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The Vapor Pressure of Deuterium Water from 20 to 230°

BY FRANCIS T. MILES AND ALAN W. C. MENZIES

Comparative measurements of the vapor pressures of ordinary water and deuterium water were undertaken in this extended range because similar comparative measurements were contemplated on the vapor pressures of saturated solutions and on the dissociation pressures of salt hydrates containing these two varieties of water.

The Material Used.—The deuterium water was prepared in this Laboratory in the manner previously reported.[1] After electrolysis the residue, which contained NaOD, was distilled three times as follows: first, after passing carbon dioxide in excess; second, after adding barium oxide to precipitate carbonate; and third, without addition of any reagent. This yielded a product of d^{25}_{25} 1.1079 as compared with 1.1074 as reported by others.[2] Each of the two experimental runs, A and B, utilized a different sample of deuterium water. The degree of dilution of these by ordinary water was estimated from melting point determinations performed upon the water after sealing it within the completed apparatus, yielding, for sample A, 3.76 ± 0.02° and, for sample B, 3.73 ± 0.03°, as measured by a Beckmann thermometer calibrated against a platinum resistance thermometer whose readings were good to 0.01°. Linear interpolation between 3.802 and 0.00°, taken as melting points[3] of deuterium and common water, respectively, indicated concentrations of D_2O of 98.9 and 98.1% for samples A and B, respectively. The observed values of vapor pressure difference were accordingly corrected by multiplying them by the ratios of 100 to these percentages.

Pressure.—Differential tensimeters of Pyrex glass were used, with mercury as manometric liquid. For temperatures up to 100°, where small differences of pressure were of greater importance, the manometer bore (apparatus A) was 12 mm., and readings were made with a cathetometer. For the higher temperatures, the manometer bore (apparatus B) was 8 mm., and readings were made against a millimeter scale without use of a telescope. Permanent gases were eliminated from the water in A by distilling the water to a portion of the apparatus cooled by solid carbon dioxide while the vacuum pump was in operation; and in B by the customary technique of boiling out. Permanent gas was likewise expelled from glass and from mercury by the customary techniques of heating, boiling and evacuation. After sealing off, when both sides of apparatus A were cooled by solid carbon dioxide, the pressure difference found was 0.02 mm. This was attributed to permanent gas, and the appropriate correction applied to the differential pressure readings. Essential absence of permanent gas from apparatus B was shown by the agreement of the differential pressure values near 100° with those yielded by apparatus A, both before and after heating to 228°. This also showed that the results were not affected to more than ±0.1% by the solution of substances from the glass which might lower the vapor pressure more on one side than on the other. Mercury pressures were reduced to 0° by use of the densities of mercury found in "International Critical Tables."[4] For the purposes of comparative study, we used the values of the vapor pressure of H_2O up to 100°

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[1] H. S. Taylor, H. Eyring and A. A. Frost, *J. Chem. Phys.*, **1**, 823 (1933).

[2] Tronstad, Nordhagen and Brun, *Nature*, **136**, 515 (1935).

[3] V. K. La Mer and W. N. Baker, THIS JOURNAL, **56**, 2641 (1934).

[4] "International Critical Tables," Vol. II, p. 457.

as given in "International Critical Tables"[5] and above 100° as given by Smith, Keyes and Gerry.[6]

Temperature.—Up to 50° a water thermostat of 320 liters capacity was used, held constant to ±0.03°. Temperatures were measured to ±0.02° by use of a Reichsanstalt certificated thermometer after redetermination of the zero point. Near 100°, four measurements were made in apparatus A immersed in a thermostat of 11 liters water content. Temperatures were read on a Beckmann thermometer whose scale was known to 0.02° by measurement of the boiling point of water at different barometric pressures. Above 100°, the tensimeter B was immersed in an oil-bath of 4 liters capacity. Temperatures were measured to ±0.1° by means of completely immersed Anschütz thermometers whose readings were converted to the scale of the Bureau of Standards by comparison with certificated Allihn thermometers, whose zero points were determined after preheating. To secure uniformity of temperature, violent stirring was especially necessary at the higher temperatures. Identical pressure values were obtained upon doubling the speed of the stirrer, and also upon reversing its direction. Inspection of Table II will show that error in pressure measurement was throughout several fold more important than that due to the uncertainty of absolute temperature reported above.

Results.—The experimental results are tabulated in the first three columns of Table I. In order to obtain a smooth curve for purposes of interpolation, we were reluctantly obliged to employ a five-constant equation

$$\log \frac{p_{D_2O}}{p_{H_2O}} = -16.998671 + \frac{268.8426}{T} + 7.4971604 \log T - 9.761107 \times 10^{-3} \times T + 4.4288 \times 10^{-6} \times T^2 \quad (1)$$

Simpler equations gave values falling outside our estimated experimental error. Column 4, Table I, gives the differences of pressure at the temperatures of experiment as derived from this equation and column 5 shows the closeness of fit.

TABLE I

VALUES OF p_{D_2O}-p_{H_2O} DETERMINED EXPERIMENTALLY

Observation number	T, °C.	$p_{D_2O} - p_{H_2O\,obsd.}$, mm.	$p_{D_2O} - p_{H_2O\,calcd.}$, mm.	$\Delta p_{obsd.} - \Delta p_{calcd.}$ mm.
A1	25.0	− 3.13	− 3.18	+0.05
A2	30.0	− 3.97	− 4.01	+ .04
A3	50.0	− 9.14	− 9.14	.00
A4	100.0	−37.7	−37.7	.0
B1	122.7	−55.5	−56.4	+ .9
B2	143.2	−73.4	−72.7	− .7
B3	166.7	−87.0	−84.9	−2.1
B4	181.9	−83.9	−84.5	+0.6
B5	204.2	−61.0	−61.3	+ .3
B6	228.7	+22.4	+22.0	+ .4

The values tabulated in Table II for each 10° interval are derived from this equation, with extrapolated values in italics. For purposes of interpolation, log p_{D_2O} and $1/T_A$ should be used as variables. Column 5 of this table shows the values of Lewis and Macdonald.[7] These authors give the normal boiling point of deuterium water as 101.42° while our equation yields 101.40 ± 0.016°. We find the temperature at which the vapor pressure of these two varieties of water is identical as 224.3°, which may be within 0.5° of the truth. Urey and Teal[8] estimated this temperature as about 160° using the data of Lewis and Macdonald;[7] while Riesenfeld and Chang's[9] estimate was about 200°.

TABLE II

VAPOR PRESSURES OF D_2O CALCULATED FROM EQUATION 1 AND COMPARED WITH THE RESULTS OF LEWIS AND MACDONALD

T, °C.	$p_{D_2O} - p_{H_2O}$ (M. & M.), mm.	p_{D_2O} (M. & M.), mm.	Estimated limit of exptl. error, mm.	$p_{D_2O} - p_{H_2O}$ (L. & M.), mm.
10	− *1.46*	*7.75*	±0.1	
20	− *2.48*	*15.06*	± .1	− 2.3
30	− 4.01	27.81	± .1	− 3.9
40	− 6.19	49.13	± .1	− 6.1
50	− 9.14	83.37	± .1	− 9.1
60	−12.97	136.41	± .2	−13.1
70	−17.8	215.9	± .3	−18.0
80	−23.5	331.6	± .3	−23.9
90	−30.2	495.6	± .4	−30.7
100	−37.7	722.3	± .4	−38.4
110	−45.7	1028.9	± .7	−47.0
120	−54.1	1435.1	±1.0	
130	−62.5	1963.8	±1.0	
140	−70.4	2640.4	±1.5	
150	−77.3	3493.4	±2	
160	−82.6	4553.9	±2	
170	−85.6	5856.1	±2	
180	−85.1	7436.9	±2	
190	−80.1	9336.3	±2	
200	−68.9	11596.3	±2	
210	−49.1	14262.5	±2	
220	−17.9	17384.6	±2	
230	+*28.8*	*21014.6*	±2	
240	+*96.2*	*25207.3*	±*5*	

Latent Heat of Vaporization.—From the simplified approximate form of the Clapeyron–Clausius equation and equation (1) we can calculate the difference between the latent heats of vaporization of D_2O and H_2O as follows

$$L_{D_2O} - L_{H_2O} = 2.303 \times RT^2 \frac{d \log (p_{D_2O}/p_{H_2O})}{dT} = -1230 + 14.90 \times T - 0.04466 \times T^2 + 4.052 \times 10^{-5} \times T^3 \quad (2)$$

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[5] "International Critical Tables," Vol. III, p. 210.

[6] L. B. Smith, F. G. Keyes and H. T. Gerry, *Proc. Am. Acad. Arts Sci.*, **69**, 137 (1934).

[7] G. N. Lewis and R. T. Macdonald, THIS JOURNAL, **55**, 3057 (1933).

[8] H. C. Urey and G. K. Teal, *Rev. Mod. Phys.*, **7**, 34 (1935).

[9] E. H. Riesenfeld and T. L. Chang, *Z. physik. Chem.*, **B28**, 408 (1935).

Values for $L_{D_2O} - L_{H_2O}$ calculated from this equation are given in Table III. The estimated limits of error given in Table III are derived from the estimated limits of error of the vapor pressure results. Since the necessary simplifying assumptions depart further from the facts with rising temperature, the degree of trust we can place upon these latent heat differences is measured by the degree of similarity of behavior of the two forms of water.

TABLE III

VALUES FOR THE DIFFERENCE OF THE LATENT HEATS OF VAPORIZATION OF HEAVY AND LIGHT WATER, $L_{D_2O} - L_{H_2O}$, CALCULATED FROM EQUATION 2

T, °C.	$L_{D_2O} - L_{H_2O}$, g. cal. per mole	Estimated limit of exptl. error, g. cal. per mole
40	300	±20
60	275	±10
80	246	±10
100	216	±10
120	186	±15
140	159	±16
160	137	±10
180	121	±10
200	113	± 5
220	115	± 4

The value for this difference reported by Lewis and Macdonald[7] was based on assumed rectilinearity of the log p_2/p_1 against $1/T$ graph between 20 and 90°, and their value agrees with ours for a temperature near 70°.

Summary

The vapor pressures of deuterium water have been compared with those of ordinary water in the range 20 to 230°. The vapor pressures are identical at about 224°.

The differences of the latent heats of vaporization are evaluated approximately from the changes of vapor pressure over the same temperature range.

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Sonic Activation in Chemical Systems: Oxidations at Audible Frequencies

BY EARL W. FLOSDORF, LESLIE A. CHAMBERS AND WM. M. MALISOFF[1]

During the past few years there have appeared numerous reports of oxidations, as well as other types of chemical reactions, induced or accelerated by intense ultrasonic vibrations.[2–4]

Schmitt, Johnson and Olson[3] observed the liberation of iodine from potassium iodide solution. They further reported that "upon the addition of radiated potassium bromide or chloride solution to starch–iodide reagent, a blue color developed which indicated either the oxidation of the bromide and chloride ions or that some other substance is produced in the presence of these salts which oxidizes the iodide ion instantaneously. Radiated distilled water produced the effect to a less marked degree." Hydrogen peroxide was found in small amount, insufficient to account for the observed rate of oxidation of halogen or of sulfide. Ozone production, if any, was in amounts too small to be detectable and consequently could not be considered as the oxidizing agent. It was further found that dissolved oxygen gas was essential to the oxidations and it was suggested that the gas was activated in association with ultrasonic cavitation. Direct absorption of energy by the molecules in solution was believed to be inconsistent with results that were obtained under pressures sufficient to inhibit visible cavitation.

Liu and Wu[4] confirmed the findings of Schmitt, Johnson and Olson, in the case of potassium iodide oxidation by ultrasonic radiation, with respect to the essential presence of dissolved oxygen gas and to the insufficient production of hydrogen peroxide or ozone to account for the observed effects. Liu and Wu presented experimental evidence in favor of the view that activation of oxygen gas is associated with cavitation. It is questionable, however, whether the conditions of radiation in a gel, whereby cavitation is suppressed and no oxidation is observed, are otherwise sufficiently comparable to justify without further evidence their conclusion concerning the influence of cavitation.

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(1) Fellow of the Josiah Macy, Jr., Foundation. Now at the Montefiore Hospital, New York City.

(2) Richards and Loomis, THIS JOURNAL, **49**, 3086–3100 (1927).

(3) Schmitt, Johnson and Olson, *ibid.*, **51**, 370 (1929).

(4) Szu-Chik Liu and Hsien Wu, *ibid.*, **56**, 1005 (1934).

Beuthe[5] also has suggested that the primary effect of ultrasonic radiation is upon the dissolved gases. He concluded, however, from his study of the ultrasonic oxidation of certain halides, that the intermediate formation of hydrogen peroxide and possibly of ozone is at least partially responsible for the liberation of the free halogen. Oyama[6] has likewise reported the oxidation of pure water by ultrasonic action.

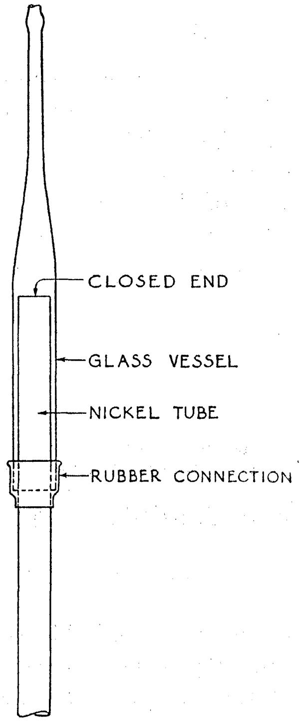

Fig. 1.—Reaction vessel, oscillator MS.

It should be emphasized that the experiments in which the above observations were made, in each case, were carried out through the use of ultrasonic vibrations (10^5 to 1.5×10^6 cycles/second). Apparatus for investigating the effects of intense sounds in the audible range (12 to 1.8×10^5 cycles/second) has been developed by Gaines[7] and used by Chambers and Gaines[8] and their collaborators, in various studies of the biological and physical actions of such audible vibrations. With this audible sound source we have extended the survey of the chemical effects of intense sound into the audible range (Flosdorf and Chambers[9]). Qualitatively, the effects produced at 9000 cycles/second seem to be similar to those previously reported for ultrasonic frequencies. Since the available sound densities are greater within the audible band the effects are greater in degree making quantitative studies less tedious and difficult and consequently more accurate.

In this paper we shall present some results of a quantitative study of certain oxidation reactions sonically activated in the audible range. We have undertaken to determine the conditions under which these sonic oxidation reactions take place in an aqueous medium, the reactants involved, the rates of reaction, and the sound intensities required. Particular attention is devoted to the question of the possible intermediate roles of hydrogen peroxide and of sonically activated oxygen. Although technical limitations have restricted the accuracy of our data, the results are instructive in a consideration of the intermediary mechanism involved not only in oxidative activation but in sonic reactions generally.

Experimental

Two types of apparatus were used, (1) the magnetostriction oscillator described by Gaines[7] and by Chambers and Gaines[8] (hereafter referred to as oscillator MS) and (2) an electromagnetic oscillator (oscillator EM).[9-11]

In oscillator MS, a cold-drawn, unannealed nickel tube, 20 mm. in diameter, vibrates in a strong electromagnetic field in resonance with a 2000 volt oscillating power circuit to which the tube imparts approximately its own natural frequency. The tubes used in these experiments, 250 mm. long, produce a frequency of about 8900 cycles per second with an acoustic output of about 15 watts (estimated) under full load. A rubber connection supports a glass vessel on the metal tube (Fig. 1). In each experiment 17–20 ml. were treated. The entire quantity was required for a single test sample which necessitated a fresh start for each time interval studied.

The diaphragm of oscillator EM is 33 cm. in diameter. The oscillator produces a frequency of about 1200 cycles per second with a maximum output of about 175 watts (Submarine Signal Co. estimate) under full load. It is of a type used in under-water signalling and depth-finding and is manufactured by the Submarine Signal Company of Boston. An iron cylinder 20 cm. deep is bolted to the periphery of the stainless steel diaphragm forming the bottom of the treatment vessel. Up to four liters of solution can be treated at one time and test samples can be removed at intervals from the same initial solution leaving sufficient for further treatment.

It has not been possible to eliminate all rubber and metal parts from contact with the reacting mixtures in either oscillator without serious impairment of intensity. Until

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(5) H. Beuthe, *Z. physik. Chem.*, **A163**, 161–171 (1933).

(6) H. Oyama, *Radio Research Japan*, **4**, 41–55 (1935).

(7) Newton Gaines, *Physics*, **3**, 209–229 (1932).

(8) Chambers and Gaines, *J. Cell. Comp. Physiol.*, **1**, 465 (1932).

(9) Earl W. Flosdorf and L. A. Chambers, THIS JOURNAL, **55**, 3051 (1933); **56**, 2795 (1934).

(10) Earl W. Flosdorf and L. A. Chambers, *J. Immunol.*, **28**, 297–310 (1935).

(11) L. A. Chambers and Earl W. Flosdorf, *J. Biol. Chem.*, **114**, 75–83 (1936).

this is accomplished the extent of catalytic action of traces of foreign substances cannot be ascertained.

It has been found that none of the sonic oxidations previously reported[9] occur in water boiled free of oxygen and accordingly all the experiments in this study, unless otherwise stated, have been carried out with free access of air to the liquid. With the energy intensities we used, cavitation is suppressed with hydrostatic pressures over six atmospheres. Since we have found the oxidations to progress only with sonic cavitation, the experiments were carried out in the presence of air at atmospheric pressure. All the results included in this report were obtained with the solutions at a temperature of 20 to 30°.

The analytical results were obtained by the following methods. *Hydrogen peroxide* was titrated in sulfuric acid solution with 0.002 *M* potassium permanganate. Results were accurate to within ±20%. *Sodium bisulfite* was determined by titration with potassium permanganate to an estimated accuracy of ±5%. *Free chlorine* (or hypochlorite) was determined colorimetrically with *o*-tolidine in hydrochloric acid solution.[12] The readings were made seven minutes after addition of the test reagent. These determinations were accurate to within ±10%. *Chlorate* was qualitatively detected after removal of chloride and hypochlorite by reduction with sodium nitrite and subsequent precipitation with silver nitrate.

Quantitative Results

(1) **Hydrogen Peroxide Formation.**—With either oscillator hydrogen peroxide has been found to be produced from water and oxygen in quantities that are of the same order of magnitude as those reported for ultrasonic frequencies.[3,4] These quantities approach 300 micro-equivalents per liter in periods under an hour; the amounts are measurably increased by vibration in acid solution such as in 0.01 *M* sodium bisulfate. Under the latter condition the reaction is interfered with, however, by the sonically accelerated side reaction of the metal of the vibrator with the acid.[9]

The rate at which the production of hydrogen peroxide takes place in pure water is illustrated in Fig. 2. Under the conditions of these experiments the estimated power output of oscillator EM was approximately ten times that of MS, whereas for EM there was twenty times the volume of water to vibrate. The amounts of chemical change per unit of energy *output* from the two sources of sound therefore appear to be about the same, in spite of the frequency difference. The spray produced as a result of the vigorous cavitation apparently is sufficient to keep the solution adequately saturated with oxygen inasmuch as the concentration of hydrogen peroxide does not reach a constant value up to the maximum duration of treatment studied. Furthermore, a stream of air bubbling through the solution during treatment produced no detectable increase in the rate.

Iodine liberation, titrated by sodium thiosulfate as used by Liu and Wu,[4] did not yield any indication of measurable production of ozone. Hydrogen peroxide, determined by permanganate titration, was produced in sufficient quantity within the limits of experimental error to account for all the iodine liberated.

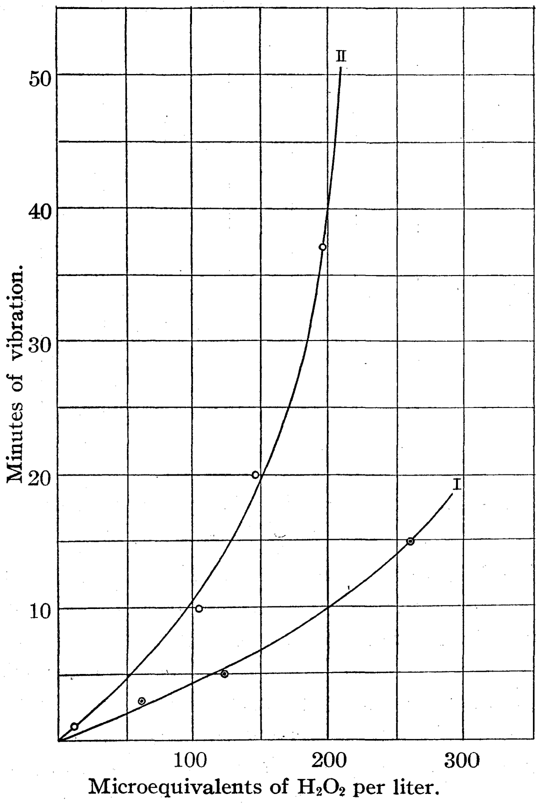

Fig. 2.—Treatment of pure water; Curve I, oscillator MS; Curve II, oscillator EM.

In alkaline solution, 0.002 *M* potassium permanganate is rapidly reduced to manganese dioxide as is to be expected on the basis of hydrogen peroxide formation. Reduction reactions of hydrogen peroxide do not lend themselves to quantitative study in the oscillators, however, because of the complicating factor introduced by the accelerated reduction reactions of the metal of the vibrators.[9] Oxidation reactions involving direct addition of oxygen therefore would seem to be simpler for study. Furthermore, in order to avoid any possible sonic action directly on a test reagent itself, analytical reagents in general

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[12] J. W. Ellms and S. J. Hauser, *J. Ind. Eng. Chem.*, **5**, 915, 1030 (1913).

should not be added to test samples until after they are removed from sonic apparatus. We shall now proceed to the results obtained from oxidation reactions involving the addition of oxygen.

(2) **Sodium Bisulfite Oxidation.**—Sodium bisulfite oxidation has not been studied in the ultrasonic range. We have found it to be oxidized relatively rapidly in the audible range in either oscillator, the rate being dependent upon the molarity of the bisulfite. A typical result obtained in oscillator EM is illustrated in Fig. 3. In Table I it will be noted that with 0.04 molar bisulfite as much as 19.2 milli-equivalents per liter have been oxidized in sixty minutes which is about seventy times as fast as hydrogen peroxide has been shown to accumulate. Upon completion of the oxidation of the sodium bisulfite we have found hydrogen peroxide is produced at about the same rate as in sodium bisulfate solution.

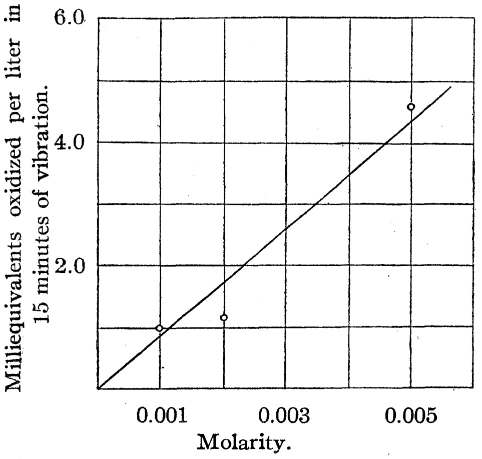

Fig. 3.—Oxidation of sodium bisulfite in oscillator EM.

Table I

Treatment of Sodium Bisulfite Solution, Oscillator MS

Molarity (approx.)	Duration, min.	Milli-equivalents oxidized per liter
0.0007	5	0.2
	15	.5
	60	1.4
.04	10	13.1
	60	19.2

Contrasted with the production of hydrogen peroxide in the two oscillators where the amounts of chemical change per unit of energy are approximately equal, the oxidation of bisulfite proceeds only about one-fifth as fast in oscillator MS as in EM. In oscillator EM there is much more vigorous spraying into the air. Because of the more rapid rate of the bisulfite reaction, this condition which controls the dissolution of oxygen to maintain the supply of gas in solution may be critical. Otherwise, we must assume that the difference in frequency is a factor in the oxidation of bisulfite and not of water.

(3) **Oxidation of Chlorides.**—In order to avail ourselves of the advantages of a system not sensitive to light, chloride was the halogen ion chosen for quantitative study. The rate of chlorine production (the test samples are acidified with the hydrochloric acid of the test reagent which completely liberates the chlorine from hypochlorite)[9] has been found to be dependent upon the concentration of chloride, Fig. 4, but not in as great degree as the bisulfite reaction. The amounts of chlorine found in solution increase with duration of treatment but reach a limiting concentration of the order of 7 to 8 microequiva-

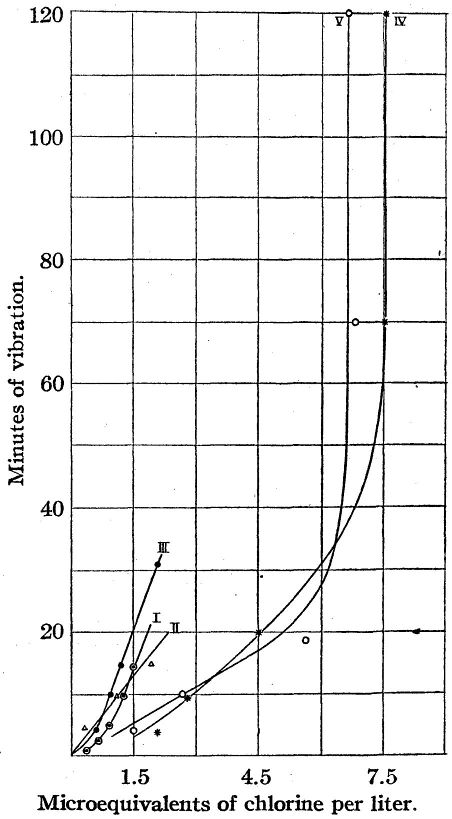

Fig. 4.—Oxidation of sodium chloride.

Chlorine determinations made after ten minutes of standing following vibration.

Oscillator MS, curve I, 0.5 Molar
Oscillator MS, curve II, 2.0 Molar
Oscillator EM, curve III, 0.5 Molar
Oscillator EM, curve IV, 2.0 Molar
Oscillator EM, curve V, 5.0 Molar

lents per liter. This is probably a result of the loss of chlorine gas from solution. In solutions of high *p*H, oxidation of chloride is very slow. In neutral solution the *p*H increases slightly during treatment because of hypochlorite formation.[9]

The quantity of chlorine found in solution is in part dependent upon the length of time of standing before the test reagents are added, subsequent to treatment. With quantities produced under 0.3 micro-equivalent per liter, the amount is doubled after standing for ten minutes. With larger quantities the amount may be increased by as much as one micro-equivalent. This suggests that accumulated hydrogen peroxide may be responsible for at least the continued effect subsequent to removal of the solutions from the oscillators. In Fig. 5 the quantities of chlorine produced by known amounts of hydrogen peroxide and sodium chloride are given. Up to 100 micro-equivalents of hydrogen peroxide per liter would be required to produce the additional chlorine found in ten minutes of standing, which is consistent with the known rate of production of peroxide. That the rate of reaction of hydrogen peroxide with chloride is slow is evident from the fact that with 2 *M* sodium chloride and 1200 micro-equivalents of peroxide per liter, the amount of chlorine produced in ten minutes is 3.7 micro-equivalents per liter and in twenty minutes is 4.5. The effect of the concentration of chloride and of peroxide is shown in Table II.

TABLE II

EFFECT OF DILUTE HYDROGEN PEROXIDE SOLUTION ON SODIUM CHLORIDE

Concentration after mixing		Time of standing before testing, min.	Chlorine produced, micro-equivalents per liter
Hydrogen peroxide, micro-equivalents per liter	Sodium chloride, molarity		
6000	0	10	0.0
6000	2	10	6.5
1200	2	10	3.7
1200	1	20	2.5
1200	2	20	4.5
1200	5	20	7.9

It is further apparent, however, that the known rate of production of peroxide cannot account for all the chlorine formed. In ten minutes in oscillator EM, three micro-equivalents of chlorine per liter are produced from 2 *M* sodium chloride, which, on the basis of Fig. 5, would require 700 micro-equivalents of peroxide per liter for the intermediate step mechanism. We have never found in either oscillator more than 200 micro-equivalents of peroxide in ten minutes. Likewise, with oscillator EM, in thirty minutes 6000 micro-equivalents of peroxide per liter would be required to yield the observed amount of chlorine, yet there never were indications of more than 300. Furthermore, peroxide is produced at a higher rate per liter in oscillator MS and we should expect, accordingly, a greater production of chlorine in this oscillator were the intermediate peroxide step essential for the production of all the observed chlorine; but more chlorine is found in oscillator EM.

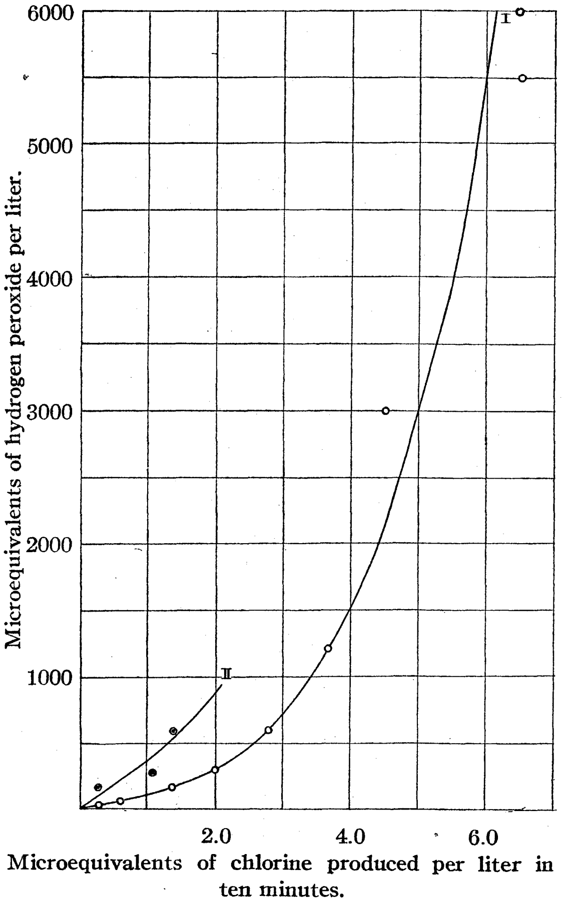

Fig. 5.—Reaction of dilute hydrogen peroxide solution with sodium chloride: curve I, 2 *M* sodium chloride; curve II, 1 *M* sodium chloride.

That sonically produced very dilute hydrogen peroxide solution can cause the production of chlorine is further evident from the data in Table III.

Water was treated by sound, removed from the apparatus after varying durations of treatment, and added to sodium chloride solution. As much as two micro-equivalents of chlorine per liter were produced. Sufficiently large samples can be ob-

Table III

Effect of Addition of Sound Cavitated Water to Sodium Chloride Solution

Oscillator	Volume treated, ml.	Duration of treatment, min.	Concn. of H_2O_2 micro-equiv. per liter Produced	Concn. of H_2O_2 micro-equiv. per liter After mixing	Concn. of NaCl after mixing, *M*	Time of standing before testing, min.	Chlorine produced, micro-equiv. per liter
MS	17	10	Insufficient sample		2	8	1.1
	20	60	Insufficient sample		2	20	2.0
EM	500	1	12	7	2	10	0.0
	450	10	106	65	2	10	0.6
	400	20	147	88	2	10	1.0
	350	37	194	124	2	10	1.1

tained from oscillator EM to permit the determination of hydrogen peroxide as well as of chlorine and, within the limits of experimental error, the quantities of both which have been found agree with the values to be expected on the basis of Table II. It is again evident, however, that the hydrogen peroxide is produced in insufficient quantity to account for all the chloride that was found to be oxidized sonically.

The possibility has not been ruled out, however, that under the influence of sound, the reaction of sonically produced hydrogen peroxide with chloride is accelerated sufficiently to account for the twenty-fold increase in the rate of production of chlorine that takes place in the oscillators. On the basis of this mechanism, however, it is difficult to account for the more rapid production of chlorine in oscillator EM which takes place in spite of a lower rate of formation of peroxide. It would be difficult to understand how there could be a difference in degree of acceleration of peroxide reaction in the two oscillators because of the frequencies when there is apparently little or no frequency effect on the production of the peroxide.

The possibility that chloride-ion catalytically increases the production of peroxide to such an extent that the latter would oxidize chloride-ion at the observed rate does not seem to be tenable. This mechanism also would involve a frequency effect.

To us it seems rather that the twenty-fold increase in rate of chlorine production, and particularly the seventy-fold increase in rate of bisulfite oxidation, suggest the possibility of a chain reaction similar to that in the thermal and in the photochemical bisulfite reactions.[13] If so, this suggests the activation of oxygen and the chains should be breakable by the usual alcohol inhibitors. These possibilities are to be investigated further.

It would seem, therefore, that there are two concurrent reactions taking place in which chloride is oxidized, *viz.*, the direct oxidation with activated oxygen and secondary oxidation with sonically produced hydrogen peroxide. On this basis the curves in Fig. 4 would represent the total effect of the two reactions. The net result would seem to be that maintenance of an adequate supply of oxygen in solution becomes the critical factor which explains the difference in rates in the two oscillators, or else there is a frequency difference responsible for more rapid oxidation of chloride in oscillator EM. More probably it is a question of oxygen supply. The sonic spray is so effective in exposing solution surface to the air for dissolution of oxygen, however, that bubbling air through the solution produces no detectable effect.

(4) **Chlorate Production.**—After standing overnight, test samples of sonically cavitated chloride solutions continue to show the presence of one to two micro-equivalents of chlorine per liter, provided they have been stored in the presence of hydrochloric acid of the concentration used in the *o*-tolidine test. Solutions of chloride to which sonically cavitated water or hydrogen peroxide solution (up to 1000 micro-equivalents per liter) has been added do not continue to show chlorine after standing overnight, the gas having been completely lost. The gas remaining in solution the next day has been attributed to the slow production of chlorine from the hydrochloric acid and sonically produced chlorate. This has been confirmed qualitatively by the detection of minute amounts of chlorate in sonically treated chloride solution by reduction with sodium nitrite after removal of chloride and hypochlorite and subsequent precipitation of the reduced chlorate with silver nitrate.

(5) **Oxidation of Organic Compounds of Chlorine.**—We have determined also that organic chlorine compounds, such as chloroform and

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[13] H. N. Alyea and H. L. J. Bäckström, This Journal, **51**, 90 (1929).

carbon tetrachloride, are oxidized as a result of sonic cavitation. Free chlorine and chloride ion are produced. Schmitt, Johnson and Olson[3] and Liu and Wu[4] have reported that a similar effect is obtained by ultrasonic vibration.

Sonic Chemiluminescence

The reaction by which light is produced as a result of the oxidation of "luminol" (3-aminophthalhydrazide) we have found to be interesting because it affords a visual confirmation of the importance of cavitation in sonic oxidation. We have determined that this reaction can be carried out sonically with dissolved oxygen gas as the only source of oxidant.

Harris and Parker[14] have shown that in the luminol reaction with hydrogen peroxide and another oxidant "the light-emitting molecule is a compound of sodium luminol and hydrogen peroxide, or this compound is the parent of the light-emitting molecule. The light-emitting molecule is brought to its energized state by reactions of the parent with some oxidizing molecule." We have found that as little as 50 micro-equivalents of hydrogen peroxide per liter is sufficient concentration to make the reaction visible in the dark without dark adaptation upon the part of the observer. It seemed reasonable, therefore, to expect luminescence by the sonic reaction in which the sound would be the sole energy source of hydrogen peroxide and oxidant. Two-tenths gram of luminol was dissolved in 20 ml. of 5% sodium hydroxide and 0.1 ml. of this stock solution in 10 ml. of distilled water was used for sonic vibration.

Upon vibration of such a solution either in oscillator MS or EM luminescence is easily visible. After allowing the observer's eyes to become dark-adapted for ten minutes the distribution of the light production becomes distinguishable. In addition to the bright glow to be seen at the top of the nickel tube (oscillator MS) streamers of light are observed to rise in spirals from the tube just as the cavitation vacuoles rise. Throughout the solution, points of light may be noticed and if these points of maximum intensity be marked and the electric lights switched on, it is seen that the spirals and the points of maximum light intensity correspond exactly with the positions of maximum cavitation. The light of greatest intensity apparently is produced in association with cavitation vacuoles.

The maximum luminescence is produced immediately or is made to vanish immediately with the turning on or off of the oscillator. After more prolonged and continuous vibration (five to ten minutes), however, a faint and homogeneous afterglow persists for five or ten minutes after the vibration ceases and it appears throughout the entire solution.

With the use of the vacuum vessel previously described in connection with the investigation of egg albumin,[11] luminescence is observed as described above. If after such vibration in which luminescence is produced, the solution in this vessel is boiled under vacuum (60 mm.) and thoroughly swept with nitrogen and finally left under one atmosphere of nitrogen, no luminescence can be observed upon subsequent sonic vibration although cavitation occurs as usual. If then this same solution is saturated once more with oxygen by bubbling air through it, luminescence is again visible as before upon sonic vibration.

It seems definitely established, therefore, that hydrogen peroxide is produced from dissolved oxygen and water upon sonic vibration and that this reacts with sodium luminol to form the light-emitting molecule or its parent substance. This parent is then brought to its energized state by reaction with some oxidizing substance. The much greater intensity of luminescence which occurs at the cavitation surface than that found existing as a faint afterglow throughout the body of the solution after more prolonged vibration (the latter presumably being entirely due to accumulated hydrogen peroxide) indicates that the oxidizing substance which brings the parent molecule to its energized state is being produced in these regions. The substance may be either activated oxygen or newly formed hydrogen peroxide in high concentrations in thin layers, as yet unmixed, or both. By analogy with the oxidation of chloride, we could expect reaction of the parent substance with both activated oxygen and with hydrogen peroxide. This greater intensity of luminescence at the cavitation surfaces by reaction with activated oxygen is analogous to that produced by potassium ferricyanide (without sonic vibration), in which case the parent substance is produced with as little as 50 micro-equivalents of hydrogen peroxide per liter.

Discussion

It is obvious from theoretical considerations

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[14] Louis Harris and A. S. Parker, THIS JOURNAL, **57**, 1939 (1935).

that the activation of dissolved oxygen may not be attributed to sound waves *per se* in the fluid. Furthermore, the experimentally established fact that such activation occurs only during sonic cavitation of the liquid and only in the immediate vicinity of such disruptive disturbances, indicates that we must be dealing with a phenomenon not easily amenable to theoretical treatment. From the evidence at hand we may conclude that oxygen is brought into a reactive state during some phase of cavitation through a process not understood at present. The activated oxygen is then free to react with either solute or solvent molecules. A similar conclusion was drawn by Schmitt, Johnson and Olson,[3] and by Liu and Wu[4] from experimental data relative to oxidations promoted by ultrasonic cavitation.

That oxygen is not the only gas capable of activation during cavitation of its solvent has been demonstrated in previous papers. For example it already has been shown[10,11] that egg albumin is denatured by sonic cavitation in the presence of carbon dioxide as well as oxygen, while in the presence of nitrogen or hydrogen, or in gas free solution, no denaturation occurs even during vigorous cavitation.

One may assume perhaps that molecules of the high energy necessary to permit the formation of hydrogen peroxide from molecular oxygen and water are created during sonic cavitation through a process of ionization or excitation. While no theoretical justification for such an hypothesis can be drawn from acoustical theory it should be remembered that, in the events accompanying cavitation, we are not dealing with acoustical phenomena *per se*. As a matter of fact the recent observation by Chambers[15] that visible light is emitted from pure polar liquids during cavitation by sound waves of the same amplitude as those used in our experiments lends credibility to the supposition that excitation or ionization may actually be occurring.

Whatever the mechanism it would appear from the evidence in hand that activation of oxygen during cavitation offers the best explanation for the chemical changes recorded in our experiments. With improvements in apparatus it should be possible to obtain further data which will permit calculation of the reaction orders and to carry out experiments of greater theoretical significance. Some means of estimating quantitatively the relative degrees of sonic cavitation produced in liquids and means for experimental variation of this factor will ultimately be necessary.

Acknowledgment.—We wish to express our appreciation to Mr. David Lackman for the assistance he has given in the chlorine determinations.

Summary

Quantitative studies of the oxidation of water and of sodium bisulfite and sodium chloride in aqueous solution by cavitation produced at audible frequencies have been carried out. The data indicate that the oxidations are accomplished through the production of activated oxygen in association with cavitation. It was determined that a compound of sodium luminol and sonically produced peroxide may be energized to produce chemiluminescence in the absence of the usual secondary oxidants, the reaction giving visual confirmation that chemical activation occurs during sonic cavitation. The results represent an elaboration of earlier work in the audible range and an extension to the audible of effects previously observed in the ultrasonic range. Some effects new at either range have been reported and certain theoretical conclusions have been drawn which probably are general for all frequencies.

PHILADELPHIA, PENNA. RECEIVED MARCH 21, 1936

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[15] L. A. Chambers, *Bull. Am. Phys. Soc.*, **11**, No. 2, 30 (1936) (Abst. 114).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary Systems KI–K_2SO_4–H_2O and NaI–Na_2SO_4–H_2O

BY JOHN E. RICCI

In addition to the purpose of obtaining solubility data for the salt pairs KI–K_2SO_4 and NaI–Na_2SO_4 in water, this brief investigation also had as its object the question of the formation of solid solutions of the alkali iodides in the corresponding sulfates. The crystals of sodium sulfate offer a considerable number of instances of the formation of solid solutions with other salts (as, with Na_2CO_3, Na_2CrO_4, Na_2S, Na_2SO_3, $Na_2S_2O_3$, Ag_2SO_4,[1] and $NaBrO_3$[2]). As to the iodides in particular, sodium sulfate has been reported[3] to form crystals of $Na_2SO_4 \cdot 10H_2O$ containing varying quantities of NaI, KI, NH_4I and LiI, held in the form of solid solution; these results, however, are based on non-equilibrium studies, in which the decahydrate was allowed to crystallize slowly from solutions of varying concentrations of the iodides, at a roughly constant temperature near room temperature. Although the fact that such crystals contain iodide (from 0.4% in the case of NaI, to 0.65% for LiI) may well be the result of simple occlusion due to lack of equilibrium, the crystals are reported to be solid solutions ("mixed crystals") on the strength of their clearness and transparency. Since on the basis of such work there seemed to be some doubt as to the actual existence of such solid solutions as stable phases in the systems, it was thought desirable to make an equilibrium study of the particular system NaI–Na_2SO_4–H_2O.

In the present work both the system KI–K_2SO_4–H_2O and the system NaI–Na_2SO_4–H_2O were studied, from the point of view of the phase rule, the first at 25°, the second at 15, 25 and 45°. The results, which represent equilibrium in the systems, show no solid solutions to be formed in either case, within the limits of the rather small experimental error of this type of work. The only solid phases encountered are the pure anhydrous or hydrated salts themselves.

Experimental Method

The experimental procedure for the solubility measurements has already been described in previous similar publications.[4] The temperature was maintained constant to within ±0.02°. The time allowed for the attainment of equilibrium varied from three days in the case of the potassium salts, to as long as fourteen days in the case of the sodium salts; the latter system was found by experiment to require from ten to fourteen days to reach equilibrium in all complexes which involved the formation of $Na_2SO_4 \cdot 10H_2O$ as solid phase. The densities reported for the potassium salt system and for some solutions of the sodium salt system, were obtained by means of volumetric pipets calibrated for delivery. For the analysis of the solutions, the iodide was determined volumetrically by titration with 0.2 *N* silver nitrate using dichlorofluorescein as indicator, the total solid was determined by evaporation to dryness, and the sulfate was then calculated by difference. In some cases of the KI–K_2SO_4–H_2O system the sulfate was determined directly by the gravimetric method, and the iodide then calculated by difference. The results of the two methods being in sufficiently close agreement, the more rapid method (titration of the iodide) was used in general. The solid phases were in each case verified by the method of algebraic extrapolation of tie-lines,[5] the average error of the extrapolations, for both systems, being 0.18%.

Results

The experimental data for the system KI–K_2SO_4–H_2O at 25° are given in Table I and Fig. 1;

TABLE I

KI–K_2SO_4–H_2O AT 25°

Original complex, wt. %		Saturated solution, wt. %			
K_2SO_4	KI	K_2SO_4	KI	Density	Solid phase
...	0.00	10.76	0.00	1.083	K_2SO_4
23.01	7.53	6.57	9.13	1.127	K_2SO_4
22.02	15.01	3.57	18.57	1.185	K_2SO_4
21.47	23.02	1.70	28.81	1.273	K_2SO_4
21.01	31.49	0.69	39.57	1.399	K_2SO_4
20.74	40.04	.25	50.35	1.553	K_2SO_4
19.99	47.03	.10	58.70	1.701	K_2SO_4
19.98	48.19	.08	59.69	1.724	K_2SO_4 + KI
12.05	57.91	.08	59.70	1.724	K_2SO_4 + KI
3.00	66.05	.08	59.67	1.720	K_2SO_4 + KI
0.59	67.98	.08	59.68	1.721	K_2SO_4 + KI
Av. (of 4)	...	.08	59.69	1.722	K_2SO_4 + KI
0.00	...	.00	59.76	1.718	KI

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(1) "International Critical Tables," Vol. IV, 1928.

(2) Ricci, THIS JOURNAL, **57**, 805 (1935).

(3) Fabris, *Ann. chim. applicata*, **17**, 321 (1927); **18**, 115, 326 (1928).

(4) Ricci THIS JOURNAL, **56**, 290 (1934).

(5) Hill and Ricci, *ibid.*, **53**, 4305 (1931).

the solubility curve consists of two simple branches, one for solutions in equilibrium with potassium sulfate, the other, extremely short, for solutions saturated with KI.

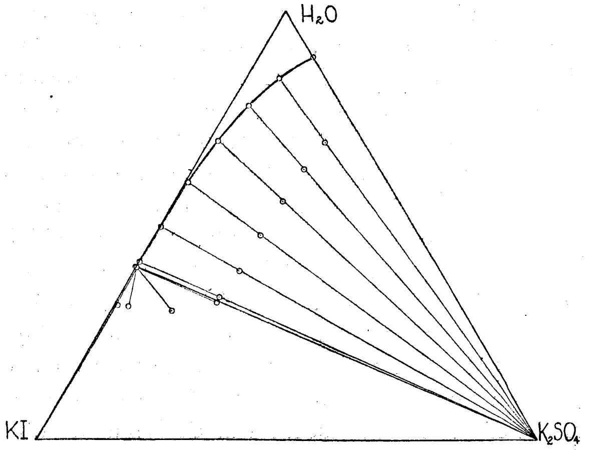

Fig. 1.—25° Isotherm: $KI-K_2SO_4-H_2O$.

The results for the system $NaI-Na_2SO_4-H_2O$, at 15, 25 and 45°, are presented in Table II, the three isotherms being shown graphically in Figs. 2, 3 and 4. As may be seen from the diagrams the only stable phases existing in the system at 45° are anhydrous Na_2SO_4 and $NaI \cdot 2H_2O$, while at

TABLE II

$NaI-Na_2SO_4-H_2O$

15°

Original complex, wt. % Na_2SO_4	Original complex, wt. % NaI	Saturated solution, wt. % Na_2SO_4	Saturated solution, wt. % NaI	Density	Solid phase
...	0.00	11.60	0.00	1.106	$Na_2SO_4 \cdot 10H_2O$
9.01	27.98	2.51	33.16	1.367	$Na_2SO_4 \cdot 10H_2O$
5.95	36.09	2.15	39.67	1.460	$Na_2SO_4 \cdot 10H_2O$
8.00	35.95	2.10	41.78	1.490	$Na_2SO_4 \cdot 10H_2O$
8.01	37.99	2.13	44.07	1.532	$Na_2SO_4 \cdot 10H_2O$
13.05	33.57	2.23	44.79	1.543	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
5.97	41.85	2.19	44.85	1.543	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
15.02	37.41	2.22	44.84	1.540	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
Av. (of 3)		2.21	44.83	1.542	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
15.09	42.99	0.93	50.15	1.613	Na_2SO_4
15.04	48.43	.15	56.92	1.733	Na_2SO_4
15.00	53.52	.02	62.89	1.875	Na_2SO_4
15.08	54.59	.01	63.33	1.881	$Na_2SO_4 + NaI \cdot 2H_2O$
4.99	64.90	.05	63.31	1.882	$Na_2SO_4 + NaI \cdot 2H_2O$
Av. (of 2)		.03	63.32	1.881	$Na_2SO_4 + NaI \cdot 2H_2O$
0.00	...	.00	63.35	1.881	$NaI \cdot 2H_2O$

25°[a]

Original complex, wt. % Na_2SO_4	Original complex, wt. % NaI	Saturated solution, wt. % Na_2SO_4	Saturated solution, wt. % NaI	Solid phase
...	0.00	21.78	0.00	$Na_2SO_4 \cdot 10H_2O$
23.91	5.15	17.54	6.77	$Na_2SO_4 \cdot 10H_2O$
23.58	8.10	14.87	11.50	$Na_2SO_4 \cdot 10H_2O$
20.09	13.94	11.83	18.46	$Na_2SO_4 \cdot 10H_2O$
15.52	17.42	10.81	20.30	$Na_2SO_4 \cdot 10H_2O$
13.11	22.20	9.37	24.81	$Na_2SO_4 \cdot 10H_2O$
13.05	23.56	8.70	26.84	$Na_2SO_4 \cdot 10H_2O$
14.03	25.00	7.94	30.05	$Na_2SO_4 \cdot 10H_2O$
13.49	27.02	7.61	31.77	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
18.05	26.02	7.66	31.74	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
12.48	29.31	7.64	31.76	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
Av. (of 5)		7.63	31.77	$Na_2SO_4 \cdot 10H_2O + Na_2SO_4$
...	0.00	33.97	0.00	Na_2SO_4 (m)[b]
36.74	6.57	26.65	7.60	Na_2SO_4 (m)
20.01	19.97	14.91	21.22	Na_2SO_4 (m)
20.13	27.11	7.97	31.21	Na_2SO_4 (m)
20.00	32.16	4.09	38.58	Na_2SO_4
20.16	36.77	2.06	45.01	Na_2SO_4
20.27	41.72	0.70	51.91	Na_2SO_4
19.94	45.45	.30	56.54	Na_2SO_4
20.06	49.73	.14	62.05	Na_2SO_4
19.96	54.55	.02	64.76	$Na_2SO_4 + NaI \cdot 2H_2O$
4.02	64.97	.07	64.76	$Na_2SO_4 + NaI \cdot 2H_2O$
2.98	72.00	.07	64.75	$Na_2SO_4 + NaI \cdot 2H_2O$
Av. (of 4)		.06	64.75	$Na_2SO_4 + NaI \cdot 2H_2O$
0.00	...	.00	64.79	$NaI \cdot 2H_2O$

45°[a]

Original complex, wt. % Na_2SO_4	Original complex, wt. % NaI	Saturated solution, wt. % Na_2SO_4	Saturated solution, wt. % NaI	Solid phase
...	0.00	32.09	0.00	Na_2SO_4
35.01	12.98	17.19	16.52	Na_2SO_4
29.87	23.88	6.73	31.73	Na_2SO_4
25.01	32.89	2.22	42.85	Na_2SO_4
20.07	41.98	0.51	52.27	Na_2SO_4
17.78	43.54	.43	52.75	Na_2SO_4
20.16	54.22	.04	67.85	Na_2SO_4
6.02	64.78	.04	68.29	$Na_2SO_4 + NaI \cdot 2H_2O$
6.00	67.92	.02	68.22	$Na_2SO_4 + NaI \cdot 2H_2O$
2.04	70.48	.06	68.25	$Na_2SO_4 + NaI \cdot 2H_2O$
Av. (of 3)		.04	68.25	$Na_2SO_4 + NaI \cdot 2H_2O$
0.00	...	.00	68.32	$NaI \cdot 2H_2O$

[a] The data for the 45°, and for part of the 25°, isotherms were obtained by Dr. Nicholas S. Yanick, formerly of this Department. [b] m = metastable solid phase.

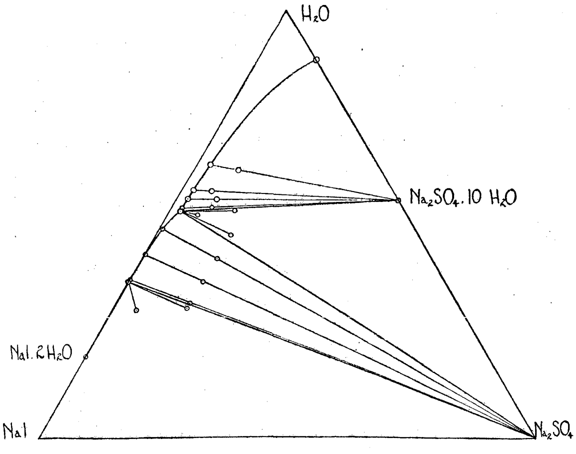

Fig. 2.—15° Isotherm: $NaI-Na_2SO_4-H_2O$.

15 and 25°, $Na_2SO_4 \cdot 10H_2O$ appears, giving three stable phases. In Fig. 3, for the 25° isotherm, the curve a-b represents the solubility of $Na_2SO_4 \cdot 10H_2O$ as stable phase in the ternary system; point b, an isothermally invariant solution in equilibrium with both hydrated and anhydrous Na_2SO_4; the curve b-c, solutions in equilibrium with anhydrous Na_2SO_4 as solid phase; point c, the isothermally invariant solution for the two solid phases Na_2SO_4 and $NaI \cdot 2H_2O$; and the very short curve c-d, the solubility curve of $NaI \cdot 2H_2O$. The curve b-e is the metastable extension of the solubility curve b-c, of Na_2SO_4, point e being the metastable solubility of anhydrous Na_2SO_4 in water at 25°.

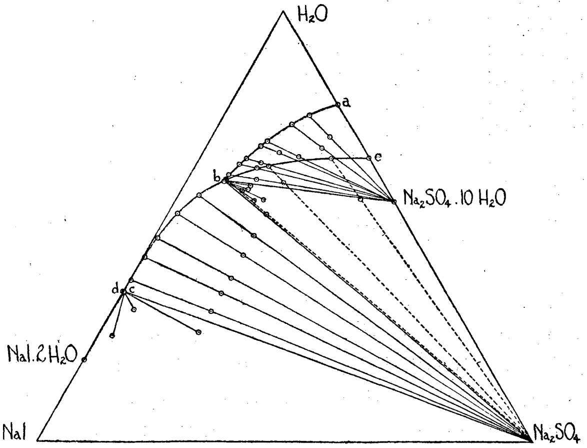

Fig. 3.—25° Isotherm: $NaI-Na_2SO_4-H_2O$.

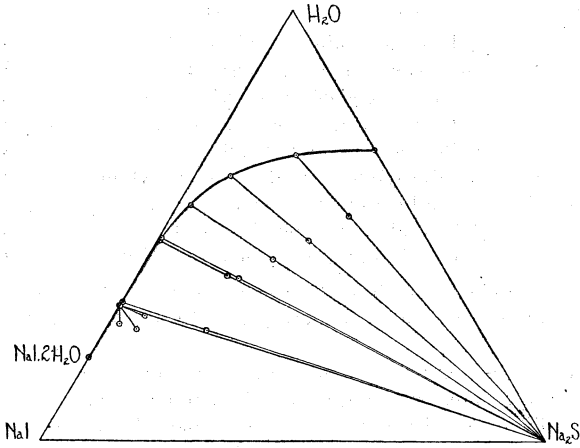

Fig. 4.—45° Isotherm: $NaI-Na_2SO_4-H_2O$.

Acknowledgment.—The author wishes to express his thanks to Dr. Nicholas S. Yanick, formerly of this Department, for his help in some of the experimental work of this paper.

Summary

Solubility measurements are given for the systems $KI-K_2SO_4-H_2O$ (at 25°) and $NaI-Na_2SO_4-H_2O$ (at 15, 25 and 45°); these salt pairs form neither double salts nor solid solutions at the temperatures reported.

NEW YORK, N. Y. RECEIVED APRIL 21, 1936

[CONTRIBUTION FROM THE LABORATORIES OF THE WM. S. MERRELL COMPANY]

Phenyl Urethan Anesthetics. II

BY E. S. COOK AND T. H. RIDER

The value of phenyl urethans as local anesthetics has been pointed out by Rider.[1] The present paper continues work in this field and deals largely with phenyl urethans of γ-dialkylaminopropanols ($R_2NCH_2CH_2CH_2OH$). Two esters of dialkylaminoisopropyl alcohols ($R_2NCH_2CHOHCH_3$) and the phenyl urethan of β-diethylaminoethanol are included.

These compounds are of particular interest because they are isomeric with the *p*-aminobenzoates, several of which have found considerable use as local anesthetics. The *p*-aminobenzoate homologs of compounds 4 and 9 (see Table I) are marketed as butyn and procaine, respectively, and the *p*-aminobenzoate homologs of compounds 2, 3,[2] and 6[3] have been prepared and found to possess local anesthetic activity.

Experimental Part

Amino Alcohols.—Beta-diethylaminoethanol, γ-diethylaminopropanol, and γ-di-*n*-butylaminopropanol were obtained from the Eastman Kodak Company and redistilled. The other γ-dialkylaminopropanols (dimethylamino-, di-*n*-propylamino-, piperidino- and methylphenethylamino-) were prepared by condensing the proper secondary amine with trimethylene bromohydrin in the absence of a solvent.

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(1) T. H. Rider, (a) THIS JOURNAL, **52**, 2115 (1930); (b) *ibid.*, **52**, 2583 (1930); (c) *J. Pharmacol.*, **39**, 457 (1930); (d) *ibid.*, **47**, 255 (1933).

(2) O. Kamm, R. Adams and E. H. Volwiler, U. S. Patents 1,358,750 and 1,358,751; E. H. Volwiler, *Science*, **53**, 145 (1921); H. L. Schmitz and A. S. Loevenhart, *J. Pharmacol.*, **24**, 159 (1924).

(3) A. C. Cope and S. M. McElvain, THIS JOURNAL, **53**, 1587 (1931).

TABLE I

PHENYL URETHAN HYDROCHLORIDES OF AMINO ALCOHOLS

	Compound, urethan hydrochloride	Formula	Chlorine, % Calcd.	Chlorine, % Found		M. p., °C. (corr.)
1	γ-Dimethylaminopropylphenyl	$C_{12}H_{19}O_2N_2Cl$	13.71	13.89	13.80	131–132.5
2	γ-Diethylaminopropylphenyl	$C_{14}H_{23}O_2N_2Cl$	12.37	12.57	12.55	140.5–142.5
3	γ-Di-*n*-propylaminopropylphenyl	$C_{16}H_{27}O_2N_2Cl$	11.27	11.33	11.31	159.5–160.5
4	γ-Di-*n*-butylaminopropylphenyl[a]	$C_{18}H_{31}O_2N_2Cl$	10.35	10.48	10.43	123–124
5	γ-Piperidinopropylphenyl	$C_{15}H_{23}O_2N_2Cl$	11.87	11.81		169–169.5
6	γ-(Methylphenethyl)-aminopropylphenyl	$C_{19}H_{25}O_2N_2Cl$	10.17	10.23	10.20	192.5–193.5
7	1-Diethylaminopropanol-2-phenyl	$C_{14}H_{23}O_2N_2Cl$	12.37	12.52	12.55	137.5–138.5
8	1-Piperidinopropanol-2-phenyl	$C_{15}H_{23}O_2N_2Cl$	11.87	11.23	11.17[b]	88–89.5
9	β-Diethylaminoethylphenyl[c]	$C_{13}H_{21}O_2N_2Cl$	13.00	13.04	13.05	142.5–143.5

[a] Previously prepared by Rider, ref. 1b. [b] Difficult completely to free from solvent. [c] Previously prepared by Rider[a] and reported by Fromherz [*Arch. Exptl. Path. Pharmakol.*, **76**, 257 (1914)]; m. p. given as 138–139°.

All were heated under reflux except dimethylamine (used as the 33% aqueous solution) which required a sealed tube. Usually no condensing agent was employed, but potassium carbonate was used successfully in several cases. The reaction mixtures were treated with potassium hydroxide solution, extracted repeatedly with ether, dried over potassium hydroxide, and the ether was removed. The alcohols were distilled either *in vacuo* or at atmospheric pressure. All of these alcohols are recorded in the literature with the exception of γ-(methylphenethyl)-aminopropanol. For this alcohol the methylphenethylamine was prepared from β-phenylethylamine, benzaldehyde, and methyl iodide by the method of Decker and Becker[4] with modifications suggested by Buck.[5] The amine was condensed with trimethylene bromohydrin as above. γ-(Methylphenethyl)-aminopropanol is a rather viscous, water-white liquid with a very slight violet fluorescence. It distils at 155–157° at 12 mm.

Anal. Calcd. for $C_{12}H_{19}ON$: N, 7.25. Found: N, 7.01.

1-Diethylamino- and 1-piperidinopropanol-2 were prepared by condensing the amines with propylene oxide. A sealed tube was necessary for the diethylamine but not for the piperidine. This method, which apparently has not been applied before to the preparation of these two compounds, gave 80% yields of amino alcohols, identical in all properties with those obtained from the corresponding chloro- or bromohydrin.

Phenyl Urethan Hydrochlorides.—Equimolar quantities of the amino alcohol and phenyl isocyanate were refluxed in absolute ether until disappearance of the odor of phenyl isocyanate. After cooling the reaction mixture, the hydrochloride was precipitated by adding a solution of hydrogen chloride in dry ether. The hydrochloride usually precipitated as a solid but 1-piperidinopropanol-2-phenyl urethan hydrochloride came down as an oil and considerable difficulty was encountered in crystallizing it. All the hydrochlorides were crystallized from a mixture of ethyl acetate and acetone except the γ-(methylphenethyl)-amino compound which was purified from absolute alcohol. The melting points and analyses of the compounds are given in Table I.

Pharmacological Properties.—In Table II data relative to the local anesthetic activity and toxicity of these compounds are given. All tests were made with 1% solutions of the hydrochlorides in distilled water. The third and fourth columns give the time in minutes required for the production of sensory and motor anesthesia in the exposed sciatic nerve of the frog.[6] The fifth column gives the duration of anesthesia after a one-minute application of the solution to the cornea of the rabbit.[6] Column six gives the approximate minimum lethal dose in milligrams per kilo by subcutaneous injection into guinea pigs.

TABLE II

PHARMACOLOGICAL PROPERTIES

Compound	*p*H, 1% Solution (quinhydrone electrode)	Time of onset of anesthesia, min. Sensory	Motor	Duration of anesthesia, min. Cornea	Toxicity mg./kg.
Cocaine	5.10	4	14	30	60
Procaine	5.50	6	18.5	Incomplete	400
1	5.82	6	36.5	Incomplete	..
2	5.98	3.5	27	14	150
3	6.46	2.75	21.75	24.5	150
4	5.93	2	10.5	65.5	150
5	5.88	3	16.5	17	150
6	5.40	3	28.75	91.5	75
7	6.48	3.25	16.5	16	150
8	5.47	3	25.5	35	200
9	6.25	3.75	14	11	150

It will be observed that the two derivatives of isopropyl alcohol (7 and 8) show some superiority over their primary alcohol isomers (2 and 5) in anesthetic activity and are less toxic as well. The one compound here reported with two dissimilar alkyl groups on nitrogen (6) has the highest anesthetic activity of the compounds tested but is extremely toxic. An increase in anesthetic power is found as the size of the nitrogen alkyls increases behavior which is duplicated in other series of anesthetics, but no progressive increase in toxicity is observed. The surprising similarity in toxici-

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(4) H. Decker and P. Becker, *Ann.*, **395**, 362 (1913).

(5) J. S. Buck, THIS JOURNAL, **52**, 4119 (1930); **54**, 3661 (1932).

(6) T. H. Rider, *J. Pharmacol.*, **39**, 329 (1930).

ties of these compounds is worthy of comment. The results were checked several times and are believed to be accurate within 30%. The diethylaminoethylphenyl urethan is less active than either of the propanol homologs, which, again, is in accord with previous observations on the influence of the length of the alcohol chain, but it is no less toxic. The propanol compounds are more effective on the exposed nerve, by the test which measures onset time rather than duration, than the corresponding mono- and diphenyl urethans of dialkylamino propanediols[1a] but the reverse is usually true with respect to corneal anesthesia. Other comparative tests indicate that the diphenyl urethans of propanediols (such as diothane) are more effective as topical anesthetics, and while giving a slower onset time likewise give considerably more prolonged duration of anesthesia following intradermal injection.

The phenyl urethans here reported are more active on the rabbit's cornea than such of the isomeric *p*-aminobenzoates as have been prepared and tested.[2,3] This same behavior has been observed for the corresponding esters of piperidinopropanediol[7] as well as for the phenyl urethan and *p*-aminobenzoate of 2-diethylamino-3-hydroxy-1,2,3,4-tetrahydronaphthalene.[8] These facts prompt the suggestion that the phenyl urethan configuration confers more topical anesthetic activity upon a molecule than does the isomeric *p*-aminobenzoate group.

Acknowledgment.—We wish to thank Dr. R. S. Shelton for assisting in the pharmacological work and Mr. Karl Bambach for the analyses.

Summary

The phenyl urethans of a number of dialkylaminopropanols have been prepared and shown to have local anesthetic properties. It is suggested that the phenyl urethan group is more active in causing anesthesia of the mucous surfaces than the isomeric *p*-aminobenzoate group.

[7] E. W. Scott and T. H. Rider, THIS JOURNAL, **55**, 804 (1933).

[8] E. S. Cook and A. J. Hill, to be published.

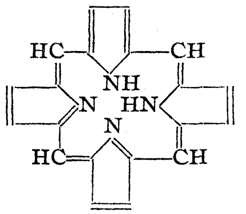
CINCINNATI, OHIO RECEIVED APRIL 6, 1936

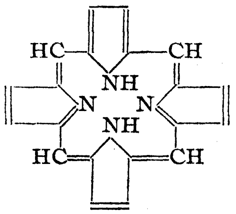
[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Studies in the Pyrrole Series. I. The Preparation of Certain N-Methyl Pyrroles[1]

BY ALSOPH H. CORWIN[2] AND WM. M. QUATTLEBAUM, JR.[3]

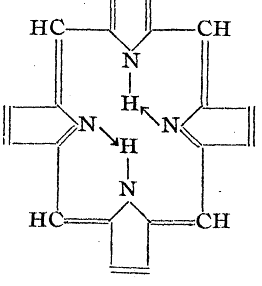
If we accept Küster's formulation of the porphyrin nucleus as proved and exclude "resonance isomers," the following isomeric forms should be possible





These will be referred to as N-isomers.

Fischer[4] has suggested the simpler possibility of N-isomerism in di-pyrryl methenes but has not demonstrated its existence. Since N-isomers of the salts of methenes with mineral acids would be "resonance isomers," a separation should be achieved only by fractionation of the free bases. Likewise with the porphyrins, the salts with acids would be "resonance isomers." As a result we should not expect to find examples of N-isomerism among the synthetic porphyrins made by acid melts unless the free bases had been fractionated subsequently by a procedure not involving the use of acid. Conant and Bailey[5] have pointed out that differences between N-isomers should be destroyed by conversion into metallic complexes but found no porphyrins which exhibited this phenomenon.



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[1] From the doctoral dissertations of Alsoph H. Corwin, Harvard University, 1932, and Wm. M. Quattlebaum, Jr., Harvard University, 1934. The authors wish to acknowledge their indebtedness to Dr. James B. Conant for suggesting this field of research and their appreciation of his advice and guidance in the direction of the work.

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[3] Present address, Carbide and Carbon Chemicals Corp., South Charleston, W. Va.

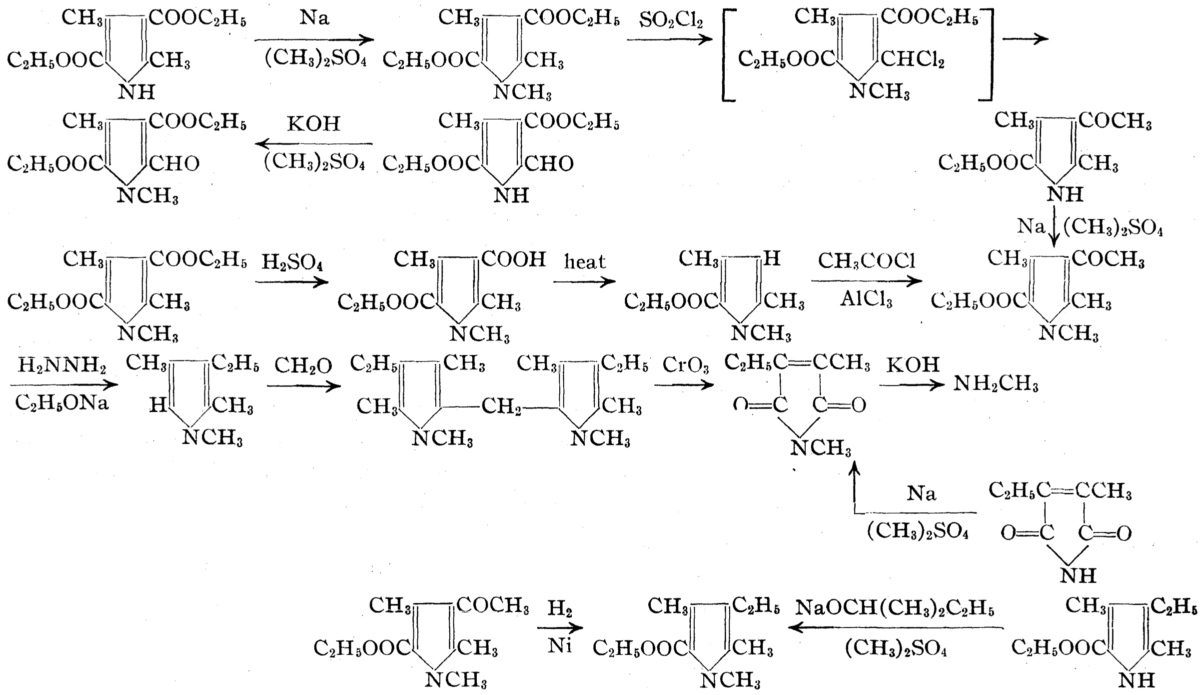
[4] Fischer, *Z. physiol. Chem.*, **128**, 63 (1923).

[5] Conant and Bailey, THIS JOURNAL, **55**, 796 (1933).

An examination of a space model of a porphyrin suggests the possibility that the adjacent secondary and tertiary nitrogens might be joined by a hydrogen bridge.

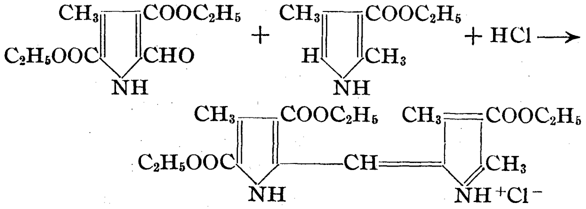
In such a case the predicated N-isomerism would not appear but might give way to another type in which the H bridges exchanged their partners.[6] Substitution of a functional group for hydrogen would destroy the latter isomerism and create the appearance that the original porphyrins were N-isomers.

To test the theoretical considerations presented, the question of N-isomerism is being submitted to experimental examination. It is proposed to synthesize porphyrins from compounds suited to the determination of the positions of the methylated nitrogens with reference to the unmethylated nitrogens. It is then proposed to N-methylate porphyrins and to compare the products with those prepared by synthesis. The first phase of this problem is the preparation and proofs of the structures of certain N-methyl pyrroles. Starting with Knorr's pyrrole (2,4-dimethyl-3,5-dicarbethoxypyrrole) the following interrelationships have been established



That the methyl group remains attached to nitrogen through all these reactions is shown by the fact that methylamine free from ammonia is obtained by the hydrolysis of N-methylmethylethylmaleic imide. The di-N-methyldipyrrylmethane indicated is the first completely alkylated dipyrrylmethane to be obtained by condensation with formaldehyde, despite many attempts.[7]

The second phase of the problem was the synthesis of N-methyl methenes. Since the simplest unsymmetrical methene containing carbethoxy groups rather than ethyl was unknown, it was prepared by the condensation



In this instance it was necessary to modify the usual methods for the preparation of methenes which failed due to the instability of this methene in solution.

The three possible combinations of the N-methyl homologs of the pyrroles in this condensation failed to yield methenes. That this failure

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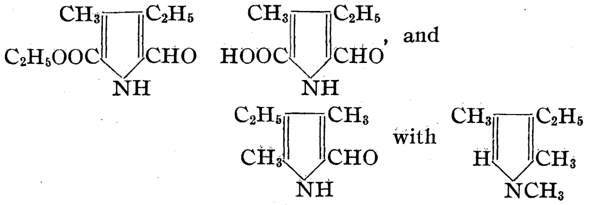
(6) The authors are indebted to Dr. Maurice L. Huggins for suggesting and critically examining the possibility of the existence of H bridges.

(7) Fischer and Bartholomäus, *Z. physiol. Chem.*, **83**, 50 (1913); Fischer and Eismayer, *Ber.*, **47**, 2021 (1914); Fischer and Nenitzescu, *Ann.*, **443**, 123 (1925); Fischer, Halbig and Walach, *ibid.*, **452**, 287 (1927).

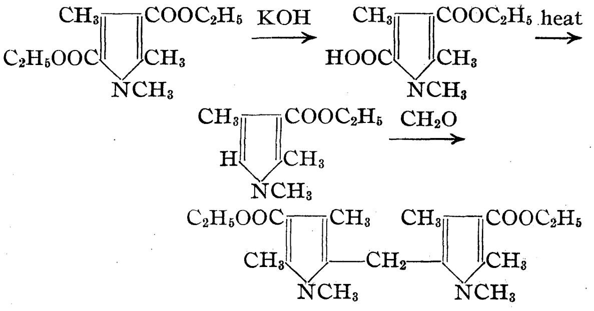
was due to a different type of reaction than that usually formulated will be shown in a separate communication.

To take advantage of the greater tendency toward methene formation exhibited by pyrroles containing only alkyl groups in the β-positions, the following combinations were tried



None of these yielded N-methyl methenes.

The failure of the aldehyde condensation led to an examination of the other general methods for methene synthesis. A di-N-methyldipyrrylmethane was prepared by the reactions



Neither the oxidation of this methane nor that of the hexamethyldiethylmethane mentioned earlier yielded a methene. The reactions of 1,2,4-trimethyl-3-carbethoxy and 1,2,4-trimethyl-3-ethylpyrroles with bromine and with formic acid again failed to yield methenes. Finally, attempts to methylate 3,5,3′,5′-tetramethyl-4,4′-dicarbethoxydipyrrylmethene were unsuccessful.

Our failure to obtain N-methylmethenes suggests the desirability of subjecting the various methene syntheses to careful scrutiny and commends to attention the possibilities of the synthesis of N-methylporphyrins by methods not involving the use of dipyrrylmethenes.

The authors are indebted to Mrs. G. Ware Wellwood for performing many of the microanalyses reported in this paper.

Experimental Part

2,4-Dimethyl-3,5-dicarbethoxypyrrole.[8]—The yield may be improved by adding sodium acetate to the zinc dust reduction to form a complex with zinc acetate and thus increase its solubility,[9] and by adding the solution of the nitroso compound to the mixture of zinc dust, sodium acetate, ethyl acetoacetate and glacial acetic acid instead of adding zinc dust to the other compounds; yield 75%.

1,2,4 - Trimethyl - 3,5 - dicarbethoxypyrrole.—Twenty-eight grams of sodium wire, 200 g. of 2,4-dimethyl-3,5-dicarbethoxypyrrole and two liters of toluene were heated with stirring for four hours on a steam-bath. The sodium salt of the pyrrole separated as a white curdy precipitate. Ninety cc. of freshly distilled dimethyl sulfate was then added dropwise and stirring and heating continued for another hour. The sodium methyl sulfate was filtered off and washed with toluene. The toluene was removed from the filtrate by steam distillation. On cooling the pyrrole crystallized out; yield 85–90%. The product may be recrystallized from methanol and water or from methanol alone by cooling with dry ice; m. p. 113–114°.

Anal. Calcd. for $C_{13}H_{19}O_4N$: C, 61.62; H, 7.56; N, 5.53. Found: C, 61.84; H, 7.95; N, 5.74.

As an alternative the sodium salt may be formed by the action of sodium tertiary amylate in tertiary amyl alcohol and subsequently methylated with dimethyl sulfate. The yield by this method was the same.

1,4 - Dimethyl - 2 - formyl - 3,5 - dicarbethoxypyrrole.—(a) Five grams of 2-formyl-3,5-dicarbethoxy-4-methylpyrrole was dissolved in a solution of 1.1 g. of potassium hydroxide in 11 cc. of methyl alcohol. Two and one-half cc. of dimethyl sulfate was added slowly below 50°. The mixture was allowed to stand for half an hour and cooled to crystallize the N-methyl aldehyde. The aldehyde was filtered off, washed with water and crystallized from methanol, m. p. 94°. This is the procedure of choice in quantity preparations.

(b) Twenty-five and three-tenths grams of 1,2,4-trimethyl-3,5-dicarbethoxypyrrole was dissolved in 127 g. of glacial acetic acid and 27 g. of sulfuryl chloride added slowly at 60°. The temperature was maintained for half an hour and the flask then cooled to 20° to permit crystallization of the aldehyde. Less pure product may be obtained by precipitating the mother liquor with water; m. p. 93°; mixed m. p. with aldehyde obtained in (a) 93°.

Anal. Calcd. for $C_{13}H_{17}O_5N$: C, 58.39; H, 6.41. Found: C, 58.34; H, 6.44.

1,2,4 - Trimethyl - 3 - carboxyl - 5 - carbethoxypyrrole.—The procedure was essentially that of Fischer and Walach[10] for the lower homolog. Twenty-five grams of 1,2,4-trimethyl-3,5-dicarbethoxypyrrole was added to 100 cc. of concd. sulfuric acid and the temperature kept below 30°: recovery 3 g.; yield 60% of the remainder; decomposition point 192°.

Anal. Calcd. for $C_{11}H_{15}O_4N$: C, 58.63; H, 6.71. Found: C, 58.99; H, 6.91.

1,2,4 - Trimethyl - 5 - carbethoxypyrrole.—The decarboxylation of the preceding compound was carried out as rapidly as possible in three times its weight of anhydrous glycerine;[11] yield 75%; m. p. 47°. The substance has a peculiar, sickening, sweetish odor.

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[8] Hans Fischer, "Organic Syntheses," Vol. XV, 1935, p. 17; Winans and Adkins, This Journal, **55**, 4167 (1933).

[9] Davidson and McAllister, *ibid.*, **52**, 507 (1930).

[10] Fischer and Walach, *Ber.*, **58**, 2820 (1925).

[11] Fischer, Berg and Schormüller, *Ann.*, **480**, 114 (1930).

Anal. Calcd. for $C_{10}H_{15}O_2N$: C, 66.25; H, 8.34. Found: C, 65.92; H, 8.34.

1,2,4 - Trimethyl - 3 - acetyl - 5 - carbethoxypyrrole.—(a) The best method for the preparation of this compound is the methylation of 2,4-dimethyl-3-acetyl-5-carbethoxypyrrole by the method given for 1,2,4-trimethyl-3,5-dicarbethoxypyrrole; yield 80%; m. p. 62° after recrystallization from ligroin.

(b) The preparation from 1,2,4-trimethyl-5-carbethoxypyrrole by the Friedel–Crafts reaction follows that of the lower homolog;[12] yield 25% after recrystallization; m. p. 60–61°; mixed m. p. with product from (a) 61°.

Anal. Calcd. for $C_{12}H_{17}O_3N$: C, 64.53; H, 7.67. Found: C, 64.46; H, 7.54.

1,2,4-Trimethyl-3-ethylpyrrole.—The procedure for preparing this from 1,2,4-trimethyl-3-acetyl-5-carbethoxypyrrole follows essentially that of Fischer, Baumann and Riedl.[13] The substance is sensitive to oxidation and should be protected by nitrogen; yield 55%; b. p. 93° at 23 mm.

Anal. Calcd. for $C_9H_{15}N$: C, 78.75; H, 11.02. Found: C, 77.85; H, 10.45.

(It appeared that this analytical discrepancy was due to the rapidity with which the substance oxidized during the weighing process.)

1,3,5,1′,3′,5′ - Hexamethyl - 4,4′ - diethyl - 2,2′ - dipyrrylmethane.—Success in preparing this compound depends upon the absence of mineral acid. The acid necessary for condensation was supplied by using old formalin which had accumulated enough formic acid to give an acid reaction to litmus.

One gram of N-methylcryptopyrrole, 2 cc. of 95% ethyl alcohol and 0.5 cc. of 40% formalin solution were stirred together without warming. The methane separated in colorless crystals. The precipitate was filtered off, washed and crystallized from methanol. It was very sensitive to air and was dried in a vacuum and stored under nitrogen; m. p. 106°.

Anal. Calcd. for $C_{19}H_{30}N_2$: C, 79.65; H, 10.56. Found: C, 79.80; H, 10.67.

N-Methylmethylethylmaleic Imide.—(a) Two grams of 1,2,4-trimethyl-3-ethylpyrrole was suspended in a saturated aqueous solution of 8 g. of CrO_3 and 50 cc. of 20% sulfuric acid added drop by drop at 60°. The flask was kept at 70° for several hours with occasional stirring and rubbing of the resinous precipitate. The solution was cooled, extracted five times with ether, the extract washed with water, dilute soda solution and again with water, dried and distilled. The imide was a colorless oil; b. p. 215–220°.

(b) 1,3,5,1′,3′,5′ - Hexamethyl - 4,4′ - diethyl - 2,2′ - dipyrrylmethane was oxidized according to the above procedure. N-methylmethylethylmaleic imide was isolated. When saponified according to the directions below and tested for ammonia the latter was found to be absent. CH_3NH_3Cl was isolated; m. p. 226–227°; mixed m. p. with CH_3NH_3Cl, 227°.

(c) One and four-tenths grams of methylethylmaleic imide was dissolved in 20 cc. of toluene and treated with 0.46 g. of sodium and then 2.52 g. of dimethyl sulfate according to the procedure for 1,2,4-trimethyl-3,5-dicarbethoxypyrrole. The toluene was removed by vacuum fractionation. The imide boiled at 215–221°.

Hydrolysis Procedure.—Two 50-cc. distilling flasks were connected through their side-arms with a small condenser. The first flask was provided with an ebullition tube, the second with a stopper containing a 12 in. length of 12 mm. glass tubing which dipped below a few cc. of distilled water in the flask. The imide was placed in the first flask with 20 cc. of normal sodium hydroxide solution and the apparatus tilted so that the condenser acted as a reflux during the hydrolysis. The solution was boiled for an hour, the apparatus tilted toward the second flask and the amine distilled slowly until most of the water had passed over. The liquid in the receiver was then tested for ammonia and methylamine by Thatcher's test.[14] No ammonia was found. A portion of the distillate was neutralized with hydrochloric acid and evaporated to dryness. A test portion of the residue was found to be completely soluble in absolute alcohol previously saturated with ammonium chloride. The residue was crystallized from hot absolute alcohol and ether; m. p. 227°; mixed m. p. with CH_3NH_3Cl, 227°.

1,2,4 - Trimethyl - 3 - ethyl - 5 - carbethoxypyrrole.—(a) This product may be prepared by the catalytic hydrogenation of 1,2,4-trimethyl-3-acetyl-5-carbethoxypyrrole in alcoholic solution with Raney's catalyst,[15] at 2500 pounds per sq. in. pressure and 150°. The pyrrole distilled at 124° at 2 mm. This is the method of choice in the preparation.

(b) The substance may be prepared by methylation of 2,4-dimethyl-3-ethyl-5-carbethoxypyrrole by the tertiary amylate method mentioned for 1,2,4-trimethyl-3,5-dicarbethoxypyrrole, b. p. 120–125° at 2 mm. Comparison of b. p. with product from (a) in the same apparatus shows them to be identical.

Anal. Calcd. for $C_{12}H_{19}O_2N$: C, 68.90; H, 9.09. Found: C, 68.65; H, 9.04.

3,5,4′ - Tricarbethoxy - 4,3′,5′ - trimethyl - 2,2′ - dipyrrylmethene.—Attempts to prepare this compound by any of the methods employed by Fischer for methene syntheses were unsuccessful. It was finally prepared by using cold ether as a solvent for the reaction and dry hydrogen chloride gas as a catalyst. The methene was so insoluble in ether that it crystallized out as rapidly as formed. It was then found that the earlier failures to obtain this methene were due to the fact that it decomposed when dissolved in alcohol or glacial acetic acid. In fact, this methene was not stable in any solvent which was investigated.

Two and five-tenths grams of 2-formyl-3,5-dicarbethoxy-4-methylpyrrole and 1.67 g. of 2,4-dimethyl-3-carbethoxypyrrole were dissolved with warming in 175 cc. of dry ether. The mixture was cooled to 10° and dry gaseous hydrogen chloride passed in for fifteen to twenty minutes. The solution was allowed to stand at 0° for several hours, the methene filtered off and washed with ether. Brilliant

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[12] Fischer and Schubert, *Z. physiol. Chem.*, **155**, 102 (1926).

[13] Fischer, Baumann and Riedl, *Ann.*, **475**, 239 (1929).

[14] Mulliken, "Identification of Pure Organic Compounds," John Wiley & Sons, Inc., 1916, Vol. II, p. 20.

[15] Raney, THIS JOURNAL, **54**, 4116 (1932); Signaigo and Adkins, *ibid.*, **58**, 710 (1936).

yellow needles were obtained. The crystals changed color at 120° and sintered gradually as the temperature was raised. The substance could not be recrystallized satisfactorily. When dissolved in cold toluene and plunged quickly into dry ice, crystals separated which were less pure than the starting product. When this methene was boiled in alcohol it decomposed to give 2-formyl-3,5-dicarbethoxy-4-methylpyrrole, m. p. 124°, and a residue which has not been identified.

Anal. Calcd. for $C_{21}H_{27}O_6N_2Cl$: C, 57.44; H, 6.20. Found: C, 58.01, 57.95; H, 6.20, 6.65.

The analytical discrepancy indicates an impurity which differs from the aldehyde used, because this has less C and H than the methene, and which probably is not 2,4-dimethyl-3-carbethoxypyrrole since this should have been removed by the ether wash used. Hence we feel that the discrepancy needs further investigation.

The attempted condensations of aldehydes and α-unsubstituted pyrroles to give N-methylmethenes followed the directions given above. The combinations tried were 2-formyl-3,5-dicarbethoxy-4-methylpyrrole with 1,2,4-trimethyl-3-carbethoxypyrrole; 1,4-dimethyl-2-formyl-3,5-dicarbethoxypyrrole with 2,4-dimethyl-3-carbethoxypyrrole and with 1,2,4-trimethyl-3-carbethoxypyrrole; 1,2,4-trimethyl-3-ethylpyrrole with 2-formyl-3-ethyl-4-methyl-5-carbethoxypyrrole, with 2-formyl-3-ethyl-4-methyl-5-carboxylpyrrole, and with 2-formyl-3,5-dimethyl-4-ethylpyrrole. These condensations led to reddish or purple oils.

1,2,4 - Trimethyl - 3 - carbethoxy - 5 - carboxylpyrrole.—Twenty-six grams of potassium hydroxide was dissolved in 300 cc. of 95% alcohol and 105 g. of 1,2,4-trimethyl-3,5-dicarbethoxypyrrole added and refluxed for two and one-half hours. The solution was poured into cold water, talc added and filtered. The pyrrole acid was precipitated with hydrochloric acid, filtered off and dried, yield 90%.

Anal. Calcd. for $C_{11}H_{15}O_4N$: C, 58.63; H, 6.71. Found: C, 58.93; H, 7.18.

1,2,4 - Trimethyl - 3 - carbethoxypyrrole.—The preparation was similar to that of 1,2,4-trimethyl-5-carbethoxypyrrole; yield 75%; m. p. 57°; mixed m. p. with the 5-carbethoxy isomer, 39°. The substance has nearly the same sickening sweet odor as its isomer. Repeated recrystallizations raised the m. p. to 62°.

Anal. Calcd. for $C_{10}H_{15}O_2N$: C, 66.25; H, 8.34. Found: C, 66.40; H, 8.59.

1,3,5,1′,3′,5′ - Hexamethyl - 4,4′ - dicarbethoxy - 2,2′ - dipyrrylmethane.—The procedure was similar to that of the corresponding 4,4′-diethylmethane except that hydrogen chloride catalyst was used and the mixture warmed. The yield was nearly quantitative, m. p. 151–152°.

Anal. Calcd. for $C_{21}H_{30}O_4N_2$: C, 67.33; H, 8.08. Found: C, 67.43; H, 8.45.

The preceding compound and its 4,4′-diethyl analog were treated with bromine in the usual manner for the preparation of methenes. Purple oils resulted from which no crystalline material could be isolated.

The method tried for the bromination of N-methyl pyrroles was essentially that of Fischer.[16] 1,2,4-Trimethyl-3-carbethoxypyrrole and 1,2,4-trimethyl-3-ethylpyrrole were tried and the products were purple oils.

The method tried for the condensation with formic acid was essentially that of Fischer and Zerweck.[17] The pyrroles used in the bromination were used in this condensation and again purple oils resulted.

3,5,3′,5′ - Tetramethyl - 4,4′ - dicarbethoxydipyrrylmethene, obtained by the formic acid condensation of Fischer and Zerweck was treated with sodium in the same manner as with Knorr's pyrrole. A bright red precipitate separated. When dimethyl sulfate was added to this the precipitate dissolved and the toluene solution turned green. When a toluene solution of the methene was treated with a small amount of mineral acid and warmed a similar green color appeared. This decomposition was even more marked in glacial acetic acid. Every attempt to recrystallize a mineral acid salt of this compound led to more or less extensive decomposition. A few minutes' boiling in glacial acetic acid was sufficient to complete this decomposition. We intend to submit this reaction to further investigation to determine whether or not this behavior is typical of dipyrrylmethenes.

Summary

1. The theoretical limits of a new type of isomerism have been discussed.

2. A program has been outlined which is designed to test the possibility of the existence of this type of isomerism.

3. The preparation of a group of N-methylpyrroles to fit into this program has been reported.

4. The formaldehyde synthesis of dipyrrylmethanes has been modified to permit the preparation of a completely alkylated dipyrrylmethane.

5. A method has been described for obtaining a dipyrrylmethene not available by older methods.

6. Attempts to prepare N-methyldipyrryl methenes have been described.

7. Certain decompositions of dipyrrylmethenes have been reported.

BALTIMORE, MD. RECEIVED MARCH 4, 1936

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[16] Fischer, *Sitz. ber. math. physik. Klasse Bayer. Akad. Wiss. München*, 410 (1915).

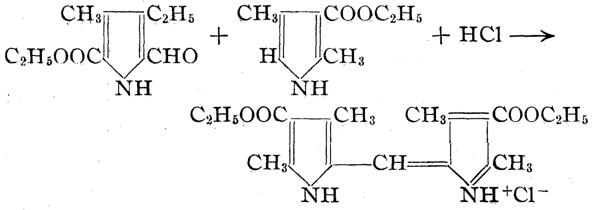
[17] Fischer and Zerweck, *Ber.*, **56**, 526 (1923).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Studies in the Pyrrole Series. II. The Mechanism of the Aldehyde Synthesis of Dipyrrylmethenes[1]

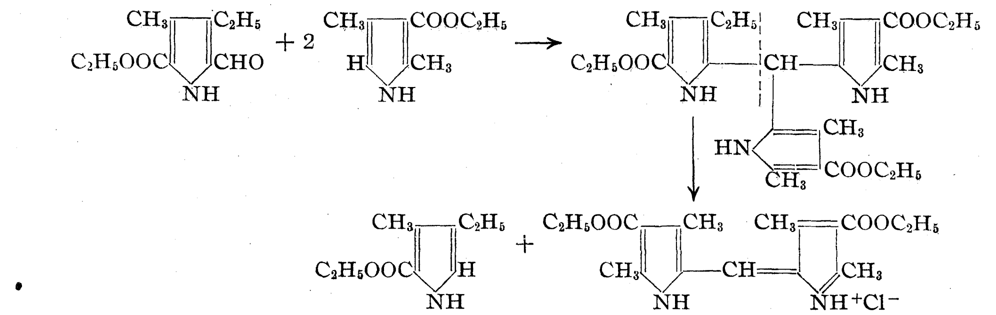
BY ALSOPH H. CORWIN AND JOHN S. ANDREWS

In the preceding paper[2] it was shown that the introduction of N-methyl groups into the pyrrole nucleus causes the aldehyde synthesis of methenes to follow a course different from that usually postulated. Fischer and Ernst[3] have also reported an anomalous aldehyde condensation



In order to account for the product obtained they assumed that the aldehyde was first hydrolyzed to yield formic acid which subsequently reacted with the 2,4-dimethyl-3-carbethoxypyrrole. This mechanism does not agree, however, with their observation that the best yield of methene resulted when two mols of the pyrrole were used for each mol of the aldehyde. These proportions suggest a tripyrrylmethane intermediate.

The suggestion of a tripyrrylmethane intermediate in the formation of methenes was unwittingly made by Piloty, Krannich and Will[4] who obtained a colorless compound as an intermediate in the synthesis of a methene and assigned to it the formula of a dipyrryl carbinol. Fischer and Ammann[5] proved this substance to be a tripyrrylmethane, substantiated Piloty's observation that hydrochloric acid would convert it into a methene but ignored his intuition that it was truly an intermediate in the reaction. If we assume a tripyrrylmethane as the intermediate in the reaction reported by Fischer and Ernst we have a complete explanation of the "abnormal" reaction by assuming cleavage at the bond which gives the symmetrical methene.



It becomes of interest, therefore, to determine whether or not tripyrryl methanes are actually intermediates in the methene syntheses. To this end we are reporting herewith a study of three reactions

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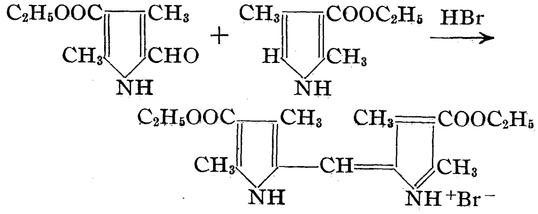

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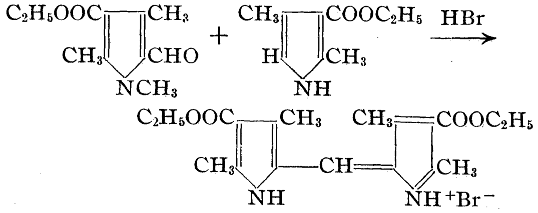

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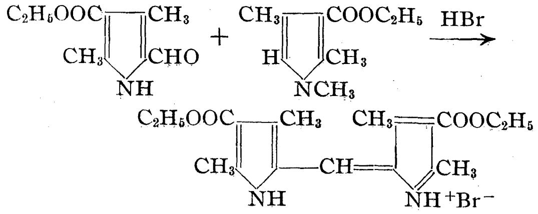

The first of these is well known. The latter two are new examples of anomalous aldehyde syntheses.

The possibility of the existence of a tripyrryl-

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[1] From the doctoral dissertation of John S. Andrews, The Johns Hopkins University, 1935.

[2] Corwin and Quattlebaum, THIS JOURNAL, **58**, 1081 (1936).

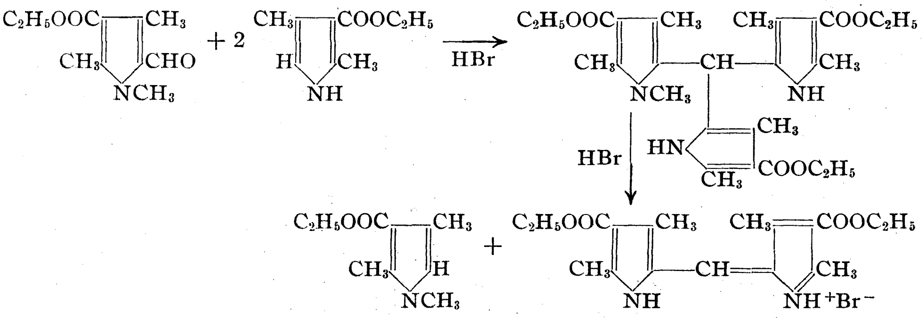
[3] Fischer and Ernst, *Ann.*, **447**, 146, 162 (1926).

[4] Piloty, Krannich and Will, *Ber.*, **47**, 2535 (1914).

[5] Fischer and Ammann, *ibid.*, **56**, 2319 (1923).

methane intermediate in the first reaction was tested by preparing the tripyrrylmethane and comparing its rate of cleavage with the rate of condensation of the aldehyde and the pyrrole. The fact that no appreciable difference in either velocity or yield could be found indicates that the tripyrrylmethane is a possible intermediate in the reaction.

In the second reaction a quantitative yield of methene was obtained when two mols of the pyrrole were used with one mol of the N-methyl aldehyde. In addition, 1,2,4-trimethyl-3-carbethoxypyrrole, predicted on the assumption of the tripyrrylmethane mechanism, was isolated in good yield. With equimolecular proportions the same products were formed but approximately half of the original aldehyde was recovered unchanged, indicating that it was not hydrolyzed to give formic acid under the conditions of the experiment. The tripyrrylmethane postulated as an intermediate was prepared and cleaved with acid under the conditions of the condensation. The same methene and N-methylpyrrole were obtained. We present these three facts as positive evidence of the existence of a tripyrrylmethane intermediate in this reaction as formulated in the following scheme



On the basis of this evidence we should predict that the condensation of the unmethylated aldehyde with the methylated pyrrole, the third reaction, should lead to an N-methyl methene. Actually, however, a new complication appears which upsets this prediction. The third reaction differs from the first two in that it is slow and does not give quantitative yields of the methene. That the postulated tripyrrylmethane is an intermediate in this reaction was proved by its actual isolation from the reaction mixture. Identification was made by comparison with a sample prepared by the Feist fusion method.[6] Cleavage of this material by acid led to the same yield of the methene as was produced in the same time by the condensation. We believe that these facts justify the formulation of the condensation given on the following page.

The three reactions which we have studied represent increasing degrees of complexity in the mechanism of the methene synthesis. They emphasize that the structures of the methenes obtained in the aldehyde condensation cannot in all cases be predicted from the starting products by the formulations previously used. The carbinol which is assumed to be formed first may undergo further condensation to give a tripyrrylmethane. This may cleave to form a second carbinol which may give either a methene or a second tripyrrylmethane. The latter may then yield a third carbinol and a third methene. The number of possible methenes resulting from the aldehyde condensation must be increased from one to three and we envisage the possibility that mixtures of these may occasionally result. The factors which influence the formation and cleavage of tripyrrylmethanes will be the subject of a later communication.

Experimental Part

Identification of 3,5,3′,5′-Tetramethyl-4,4′-dicarbethoxydipyrrylmethene (Piloty's Methene).—The recorded melting point of the hydrochloride[7] is not a true melting point but an irreversible decomposition point as noted by Fischer and Schubert.[8] Likewise the "melting point" of the free base, 190°, is the point of an irreversible decomposition. Thus the identification of the methene with unknown samples by the method of mixed melting points is theoretically unjustifiable. The method of mixed solubilities cannot be used on solutions of the methene hydrochloride for these darken and decompose on standing even at room temperature, thus precluding long contact of a solution with crystals to obtain a saturated solution. While a solution of the free base in methyl alcohol

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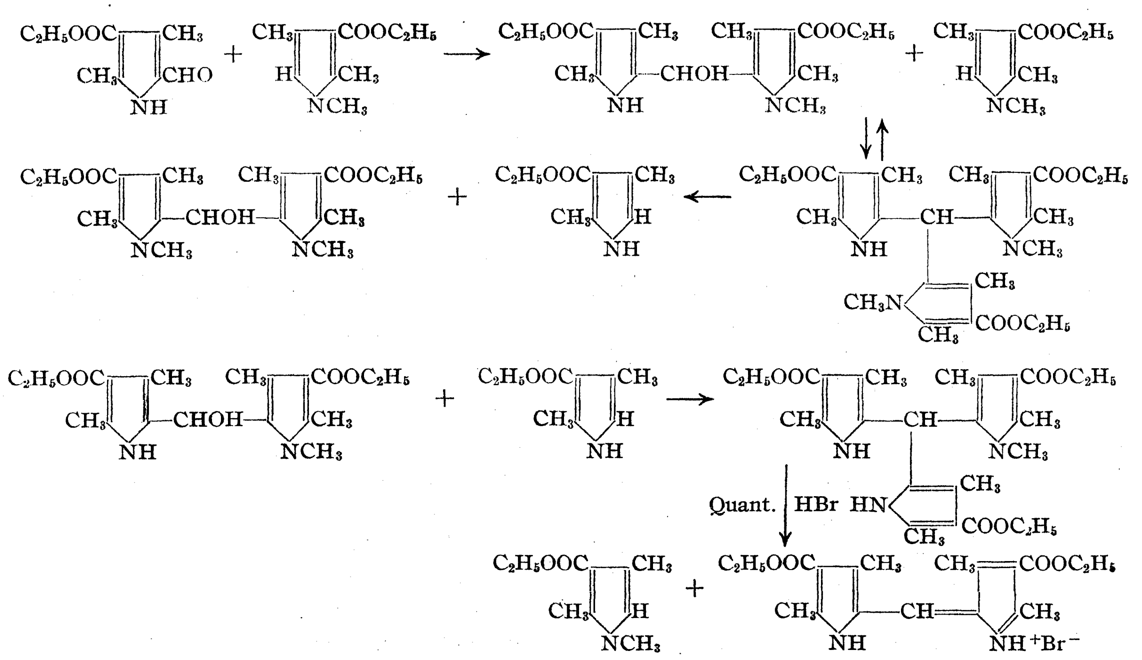
(6) Feist, *Ber.*, **35**, 1647 (1902).

(7) (a) Ref. 4, p. 2545; (b) Fischer and Zerweck, *ibid.*, **55**, 1947 (1922); (c) *ibid.*, **56**, 526 (1923); (d) Fischer and Heyse, *Ann.*, **439**, 255 (1924); (e) Fischer, Schormüller and Windecker, *ibid.*, **498**, 289 (1932).

(8) Fischer and Schubert, *Ber.*, **56**, 1209–1210 (1923).



appears to be stable so that the method of mixed solubilities might be used for a comparison of the bases, it was found more convenient to resort to catalytic reduction to the methane. By this method a substance with a true melting point was obtained which was suitable for purposes of identification. The method of Fischer and Ammann[5] (p. 2324) was modified by the substitution of alcohol for glacial acetic acid as a solvent, under which conditions no green by-product was formed. Adams catalyst was used; yield of the methane, 85%; m. p. 230°.

3,5,3′,5′,3″,5″ - Hexamethyl - 4,4′,4″ - tricarbethoxytripyrrylmethane.—The method of Fischer and Heyse[7d] (p. 246) was used. Repeated recrystallizations from alcohol–water alternated with methanol increased the purity of the compound. The substance sintered at 195° and melted with decomposition at 220–225°.

Anal. Calcd. for $C_{28}H_{37}O_6N_3$: C, 65.71; H, 7.29. Found: C, 65.70; H, 7.28.

Parallel Cleavage of Tripyrrylmethane and Aldehyde Condensation.—0.197 g. of hexamethyltricarbethoxytripyrrylmethane and 0.075 g. of 2,4-dimethyl-3-carbethoxy-5-formylpyrrole were dissolved in 20 cc. of methanol. Another solution was prepared by dissolving 0.15 g. of the aldehyde and 0.13 g. of 2,4-dimethyl-3-carbethoxypyrrole in the same amount of methanol. One cc. of hydrobromic acid solution, prepared by adding 3 cc. of saturated aqueous hydrobromic acid to 10 cc. of methanol, was added to each solution. Almost simultaneously and in less than one minute precipitates of the methene were formed in each tube. Filtration and washing with methanol yielded 0.27 g. of the hydrobromide of Piloty's methene in each case.

2,4-Dimethyl-3-carbethoxy-5-formylpyrrole.—The modification of the Gattermann synthesis introduced by Adams[9] is advantageous in this preparation. Fifty grams of 2,4-dimethyl-3-carbethoxypyrrole was dissolved in 500 cc. of anhydrous ether. Seventy-five grams of zinc cyanide was added, the mixture cooled to 10° and dry hydrogen chloride passed in rapidly until the solution was saturated (about three hours). The solution was allowed to warm to room temperature and to remain at this temperature for at least three hours. The supernatant liquid should be only slightly yellow colored. The imide hydrochloride was filtered off and washed with dry ether. It was then dissolved in 3.5 liters of cold water and filtered. Upon heating to 40° the solution deposited 53–54 g. of crystalline aldehyde. This was recrystallized from ethanol; m. p. 164°. Repeated recrystallizations raised the m. p. to 167°.

1,2,4 - Trimethyl - 3 - carbethoxy - 5 - formylpyrrole.—Twenty grams of 2,4-dimethyl-3-carbethoxy-5-formylpyrrole was dissolved in 200 cc. of dry commercial benzene, 7 g. of sodium monoxide was added and the suspension refluxed for one hour. Twelve cc. of freshly distilled dimethyl sulfate was added dropwise with vigorous mechanical stirring. The gelatinous mixture was refluxed for one hour, the sodium sulfate filtered off and washed with benzene and the filtrate allowed to stand overnight. About 3 g. of starting product crystallized out. The filtrate was steam distilled and the residual oil cooled until it solidified, filtered off and recrystallized from 80 cc. of methanol; yield, first crop, 8.5 g.; m. p. 97°. The mother liquor was cooled in dry ice and 6 g. of additional yield obtained.

Anal. Calcd. for $C_{11}H_{15}O_3N$: C, 63.18; H, 7.23. Found: C, 63.19; H, 7.28.

Condensations of 1,2,4-Trimethyl-3-carbethoxy-5-formylpyrrole with 2,4-Dimethyl-3-carbethoxypyrrole.—First experiment, 1:2 ratio: 1 g. of the N-methyl aldehyde and 1.65 g. of 2,4-dimethyl-3-carbethoxypyrrole were dissolved in 100 cc. of warm hexane. After cooling to room temperature dry hydrogen chloride gas was passed in for fifteen seconds and the resulting methene hydrochloride filtered

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[9] Adams and Levine, THIS JOURNAL, **45**, 2373 (1923); Adams and Montgomery, *ibid.*, **46**, 1518 (1924).

off and washed with a little hexane; yield, 1.90 g. or 100%; identified by reduction to the methane, m. p. 230°. The faintly yellow filtrate was evaporated on the steam-bath to about 20 cc. Chilling in dry ice–ethanol mixture yielded 0.6 g. of a nearly colorless crystalline solid, m. p. 57°. A mixed m. p. with 1,2,4-trimethyl-3-carbethoxypyrrole, m. p. 57°, gave no depression.

Second experiment, 1:1 ratio: 1 g. of the N-methyl aldehyde and 0.8 g. of the pyrrole were dissolved in 100 cc. of hexane and treated with dry hydrogen chloride for about thirty seconds. The methene was filtered off after five minutes and washed with hexane until the washings were nearly colorless; 0.9 g. of Piloty methene salt was obtained and identified by reduction to the methane. The filtrate was chilled in dry ice–ethanol mixture and 0.6 g. of colorless needles were obtained, m. p. 65–80°. This product was recrystallized by dissolving in ether at room temperature and cooling in dry ice mixture; 0.3 g. of colorless crystals was obtained, m. p. 94°, mixed m. p. with 1,2,-4-trimethyl-3-carbethoxy-5-formylpyrrole, no depression. By evaporation of the hexane filtrate from which the crude N-methyl aldehyde had been removed a nearly colorless residue was obtained. Recrystallization from 3–4 cc. of hexane by chilling in dry ice yielded 0.1 g. of material, m. p. 57°, mixed m. p. with 1,2,4-trimethyl-3-carbethoxypyrrole, no depression.

1,2,4,2′,4′,2″,4″ - Heptamethyl - 3,3′,3″ - tricarbethoxytripyrrylmethane.—The preparation was analogous to that of the hexamethyltricarbethoxytripyrrylmethane above. A preliminary purification was obtained by dissolving the product in chloroform and precipitating with petroleum ether. Crystallization from methanol yielded 1.6 g. of the methane and 0.3 g. additional was obtained from the mother liquor. Three recrystallizations from ethanol-water gave a colorless product, m. p. 177°.

Anal. Calcd. for $C_{29}H_{39}O_6N_3$: C, 66.24; H, 7.48. Found: C, 66.25, 66.29; H, 7.44, 7.44.

Cleavage.—Two-tenths gram of the heptamethyltricarbethoxytripyrrylmethane was dissolved in 50 cc. of hot methanol, cooled to 40°, and to it added 1 cc. of saturated aqueous hydrobromic acid. Within one minute the formation of a red precipitate was observed. This was filtered off after five minutes and washed with methanol; yield 0.16 g. or 95%. The product was identified by reduction to the methane, m. p. 230°.

Condensations of 2,4-Dimethyl-3-carbethoxy-5-formyl Pyrrole with 1,2,4-Trimethyl-3-carbethoxypyrrole.—Five grams of the aldehyde and 4.6 g. of the N-methylpyrrole were dissolved in 150 cc. of hot methanol and 0.5 cc. of saturated aqueous hydrobromic acid was added and the mixture allowed to stand at 70°. The precipitate which formed was reddish-purple even after washing with ether; yield 4.05 g. of methene hydrobromide, melting with decomposition at 213–215°. This was identified as Piloty methene by catalytic reduction to the methane, m. p. 230°, mixed m. p. with an authentic sample, 230°. The yield of methane from the discolored methene was identical with that from pure methene.

Parallel Test of Aldehyde with the N-Methylpyrrole and Aldehyde without the N-Methylpyrrole.—To test the possibility that the formation of Piloty's methene might be due to the cleavage of the aldehyde discovered by Fischer and Zerweck[7d] the course of the reaction of the aldehyde with and without the N-methylpyrrole was studied. Formation of the methene in the presence of the N-methylpyrrole takes place at a lower temperature than the cleavage of the aldehyde in the absence of the pyrrole. At a higher temperature, where both reactions proceed, the methene is formed more rapidly and in greater yield in the presence of the N-methylpyrrole than in its absence. A typical experiment follows.

Two-tenths gram of 2,4-dimethyl-3-carbethoxy-5-formylpyrrole and 10 cc. of methanol were mixed in each of two flasks. To the first, 0.185 g. of 1,2,4-trimethyl-3-carbethoxypyrrole was added. Both flasks were warmed until all the aldehyde dissolved and then held at about 50°; 0.1 cc. of 48% hydrobromic acid was added to each. The flask containing the N-methylpyrrole assumed a deep red color immediately. After about ten minutes it began to deposit colored crystals. A few minutes later the flask containing the aldehyde alone started to deposit similar crystals. After half an hour the crystals from both flasks were filtered off and weighed. From the flask containing aldehyde and pyrrole, 0.075 g. of the methene was obtained. From the flask containing the aldehyde alone, 0.040 g. of the methene was obtained.

Isolation of Tripyrrylmethane Intermediate in the Reaction.—If the flask containing the mixed aldehyde and N-methylpyrrole be cooled soon after the appearance of the deep red color mentioned above, tripyrrylmethane can be isolated as an intermediate. To favor this reaction, however, three mols of N-methylpyrrole was used to one mol of the aldehyde: 1 g. of the aldehyde and 2.75 g. of the N-methylpyrrole were dissolved in 35 cc. of hot methanol and 0.5 cc. of saturated aqueous hydrobromic acid added. The solution instantly became intensely red and, upon chilling in dry-ice and alcohol, deposited a large amount of a colorless precipitate. Upon warming to room temperature this deposit did not dissolve; yield, 2.5 g.; m. p. 146°. This was identified as 2,4,1′,2′,4′,1″,2″,4″-octamethyl-3,3′,3″-tricarbethoxytripyrrylmethane by a mixed m. p. with material made by the Feist fusion method given below. The yield was thus 88%.

2,4,1′,2′,4′,1″,2″,4″ - Octamethyl - 3,3′,3″ - tricarbethoxytripyrrylmethane.—One gram of 2,4-dimethyl-3-carbethoxy-5-formylpyrrole and 1.85 g. of 1,2,4-trimethyl-3-carbethoxypyrrole were fused at a temperature not exceeding 150° with about 0.1 g. of potassium bisulfate as a catalyst according to Feist's method. The product was purified by dissolving in methanol, adding ether and chilling in dry ice; yield, 1.5 g.; m. p. after several recrystallizations from C_2H_5OH–H_2O, 147–148°; mixed m. p. with substance from hydrobromic acid condensation above, no depression.

Anal. Calcd. for $C_{30}H_{41}O_6N_3$: C, 66.75; H, 7.66. Found: C, 66.67; H, 7.61.

Cleavage.—One and forty-five-hundredths grams of the di-N-methyltripyrrylmethane was dissolved in 25 cc. of hot methanol and when cool this solution was diluted with 50 cc. of ether. Five-tenths cc. of saturated aqueous hydrobromic acid was added and the solution allowed to stand at room temperature. A red coloration appeared very slowly and after one hour purple needles began to be deposited. After twenty hours these were filtered off and washed with ether yielding 0.3 g. of red-purple needles.

The material was identified as Piloty's methene salt by catalytic reduction to the methane, m. p. 230°. The yield was therefore 53%; mixed m. p. with 3,5,3',5'-tetramethyl-4,4'-dicarbethoxydipyrrylmethane, 230°. A parallel test using 1 g. of aldehyde and 1.85 g. of N-methylpyrrole under these conditions yielded 0.57 g. of methene or 52%.

Condensation of 1,2,4-Trimethyl-3-carbethoxy-5-formylpyrrole with 1,2,4-Trimethyl-3-carbethoxypyrrole.—When this condensation was carried out in acid media, highly colored tars resulted from which no crystalline compound could be isolated.

Summary

1. It has been demonstrated that tripyrrylmethanes can be and in two cases are intermediates in the formation of dipyrrylmethenes by Piloty's aldehyde synthesis.

2. As a result of the three possibilities for cleavage of a tripyrrylmethane of this type, the number of normally expected methenes from this reaction must be increased from one to three.

3. Experiments have been performed in which the substituent groups were so modified as to give each of the three possibilities.

BALTIMORE, MD. RECEIVED MARCH 4, 1936

[CONTRIBUTION FROM THE TECHNICAL DIVISION OF SHARP AND DOHME, INC.]

Thiobarbiturates. II

BY ELLIS MILLER, JAMES C. MUNCH, FRANK S. CROSSLEY AND WALTER H. HARTUNG

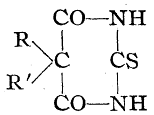
In an earlier communication[1] it was pointed out that in spite of the unfavorable indications obtained with diethyl thiobarbituric acid,[2-4] the sulfur analogs of the well-known barbituric acids gave promise of therapeutic value and merited further investigation. This is confirmed by a subsequent report of Tabern and Volwiler.[5]

Prior to the publication of their paper, only a few thiobarbituric acid derivatives were described in the literature, namely, the unsubstituted acid itself,[6,7] 5-methyl,[9] 5-ethyl,[8,9] 5-trimethylene,[10] 5,5-diethyl,[11,12] and 5,5-dipropyl thiobarbituric acids.[13]

Twenty new thio analogs of known barbituric

TABLE I

5,5-DISUBSTITUTED THIOBARBITURIC ACIDS



No.	R =	R' =	M. p., °C.	Empirical formula	Nitrogen, % Found (Kjeldahl)		Calcd.
1	CH_3CH_2-	CH_3CH_2-	174.5	$C_8H_{12}O_2N_2S$	13.48	13.53	14.0
2	CH_3CH_2-	$CH_3CH_2CH_2$-	174.5	$C_9H_{14}O_2N_2S$	13.01		13.08
3	CH_3CH_2-	$(CH_3)_2CHCH_2$-	170.5	$C_{10}H_{16}O_2N_2S$	12.42	12.48	12.28
4	$CH_3CH_2CH_2$-	$(CH_3)_2CH$-	168.5	$C_{10}H_{16}O_2N_2S$	12.19	12.30	12.28
5	$CH_3CH_2CH_2$-	$CH_2{=}CHCH_2$-	138	$C_{10}H_{14}O_2N_2S$	12.26	12.44	12.39
6	$CH_3CH_2CH_2$-	$CH_3CH_2CH_2CH_2$-	135.5	$C_{11}H_{18}O_2N_2S$	11.20	10.92	11.57
7	$CH_3CH_2CH_2$-	$(CH_3)_2CHCH_2$-	132	$C_{11}H_{18}O_2N_2S$	11.50	11.43	11.57
8	$CH_3CH_2CH_2$-	$CH_3CH_2\underset{\displaystyle CH_3}{\underset{\vert}{CH}}$-	165	$C_{11}H_{18}O_2N_2S$	11.30		11.57
9	$CH_3CH_2CH_2$-	$CH_3(CH_2)_4CH_2$-	114.4	$C_{13}H_{22}O_2N_2S$	10.76		10.40
10	$(CH_3)_2CH$-	$CH_2{=}CHCH_2$-	176.5	$C_{10}H_{14}O_2N_2S$	12.28	12.30	12.39
11	$(CH_3)_2CH$-	$(CH_3)_2CHCH_2$-	115–117	$C_{11}H_{18}O_2N_2S$	10.71		11.67
12	$(CH_3)_2CH$-	$CH_3(CH_2)_3CH_2$-	98.5	$C_{12}H_{20}O_2N_2S$	11.08	10.90	10.93
13	$CH_2{=}CHCH_2$-	$CH_3(CH_2)_2CH_2$-	120–121	$C_{11}H_{16}O_2N_2S$	11.87	11.90	11.66
14	$CH_2{=}CHCH_2$-	$(CH_3)_2CHCH_2$-	147	$C_{11}H_{16}O_2N_2S$	11.61	11.62	11.66
15	$CH_2{=}CHCH_2$-	$CH_3(CH_2)_3CH_2$-	112.5	$C_{12}H_{18}O_2N_2S$	11.15	11.09	11.02

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(1) Miller, Munch and Crossley, *Science*, **81**, 615 (1935).

(2) Fischer and v. Mering, *Therapie der Gegenwart*, **101**, 97 (1903).

(3) Fraenkel, "Die Arzneimittelsynthese," 6th ed., 1927, p. 510.

(4) Ostwald, "Chemische Konstitution und pharmakologischer Wirkung," Gebrüder Borntraeger, Berlin, 1924, p. 130.

(5) Tabern and Volwiler, THIS JOURNAL, **57**, 1961 (1935).

(6) Johnson and Johns, *ibid.*, **36**, 973 (1914).

(7) Dox and Plaisance, *ibid.*, **38**, 2156, 2164 (1916).

(8) Wheeler and Jamieson, *Am. Chem. J.*, **32**, 352 (1904).

(9) Einhorn, *Ann.*, **359**, 171 (1908).

(10) Dox and Yoder, THIS JOURNAL, **43**, 683 (1921).

(11) Fischer and Dilthey, *Ann.*, **335**, 350 (1904); *Chem. Centr.*, **75**, II, 1381 (1904).

(12) German Patents 162,219, 171,292, 182,764, 234,012, 235,801.

(13) German Patents 182,764, 234,012, 235,801; ref. 9, p. 177.

acid derivatives have been prepared in our laboratories. Six of these (the ethyl isopropyl, ethyl allyl, ethyl *n*-butyl, ethyl isoamyl, ethyl phenyl and allyl *s*-butyl thiobarbituric acids) are included in the list given by Tabern and Volwiler, and since their properties agree substantially with those already described, they need not be repeated here.

The synthesis of these compounds follows a single pattern, and one example will illustrate the method.

Ethyl *n*-Propyl Thiobarbituric Acid.—In a 1-liter, 3-necked round-bottomed flask, equipped with a mechanical stirrer and reflux condenser, is placed 276 ml. of anhydrous ethanol, and in it is dissolved 13.8 g. (0.6 mole) of metallic sodium. 24 3 g. (0.32 mole) of thiourea is added, while stirring. With continued stirring, 46 g. (0.2 mole) of ethyl *n*-propyl malonic ester is added quickly. Stirring is continued and the mixture is gently heated to incipient refluxing over a period of six to seven hours. After standing overnight the reaction mixture is concentrated on a steam-bath to about 150 ml. and diluted with 75 ml. of water. Concentrated hydrochloric acid is now added until the mixture is strongly acid to litmus paper, whereupon the desired ethyl *n*-propyl thiobarbituric acid precipitates out. The crystals, after drying and recrystallizing from toluene, melt at 174–174.5° (uncorr.).

By substituting an equimolar amount of the appropriate malonic ester in the above reaction, other desired 5,5-disubstituted thiobarbituric acids have been obtained. In general the yield is somewhat higher than that obtained for the oxygen analogs.

The thiobarbituric acid derivatives are listed in Table I.

The intermediate dialkyl malonic esters have all been described in the literature. They were purchased where possible, or synthesized by well-known procedures. Of the esters synthesized, it may be said that in general the yields are satisfactory, except when a second alkyl group is being introduced into secondary-alkylmalonic ester.

Summary

Twenty 5,5-disubstituted thiobarbituric acids have been prepared and their chemical characteristics determined. Of these, six have recently been described by others. The method of preparation corresponds to that used for the oxygen analogs, but the yields are generally somewhat higher. A pharmacological study of these compounds has been completed and will be presented elsewhere.

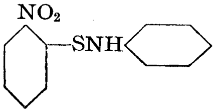
GLENOLDEN, PENNA. RECEIVED MARCH 7, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Molecular Rearrangement of Sulfenanilides.[1] III

BY MAURICE L. MOORE[2] AND TREAT B. JOHNSON

In previous communications[3] from this Laboratory, the authors have discussed the rearrangement of certain aromatic sulfenanilide compounds of Type I. They have shown that on heating these alone or in the presence of an excess of the corresponding amine, they undergo rearrangement to *p*-aminophenyl sulfides II, whereas by digestion in alcoholic sodium hydroxide solution they give the corresponding *o*-mercaptodiphenylamines III. We have now extended the study of these molecular rearrangements to other compounds of similar structure, and in this paper we shall discuss the results of some new experiments in which we have accomplished molecular rearrangements under the influence of heat.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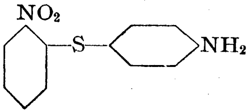
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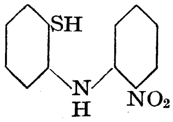
III

In addition to the compounds of Type I, previously studied by the authors, many others examined give the same type of change upon heating. Thus, 2,4-nitrochlorobenzene-sulfenanilide, prepared by the action of 2,4-nitrochlorobenzenesulfenyl chloride upon aniline, gave 2,4-nitrochlorophenyl-4′-aminophenyl sulfide when heated at a temperature of 150–160° or when heated with an excess of aniline at a temperature of 180–190°. The corresponding *o*-toluidide underwent

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[1] In our previous papers we have observed the nomenclature of the earlier workers in related fields in naming these sulfur compounds, but we have noticed that the abstractors for the *Chemical Abstracts* prefer and have applied another nomenclature. In order to be consistent and to maintain uniformity of spelling, in our Journals, we are, therefore, now following their system, as indicated in the Abstracts of our previous papers, and also in the last edition of "Organic Syntheses," Vol. XV, 1935, p. 45.

[2] A. Homer Smith Research Fellow in Organic Chemistry, 1935–1936.

[3] Moore and Johnson, THIS JOURNAL, **57**, 1517, 2234 (1935); see also *Science*, **81**, 643 (1935).

a similar rearrangement, giving the isomeric *p*-aminophenyl sulfide. 2-Nitrobenzene-sulfen-*o*-chloroanilide and 4-nitrobenzene-sulfen-*o*-chloroanilide were prepared by the action of the nitrobenzene-sulfenyl chloride on *o*-chloroaniline and both have been rearranged successfully to the corresponding sulfides by heating.

It is now quite apparent from our studies that the -S-NH- linkage between aromatic nuclei is very susceptible to a change of structure by application of heat, forming aminophenyl sulfides II and that the transformation involved is universal to compounds of Type I. Substituents in either benzene nucleus of the sulfenanilide I do not seem to have any influence in affecting a successful molecular rearrangement as long as there is at least a para or an ortho position open in the aromatic nucleus. Rearrangement, however, to the para position predominates. If this position is occupied then an ortho substituted sulfide is formed.

In the case of the methylene type of rearrangement studied by Cohn and Fischer[4] it has been shown that the anilide group in the molecule can be displaced by another aromatic amine which will then undergo rearrangement when digested in an acid solution of the amine hydrochloride. For example, when *p*-aminobenzyl-anilide IV is digested on the steam-bath with a hydrochloric acid solution of *o*-toluidine, diamino-phenyl-tolyl-methane V is formed in excellent yield. This displacement of amine and subsequent rearrangement is explained upon the basis of the following intermediate reactions

$$NH_2C_6H_4—CH_2—NHC_6H_5 \xrightarrow[\text{hydrolysis}]{\text{Acid}} \underset{\text{IV}}{NH_2C_6H_4CH_2OH} + C_6H_5NH_2$$

$$NH_2C_6H_4CH_2OH + NH_2C_6H_4CH_3(o) \xrightarrow{\text{Acid}} \underset{\text{V}}{NH_2C_6H_4CH_2C_6H_3(CH_3)NH_2}$$

In continuing the study of the rearrangement of sulfenanilides I, it was our prediction that these compounds would likewise suffer displacement of the anilide group in the molecule with subsequent rearrangement when heated in the presence of an excess of certain amines. This assumption has been confirmed. For example, when 2-nitrobenzene-sulfenanilide I was heated at a temperature of 180–190° with an excess of *o*-toluidine, 2-nitrophenyl-3′-methyl-4′-aminophenyl sulfide was formed. 2-Nitrobenzene-sulfen-*o*-toluidide and the corresponding *p*-toluidide also responded to similar reactions when treated with different aromatic amines. Aniline, *o*-toluidine and *p*-toluidine are able to displace each other from the respective sulfenanilide molecule.

Notwithstanding this similarity in chemical behavior of the two different types of compounds when they interact with amines, it does not seem plausible to explain our sulfenanilide reactions upon the theoretical basis of the mechanism suggested above and involving first an hydrolysis. When compounds of Type I are heated in acid solution the amine radical is removed and a disulfide is formed smoothly. No rearrangement takes place in an acidic, aqueous or alcoholic medium. Heating with an amine alone leads to a normal rearrangement forming a sulfide in good yield. In an alkaline solution the sulfenanilide I is unstable and undergoes a diphenylamine rearrangement III. These results seem to preclude any initial hydrolysis of I taking place in the displacement and subsequent rearrangement reaction although there must be some dissociation of the sulfenanilide molecule I before an intramolecular change can take place.

We have also found that the amine, *o*-chloroaniline, will not displace the anilide group in sulfenanilide compounds I although a normal rearrangement does take place upon heating. Thus, if 2-nitrobenzene-sulfenanilide I is heated at 180–190° with an excess of *o*-chloroaniline rearrangement takes place with formation of the sulfide II. Under similar conditions the corresponding sulfen-*o*- and *p*-toluidides undergo a similar rearrangement without being displaced from the molecule by the *o*-chloroaniline. It was found, however, that the *o*-chloroanilide group, when present in the sulfenanilide molecule, is easily displaced by other amines. For example, 2-nitrobenzene-sulfen-*o*-chloroanilide gave the sulfide II when heated at a temperature of 180–190° in the presence of an excess of aniline. Similar transformations were accomplished by heating the *o*-chloroanilide with *o*- and *p*-toluidine. In all three cases the *o*-chloroaniline group was displaced smoothly. These results indicate that the reactivity of the aromatic amines used determines whether there is a displacement of the group already present in the sulfenanilide molecule before a rearrangement takes place.

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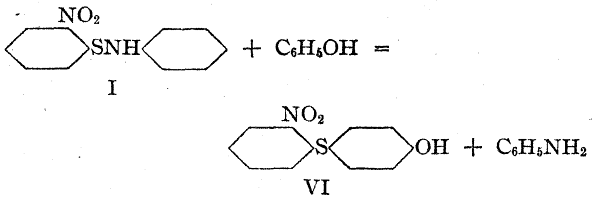
(4) Cohn and Fischer, *Ber.*, **33**, 2586 (1900).

An attempt was made to prepare directly aromatic sulfide phenols VI by heating compounds of the sulfenanilide type I with an excess of a phenol



but without success. The phenol served merely as a solvent and the final result under such experimental conditions is a normal rearrangement of the sulfenanilide I to its isomeric aminophenyl sulfide II.

Experimental Part

2,4-Nitrochlorobenzene-sulfenanilide.—The 2,4-nitrochlorobenzene-sulfenyl chloride used here was prepared by allowing chlorine gas to react with di-(2,4-nitrochlorophenyl) disulfide[5] according to the method of Zincke.[6] 2,4-Nitrochlorobenzene-sulfenyl chloride (25 g.) dissolved in anhydrous ether (500 ml.) was allowed to react with aniline (23 g.) dissolved in ether (50 ml.). The aniline solution was added slowly through a reflux condenser to the 2,4-nitrochlorobenzene-sulfenyl chloride solution. A precipitate of aniline hydrochloride immediately formed and sufficient heat was evolved to boil the ether. After standing for one hour the aniline hydrochloride was then removed by filtration and the ether expelled by distillation when the sulfenanilide crystallized as an orange-yellow solid; yield 33 g. It crystallized from alcohol, m. p. 102° and was soluble in the ordinary organic solvents but insoluble in dilute hydrochloric acid.

Anal. Calcd. for $C_{12}H_9O_2N_2SCl$: N, 9.98; S, 11.41; Cl, 12.66. Found: N, 9.82, 9.97; S, 11.15, 11.25; Cl, 12.46, 12.63.

2,4-Nitrochlorobenzene-sulfen-*o*-toluidide.—From 2,4-nitrochlorobenzene-sulfenyl chloride (25 g.) and *o*-toluidine (24 g.); yield 28 g. It crystallized from alcohol as bright glistening orange-red platelets; m. p. 127°.

Anal. Calcd. for $C_{13}H_{11}O_2N_2SCl$: N, 9.51; S, 10.87; Cl, 12.06. Found: N, 9.54, 9.67; S, 10.47, 10.70; Cl, 12.02, 12.14.

2-Nitrobenzene-sulfen-*o*-chloroanilide.—From 2-nitrobenzene-sulfenyl chloride (25 g.) as previously prepared[7] and *o*-chloroaniline (32 g.). This reaction proceeded much slower than expected and the *o*-chloroaniline hydrochloride did not settle out completely until after the ether solution had stood for at least two hours; yield 33 g. It crystallized from alcohol in bright yellow crystals melting at 130°. The compound is only slightly soluble in alcohol but is easily soluble in the ordinary organic solvents.

Anal. Calcd. for $C_{12}H_9O_2N_2SCl$: N, 9.98; S, 11.41; Cl, 12.66. Found: N, 10.11, 10.14; S, 11.62, 11.48; Cl, 12.95, 12.80.

4-Nitrobenzene-sulfen-*o*-chloroanilide.—*p,p′*-Dinitrodiphenyl disulfide[8] (25 g.) was suspended in ice-cold anhydrous chloroform (250 ml.) and treated with chlorine gas until all the solid was dissolved. The excess of chlorine gas was then removed by distillation of the chloroform under reduced pressure to a volume of 150 ml. and then made up to a volume of 400 ml. with anhydrous ether. This solution of 2-nitrobenzene-sulfenyl chloride was subsequently treated with *o*-chloroaniline (32 g.) dissolved in ether (100 ml.) when the sulfenanilide above was obtained in a yield of 23 g. of crude material. This was contaminated with 4,4′-dinitrodiphenyl disulfide and after final purification by washing with ether the yield was reduced to 8 g. This was recrystallized from alcohol, m. p. 99–101°. It is immediately converted to 4,4′-dinitrodiphenyl disulfide by treatment with dilute hydrochloric acid.

Anal. Calcd. for $C_{12}H_9O_2N_2SCl$: N, 9.98; S, 11.41; Cl, 12.66. Found: N, 9.84, 10.06; S, 11.20, 11.31; Cl, 12.51, 12.40.

Rearrangements by Heating. 2,4-Nitrochlorophenyl-4′-aminophenyl Sulfide.—From 2,4-nitrochlorobenzene sulfenanilide (10 g.) when heated for six hours at 150–160°, according to our previous procedure.[6] Recrystallization from alcohol gave a product crystallizing as bright, glistening yellow plates, m. p. 127–129°. The sulfide was easily soluble in the ordinary organic solvents, and the hydrochloride was difficultly soluble in water. The hydrochloride was obtained in crystalline form by dissolving the free base in ether solution and slowly adding concentrated hydrochloric acid, m. p. 215–225°.

Anal. Calcd. for $C_{12}H_9O_2N_2SCl$: N, 9.98; S, 11.41; Cl, 12.66. Found: N, 9.96, 9.89; S, 11.30, 11.14; Cl, 12.90, 12.79.

The sulfide was obtained with better results by heating the sulfenanilide (10 g.) with an excess of aniline (20 ml.) at 180–190° for six hours. The mixture was worked up according to the previous procedure and 5 g. of material obtained. It was purified by crystallizing from alcohol after decolorizing with norite, m. p. 129°.

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(5) This compound was prepared by the procedure given for *o,o′*-dinitrodiphenyl disulfide as described by Bogert and Stull, "Organic Syntheses," John Wiley & Sons, Inc., New York, 1928, Vol. VIII, p. 64.

(6) Zincke, *Ann.*, **416**, 111 (1918).

(7) Moore and Johnson, THIS JOURNAL, **57**, 1517 (1935).

(8) This compound was prepared by the procedure given for *o,o′*-dinitrodiphenyl disulfide[4] as used by Foss, Dunning and Jenkins [THIS JOURNAL, **56**, 1978 (1934)]. The results of this procedure are very unsatisfactory due to the formation of many by-products during the reaction. Fromm and Wittmann [*Ber.*, **41**, 2264 (1908)] have studied the conditions of this reaction in some detail. They have reported the isolation of 4,4′-dinitrodiphenyl sulfide, m. p. 154°, 4,4′-nitroaminodiphenyl sulfide, m. p. 142°, and the dinitrophenyl ether of azophenyl-*p*-dimercaptan, m. p. 164°, as well as the desired compound, 4,4′-dinitrodiphenyl disulfide, m. p. 181°. The Russian workers Voraghtzow and Krihov [*J. Gen. Chem.* (U. S. S. R.), 2939 (1932)] have isolated and identified two isomers of the disulfide present in the mixture, *i. e.*, $(NO_2C_6H_4)_2S{:}S$, m. p. 134° and the symmetrical compound, m. p. 181°. In our results following the above procedure we have isolated all of the above substances in varying quantities but have found the largest quantity present to be the dinitrodiphenyl sulfide. We have separated 60–75 g. of the desired disulfide, m. p. 181°, from 200 g. of the reaction product (m. p. 120–130°) by treatment with boiling benzene. All of the above materials will dissolve in the benzene except the symmetrical disulfide. This is obtained in fair purity, m. p. 172–179°, in this one step but the yield is relatively low. Further separation of the desired material from the soluble mixture involves considerable time and effort.

TABLE I

In these first eight experiments it is shown that the excess of amine present could displace the anilide group in the sulfenanilide molecule followed by rearrangement to give an "aminophenyl sulfide" when heated at 180–190°. In experiments 9, 10 and 11 it is shown that *o*-chloroaniline is not able to displace the anilide group in the sulfenanilide but that a normal rearrangement takes place without the *o*-chloroaniline taking part in the change.

	Sulfenanilide	Amine	Sulfide	M. p., °C.	Yield, %
1	2-Nitrobenzene-sulfenanilide[6]	*o*-Toluidine	2-Nitrophenyl-3′-methyl-4′-	101–103	60
2	2-Nitrobenzene-sulfenanilide	*p*-Toluidine	2-Nitrophenyl-5′-methyl-2′-	105–107	55
3	2-Nitrobenzene-sulfen-*o*-toluidide	Aniline	2-Nitrophenyl-3′-	103–105	65
4	2-Nitrobenzene-sulfen-*o*-toluidide	*p*-Toluidine	2-Nitrophenyl-5′-methyl-2′-	105–107	60
5	2-Nitrobenzene-sulfen-*p*-toluidide	Aniline	2-Nitrophenyl-4′-	103–105	70
6	2-Nitrobenzene-sulfen-*p*-toluidide	*o*-Toluidine	2-Nitrophenyl-3′-methyl-4′-	101–103	60
7	2-Nitrobenzene-sulfen-*o*-chloroanilide	*o*-Toluidine	2-Nitrophenyl-3′-methyl-4′-	101–103	40
8	2-Nitrobenzene-sulfen-*o*-chloroanilide	*p*-Toluidine	2-Nitrophenyl-5′-methyl-2′-	105–107	35
9	2-Nitrobenzene-sulfenanilide	*o*-Chloroaniline	2-Nitrophenyl-4′-	105–106	70
10	2-Nitrobenzene-sulfen-*o*-toluidide	*o*-Chloroaniline	2-Nitrophenyl-3′-methyl-4′-	101–103	70
11	2-Nitrobenzene-sulfen-*p*-toluidide	*o*-Chloroaniline	2-Nitrophenyl-5′-methyl-2′-	105–107	60

2,4-Nitrochlorophenyl-3′-methyl-4′-aminophenyl Sulfide.—From 2,4-nitrochlorobenzene-sulfen-*o*-toluidide (10 g.) when heated with *o*-toluidine (15 ml.) in a yield of 6 g. Purification from alcohol after digesting with norite gave bright yellow prisms, m. p. 113–115°. A portion of the aminophenyl sulfide readily dissolved in ether and upon the addition of concentrated hydrochloric acid, gave a colorless precipitate of the hydrochloride, m. p. 216–220°.

Anal. Calcd. for $C_{13}H_{33}O_2N_2SCl$: N, 9.51; S, 10.87; Cl, 12.06. Found: N, 9.41, 9.36; S, 10.94, 10.80; Cl, 12.06, 12.20.

4-Nitrophenyl-3′-chloro-4′-aminophenyl Sulfide.—From the 4-nitrobenzene-sulfen-*o*-chloroanilide (m. p. 99–101°) when heated with boiling *o*-chloroaniline. The material was purified by dissolving in a mixture of ether–petroleum ether, boiling with norite and slowly evaporating. Yellow crystals were obtained, m. p. 127–129°. The free base was readily soluble in ether and gave a colorless crystalline hydrochloride.

Anal. Calcd. for $C_{12}H_9O_2N_2SCl$: N, 9.98. Found: N, 10.37, 10.11.

Rearrangement of Sulfenanilides by Heating in the Presence of an Excess of Aromatic Amines.—Our general procedure was to place 5 g. of the sulfenanilide in 10 ml. of the aromatic amine and heat on an oil-bath at a temperature of 180–190° for four hours. The reaction fluid was then poured into dilute hydrochloric acid solution with vigorous stirring and cooled in an ice-bath. The solid hydrochloride of the rearrangement product was filtered off and dissolved in alcohol. This solution was then neutralized with 5% sodium hydroxide solution, decolorized by boiling several times with norite, and the free aminophenyl sulfide separated by crystallization after cooling in an ice-bath. The reaction product in each case was identified by mixed melting points with the known amino sulfides. The results are tabulated in Table I.

Reaction in Acidic Alcoholic Solution.—2-Nitrobenzenesulfenanilide I (5 g.) was dissolved in alcohol (25 ml.) and gently refluxed after concentrated hydrochloric acid (3 ml.) was added. If the refluxing was discontinued at the end of fifteen minutes the sulfenanilide was recovered whereas if the refluxing was continued for some time, *o,o*′-dinitrodiphenyl disulfide began to be formed and at the end of about two hours all the sulfenanilide had been converted into the insoluble disulfide, m. p. 193–195°.

Summary

1. A study of the rearrangement of the sulfenanilide type of compounds to their isomeric aminophenyl sulfides has been continued, and several new applications have been made of the rearrangement.

2. These rearrangements are influenced by the presence of other aromatic amines. The anilide group is replaceable when the sulfenanilide is warmed with another amine giving the corresponding aminophenyl sulfide.

3. The amine, *o*-chloroaniline, fails to respond in this replacement reaction. On the other hand its rearrangement is possible when it occurs in sulfenanilide combinations.

4. All sulfenanilides are decomposed by action of acids with formation of organic disulfides and an amine.

NEW HAVEN, CONN.

RECEIVED MARCH 20, 1936

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

The Effect of Oxygen on the Reaction between Bromine and Butadiene

BY G. B. HEISIG AND H. M. DAVIS

That oxygen influences the rate of the addition of bromine to unsaturated hydrocarbons was shown by the work of H. S. Davis[1] on the determination of acetylenes by titration with bromine. Schultze[2] also showed the disturbing influence of oxygen in the titration of cyclopentadiene with bromine. More recently, Bauer and Daniels[3] reported that the rate of the reaction between solutions of bromine and cinnamic acid in carbon tetrachloride was rapid, even in the dark, in the absence of oxygen, but slow in its presence. These observations, together with the remarkable effects produced by the presence of oxygen and peroxides noted by Kharasch and his collaborators,[4] serve to emphasize the importance of the presence of oxygen on the rates of reactions. That this effect may not be general is suggested in the note of Deanesly,[5] which states that oxygen fails to produce any inhibitory effect on the addition of chlorine to olefinic hydrocarbons such as beta-butylene, although he admits that the reaction may be so fast that a retardation by oxygen may be difficult to detect. Since there were no quantitative data available to show whether oxygen affects the rate of addition of a halogen to an unsaturated hydrocarbon in the gas phase, it seemed desirable to investigate the problem. The reaction between gaseous bromine and butadiene in the presence of nitrogen containing about 0.3% of oxygen, studied by Heisig and Wilson,[6] was chosen for the investigation. The reaction between equal numbers of molecules of bromine and butadiene is bimolecular and occurs largely on the surface of the reaction vessel. The product is 1,4-dibromobutene. This study is of more than usual interest since it involves the effect of oxygen on the addition of bromine to a conjugated system.

The apparatus used in the previous investigation was altered to permit the preparation of gaseous reaction mixtures with increased oxygen content or with oxygen completely absent. In the first runs of the present study, the oxygen content of the reaction mixtures was increased from a partial pressure of 2 mm. of mercury to 375 mm. by using purified, dry, tank oxygen instead of nitrogen as the diluting gas employed to bring the initial pressure in the reaction sphere up to that of the atmosphere. The product under these conditions had a melting point of 46–47° instead of the 51–52° found for the product obtained from mixtures containing 0.3% of oxygen or from mixtures from which oxygen was excluded. Also, the rate of the reaction was somewhat slower than that observed when the partial pressure of the oxygen was 0.3%, as can be seen in Tables I and II.

TABLE I

TYPICAL RUNS. REACTION BETWEEN BROMINE AND BUTADIENE WITH VARIOUS CONCENTRATIONS OF OXYGEN

Press. O_2 mm....		375	2	Trace	Small trace	0
Run............		8	10	11	12	13
Min.	Sec.	Pressure drop of alpha-bromonaphthalene, mm.				
0	5	1.8	3.5	3.5	7.8	12.0
	10	3.5	6.2	6.2	11.4	15.0
	20	6.6	9.9	11.0	14.6	18.0
	30	9.3	12.4	14.5	16.7	19.8
	40	11.4	14.3	16.8	18.1	20.9
	50	12.9	15.8	18.5	18.8	21.6
1	0	14.2	17.1	19.8	19.4	22.1
1	30	16.8	20.1	22.5	20.6	22.8
2		18.6	21.9	24.3	21.4	23.3
2	30	19.8	23.1	25.6	21.9	23.5
3		20.8	24.0	26.5	22.2	23.7
4		21.9	25.2	27.6	22.6	23.9
5		22.9	25.9	28.2	22.8	24.5
7		24.1	26.8	29.0	22.9	24.6
10		25.0	27.3	29.7	23.3	24.7
15		26.0	27.9	30.1	23.6	25.0
20		26.2	28.3	30.3	23.9	25.3
30		27	28.6	30.8	24.4	25.7
∞		28.7	29.6	31.5	25.3	27.0

The apparatus was then modified so that the tank nitrogen was passed over hot, freshly reduced copper gauze. All parts of the apparatus were evacuated and then thoroughly flushed with the oxygen-free nitrogen. When nitrogen so treated was the only diluent used, the reaction rate was greater than that obtained when (untreated) tank nitrogen was the diluent. Moreover, the rate increased with subsequent runs, as would be expected with the progressive removal of the last traces of oxygen from the purifying

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(1) H. S. Davis, *et al.*, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 108 (1931).

(2) Schultze, THIS JOURNAL, **56**, 1552–56 (1934).

(3) Bauer and Daniels, *ibid.*, **56**, 2014 (1934).

(4) Kharasch and Potts, *ibid.*, **58**, 57 (1936). This is the last published article.

(5) Deanesly, *ibid.*, **56**, 2501 (1934).

(6) Heisig and Wilson, *ibid.*, **57**, 859–63 (1935).

TABLE II

COMPARISON OF THE CURVES. TYPICAL DATA

				Slope when reaction is 80% completed			Slope when reaction is 67% completed		
Run	P_{O_2} mm.[a]	Total $-\Delta P$, exptl., mm.[b]	Δt to initial reading, sec.	$-\Delta P$ of slope, mm.[b]	Δt since start of reactn., sec.	Slope of tangt.	$-\Delta P$ of slope, mm.[b]	Δt since start of reactn., sec.	Slope of tangt.
8	375	28.7	25	17.2	120	17°55′	9.7	57	48° 5′
10	2	29.6	30	18.3	101	27° 8′	10.8	53	52°46′
11	0 (trace)	31.5	25	20.2	88	27°38′	12.7	49	59°59′
12	0 (small trace)	25.3	20	14.0	38	53°17′	6.5	24	80°30′
13	0	27.0	20	15.7	32	60°28′	8.2	22	84°12′

[a] Pressure given in mm. of mercury. [b] Pressure given in mm. of alpha-bromonaphthalene.

train. The product had the same appearance and melting point as that obtained when tank nitrogen (0.3% oxygen) was used.

The reaction was fast in all cases; in fact, somewhat more than half of the reaction took place in the twenty to thirty seconds required to mix the gases before the first reading could be made. The vapor pressure of the product is about 13 mm. of alpha-bromonaphthalene. When the first reading is made the gases in the reaction sphere are already saturated with product and a sufficient amount has been formed to cover the surface with a monomolecular layer.

It will be noted in Table II that the total observed pressure drop is somewhat smaller in the runs in which no oxygen was present, although the time required to make the first reading is less. This is in agreement with the other evidence that the reaction is faster in the absence of oxygen, since it indicates that a greater part of the reaction occurs before the first reading can be taken.

For ready comparison of the rates of the reactions, a curve for each experiment was prepared by plotting observed pressure drop against time. The slopes of the tangents to the curves when 80% of the calculated pressure drop has occurred, increase as the proportion of oxygen in the mixture decreases, as can be seen from column 7 in Table II. The greater the angle, the more rapidly is the reaction taking place. This is not a fortuitous coincidence, for the slopes determined when 66.7% of the reaction is completed increase in the same order. Furthermore, the time required for 80 and 66.7% of the reaction to take place decreases with the amount of oxygen present, as can be seen in columns 6 and 9 of Table II.

Since the rate of the reaction is sensitive to a small concentration of oxygen, and since the earlier work showed that the reaction occurred largely on the surface, a reasonable mechanism is that chains are initiated at the wall of the reaction vessel, and are broken by the oxygen. The data however do not exclude a mechanism in which the reaction occurs wholly on the surface and the rate of the reaction is decreased because of the occupation of the "active spots" on the surface by oxygen.

Experimental.—The apparatus was that described by Heisig and Wilson.[6] It was modified by the introduction of an electrically heated roll of copper screen to remove the 0.3% of oxygen in the tank nitrogen before it passed into the purifying and drying train. Before each run, the hot copper gauze was subjected to a long treatment with a stream of hydrogen under a pressure of one atmosphere, thus ensuring an active surface. A connection was also provided to permit purified oxygen to be mixed with the butadiene used in the experiment. This was a metal-to-glass connection. The oxygen was scrubbed by passage through three double wash bottles filled with a 40% solution of potassium hydroxide, and was dried by passage through calcium chloride and then through resublimed phosphorus pentoxide. The butadiene and bromine were portions of preparations of these substances used in the previous investigation. The reaction vessel had a volume of 53.8 cc. The slopes of the tangents to the curves were determined by a variation of the method described by Lipka.[7]

A grant was received from the Research Funds of the Graduate School to aid in carrying out this work.

Summary

The reaction between equimolar mixtures of bromine and butadiene has been studied in the presence of a partial pressure of oxygen at 375 mm., 2 mm. (Hg), and in the absence of oxygen, the total pressure of the reaction mixture being equal to that of the atmosphere.

The rate of the reaction as measured by the

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(7) Joseph Lipka, "Graphical and Mechanical Computation," John Wiley and Sons, Inc., New York (*ca.* 1919): Part II, Article 110, page 255.

slopes of the tangents to the curves (of pressure-drop against time) when 80 and 67% of the gases have reacted, increases with the decrease of oxygen in the mixture. The increase in the rate is especially noticeable when the partial pressure of oxygen is well below 2 mm.

The sensitivity of the rate of the reaction to small amounts of oxygen, together with the evidence that the reaction occurs largely at the surface, suggests a chain mechanism with short chains initiated at the surface.

MINNEAPOLIS, MINN. RECEIVED APRIL 30, 1936

[CONTRIBUTION FROM THE UNIVERSITY OF TEXAS]

Organic Nitrogen Bases from Pyrolysis of Cottonseed Meal[1]

BY IVY PARKER, C. L. GUTZEIT, A. C. BRATTON AND J. R. BAILEY

Introduction

Research on the bases in petroleum distillates[2] has shown a preponderance of non-aromatic types, not previously obtained from any other natural source. On the assumption that petroleum is of vegetable or animal origin, it may be assumed that carbohydrates and fats, as well as proteins, contributed to the formation of nitrogen compounds; in any event an explanation of the genesis of non-aromatic petroleum bases, among which are probably compounds of cyclopentane structure, might have an important bearing on the origin of petroleum itself.

In an attempt to determine whether similar non-aromatic bases would result from pyrolysis of a material containing proteins, carbohydrates and fats, the present investigation was undertaken. The Union Oil Company of California contributed 337 pounds of crude bases obtained from the distillation of 23 tons of cottonseed meal with nitrogen-free lubricating oil as a liquid medium, through which low temperature pyrolysis could be controlled.[2a]

Previous work by other investigators on bases formed in protein pyrolysis are of little interest as concerns the present investigation, because in these studies pure proteins were employed.[3]

The complexity of the cottonseed meal bases is comparable with that of petroleum bases. An unexpected difference is that, unlike bases from other important natural products, those from protein material are at least 50% *petroleum ether insoluble* and, besides, the higher boiling fractions have a much greater nitrogen content than can be accounted for on the assumption of a single nitrogen in the molecule. Furthermore, there is no evidence of naphthenic structure, such as is highly probable for certain petroleum bases. From the lower boiling fractions there have been isolated pyridine, and a number of its homologs, identical with products from coal, shale or bones.

The coal tar bases, quinoline, isoquinoline, quinaldine and lepidine, along with the kero base, 2,3,8-trimethylquinoline[2b] (p. 1245), have been found. A beautifully crystallizing diazine, $C_{11}H_{14}N_2$, of undetermined structure is probably a dihydroquinazoline, as indicated by its amphoteric character.

Upon vacuum distillation of the high boiling protein bases in an atmosphere of nitrogen, colorless distillates are obtained which, unlike corresponding petroleum base cuts, soon darken and precipitate tar. This instability renders difficult the isolation of individual products. So far the petroleum ether insoluble bases have been only superficially studied.

In the boiling range of 135 to 172° a total of 876 cc. (14 fractions) of petroleum ether soluble material was available with $d^{25}{}_4$ values between 0.9418 and 0.9652 and $n^{25}{}_D$ values between 1.4947 and 1.4992. These physical constants clearly indicate a preponderance of pyridines. From the high nitrogen content of these fractions pyrazines and pyrimidines were suspected but a search for diazines was fruitless. The comparatively small volume of material in this range can be attributed

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[1] In part from dissertations submitted by Ivy May Parker and C. L. Gutzeit to the Faculty of the Graduate School of the University of Texas in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1935.

[2] (a) E. J. Poth, W. D. Armstrong, C. C. Cogburn and J. R. Bailey, *Ind. Eng. Chem.*, **20**, 83 (1928); (b) E. J. Poth, W. A. Schulze, W. A. King, W. C. Thompson, W. W. Floyd and J. R. Bailey, THIS JOURNAL, **52**, 1239 (1930); (c) W. C. Thompson and J. R. Bailey, *ibid.*, **53**, 1002 (1931); (d) B. F. Armendt and J. R. Bailey, *ibid.*, **55**, 4145 (1933); (e) G. R. Lake and J. R. Bailey, *ibid.*, **55**, 4143 (1933); (f) T. S. Perrin and J. R. Bailey, *ibid.*, **55**, 4136 (1933); (g) B. S. Biggs and J. R. Bailey, *ibid.*, **55**, 4141 (1933); (h) R. W. Lackey and J. R. Bailey, *ibid.*, **56**, 2741 (1934).

[2a] The preliminary work in this connection was carried out in the Texas Laboratory by Ivy Parker.

[3] Pictet and Cramer, *Helv. Chim. Acta*, **2**, 188 (1919); T. B. Johnson and Daschavsky, *J. Biol. Chem.*, **62**, 197 (1924).

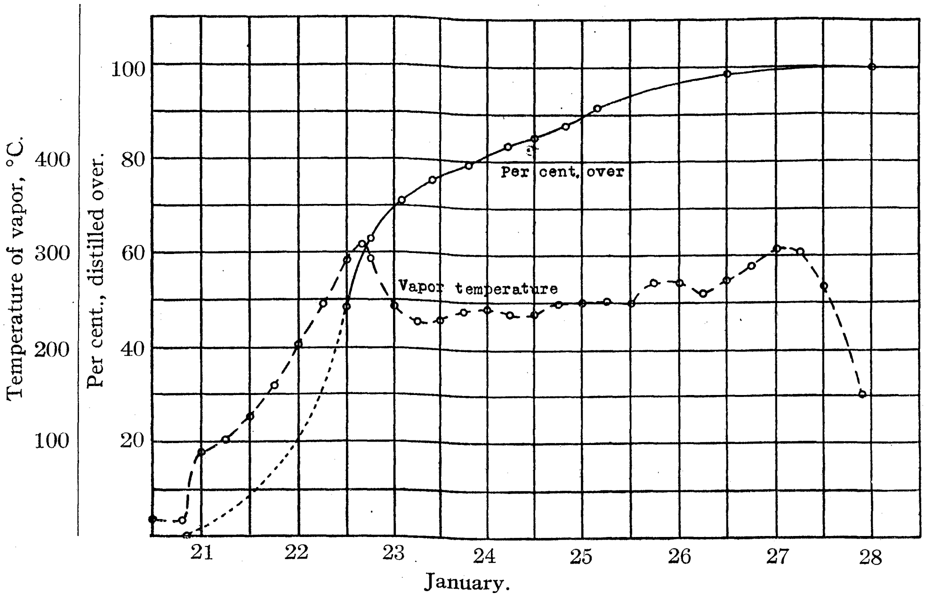

Fig. 1.—Distillation of cottonseed meal.

to the fact that no attempt was made at the Union Oil Company plant to isolate water soluble bases.

In the 172 to 215° range 2468 cc. of material (17 fractions) was available. Here there exists a progressive exaltation of the $d^{25}{}_4$ values from 0.9514 to 1.0189 and of the $n^{25}\text{D}$ values from 1.5010 to 1.5375. These constants, taken with an abnormally high nitrogen content, exclude the presence in quantity of pyridines, as well as quinolines.

The results of this investigation should not be accepted as proof that so-called petroleum bases are not of vegetable or animal origin. From the assumption that the complex nitrogen compounds in crude oil came from protein material, it does not follow that a high temperature was involved in their formation; it is more probable that they resulted from bacteriological decay at ordinary temperature;[4] at least, so far as California petroleum is concerned, the nitrogen does not exist in preformed *basic* compounds beyond a negligible amount and, therefore, the bases first encountered in distillates, are products of pyrolysis.[5,2a,b]

A recently developed practical method of indirect micro distillation, termed Amplified Distillation,[6] has proved of indispensable service in processing the cottonseed meal bases. In this process, which is even more effective than straight distillation, a fraction of bases is added to petroleum hydrocarbon oil boiling evenly over a somewhat broader range than the bases. After fractional distillation, the bases are withdrawn from the hydrocarbon fractions with sulfurous acid and then precipitated in the form of picrates or other suitable salts. In this way the components of a complex mixture, even where the total volume is only a fraction of a cubic centimeter, can be segregated in the order of their boiling points.

Another general method employed in resolving mixtures of protein bases, termed Cumulative Extraction,[2e] depends on the relative distribution ratio of base hydrochlorides between chloroform and water. This process enables a very satisfactory separation into aromatic and non-aromatic types.

The improved laboratory technique now available in this line of research, coupled with the advances made in our knowledge of the types and properties of the bases to be expected, should attract the attention of other investigators to the study of protein pyrolysis, especially the biochemist, whose interest in this practically unexplored domain of organic chemistry need not be emphasized.

To chemists who may become interested in protein pyrolysis as an attractive field for re-

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(4) *Cf.* McKensie Taylor, *J. Inst. Petr. Tech.*, **14**, 825 (1928); B. T. Brooks, *ibid.*, **20**, 177 (1934).

(5) D. T. Day, "Handbook of the Petroleum Industry," Vol. I, 1922, p. 530.

(6) A. C. Bratton, W. A. Felsing and J. R. Bailey, *Ind. Eng. Chem.*, **28**, 424 (1936).

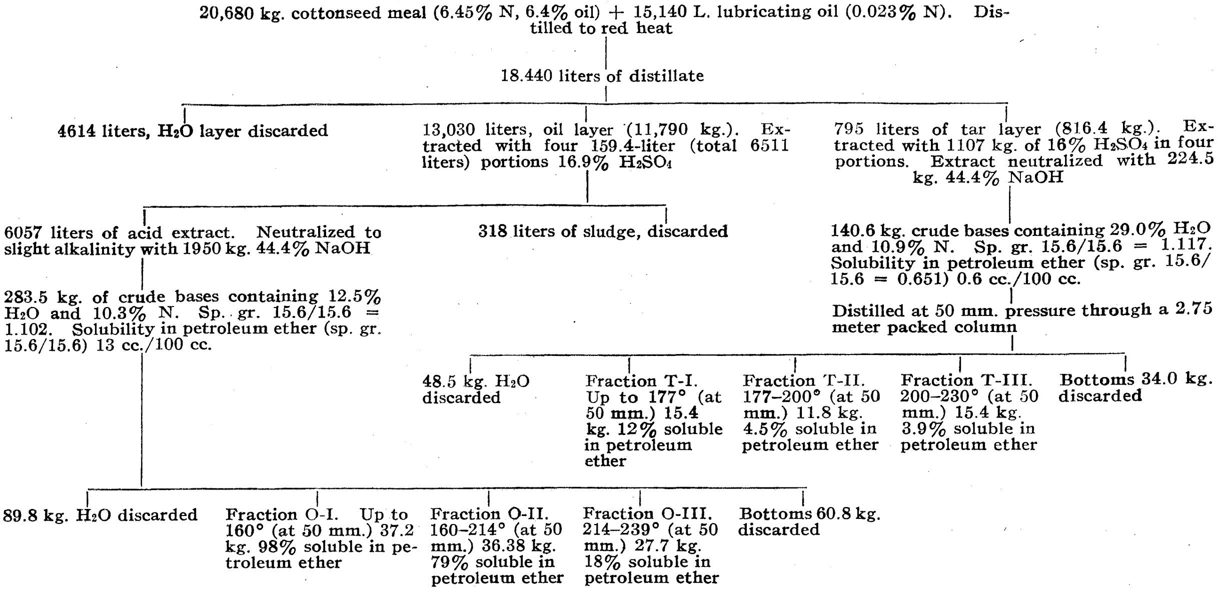

Fig. 2.

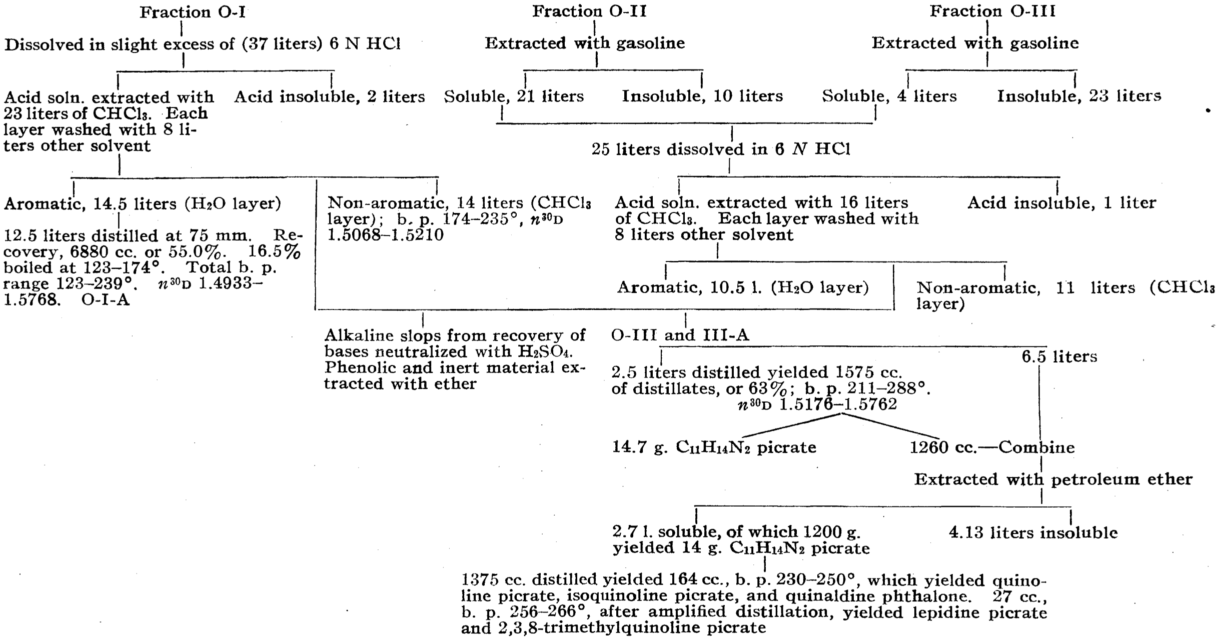

Fig. 3.

search, it may be emphasized that the cost of neither material nor equipment is prohibitive. In our preliminary investigation, an insulated iron still 3 feet (94 cm.) in height, 2 feet (61 cm.) in diameter and provided with a stirrer was used. For each of the six runs made, the charge consisted of 100 pounds (45 kg.) of cottonseed meal ($25–35 per ton (910 kg.)) and 8 gallons (30 liters) of lubricating oil. The distillates from 600 pounds (272 kg.) of meal processed in the usual way yielded a total of 5.5 liters of crude bases.

One of the most important considerations, especially where the distillation is carried out in the laboratory, is the obnoxious mercaptan odor developed. This nuisance can be suppressed conveniently by the use of two filter flasks connected separately with water pumps and serving interchangeably as receivers.

TABLE I

DISTILLATION OF O-I-A BASES

No.	Temp. range, °C.	Press., mm.	Vol., cc.	d^{25}_4	$n^{25}_{\rm D}$	N, %	Bases isolated
1	100–135	750	1				Pyridine 2-Methylpyridine
2	135–140	750	8	0.9522	1.4968	17.41	4-Methylpyridine
3	140–142.5	751	10	.9503	1.4978	17.36	3-Methylpyridine 2,6-Dimethylpyridine
4	142.5–145	751	16	.9511	1.4989	15.65	
5	145–147.5	752	25	.9652	1.4968	16.03	
6	147.5–150	752	20	.9652	1.4968	16.34	
7	150–152.5	753	37	.9507	1.4990	15.84	
8	152.5–155	753	45	.9522	1.4947	17.66	
9	155–157.5	754	38	.9418	1.4990	17.71	2,4-Dimethylpyridine
10	157.5–160	754	44	.9442	1.4990	16.92	
11	160–162.5	755	59	.9556	1.4968	15.22	
12	162.5–165	755	119	.9480	1.4962	15.24	
13	165–167.5	756	130	.9531	1.4988	15.96	3-Ethylpyridine
14	167.5–170	756	189	.9491	1.4990	15.98	3,5-Dimethylpyridine 2,4,6-Trimethylpyridine
15	170–172.5	756	136	.9504	1.4992	14.77	
16	172.5–175	758	157	.9514	1.5010	13.93	
17	175–177.5	758	170	.9559	1.5025	13.65	
18	177.5–180	758	120	.9594	1.5055	13.36	
19	180–182.5	758	133	.9598	1.5090	13.85	
20	182.5–185	757	160	.9612	1.5119	13.86	
21	185–187.5	757	200	.9631	1.5140	14.71	
22	187.5–190	757	99	.9677	1.5160	14.66	
23	190–192.5	756	191	.9716	1.5170	13.31	
24	192.5–195	756	140	.9781	1.5199	13.34	
25	195–197.5	756	183	.9820	1.5212	13.25	
26	197.5–200	756	162	.9882	1.5260	12.84	
27	200–202.5	757	221	.9917	1.5270	12.89	
28	202.5–205	757	130	.9971	1.5303	12.53	
29	205–207.5	757	92	1.0026	1.5328	12.14	
30	207.5–210	758	144	1.0093	1.5342	13.23	
31	210–212.5	758	106	1.0165	1.5363		
32	212.5–215	758	60	1.0189	1.5375		
33	Residue	758	20				

Experimental

In the production of nitrogen bases from cottonseed meal at the Oleum Plant of the Union Oil Company,[7] a shell still, 8 by 29 feet (2.5 × 8.8 meters) was used in distillation of the cottonseed meal–lubricating oil mixture, air from the spider of the still being used for agitation. The still run occupied seven days; however, most of the distillate was collected in four days. After completion of the distillation, the still was allowed to cool for four days and even then difficulty was experienced in handling the coke,[8] due to a tendency to spontaneous combustion. Distillation temperature and rate are summarized in Fig. 1. Acid extraction and distillation data, along with yields of base fractions are compiled in Fig. 2.

Fractions O-I, O-II and O-III, Fig. 2, were processed through petroleum ether extraction, cumulative extraction and fractional distillation, as shown in Fig. 3.[9] The material O-I-A, Fig. 3, boiling below 215° was carried through exhaustive fractionation by three separate distillations in a carbon dioxide atmosphere under reflux through a spirally indented column, 1 × 105 cm.

Volumes, boiling points, nitrogen content, d^{25}_4 values and $n^{25}_{\rm D}$ values of the 33 fractions obtained are collected in Table I.[10]

Investigation of O-I-A Forerun

BY A. C. BRATTON

The small volume of forerun (1 cc. of bases in 9 cc. of water) precluded direct fractional distillation under reflux. Amplified distillation was conceived to obviate the difficulty, and this first experiment in its use as an indirect method of microdistillation was carried out successfully as follows: to the 1 cc. of bases, 25 cc. of acid-and-caustic-washed hydrocarbon oil, b. p. 80–140°, was added and the mixture was distilled through a 0.5 × 100 cm. column packed with a copper spiral. The rate of distillation was

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(7) The data in this connection were furnished by Mr. T. F. Ott, Assistant Manager of Research at Oleum, California.

(8) This proved a very effective decolorant.

(9) This work was carried out by Ivy Parker.

(10) This work was carried out by A. C. Bratton and C. L. Gutzeit.

0.6 cc. per hour, and nine 2.5-cc. cuts and a 3-cc. residue were collected in the ranges shown in Table II.

TABLE II

AMPLIFIED DISTILLATION OF THE BASES IN O-I-A FORERUN

Cut no.	B. p. base-hydrocarbon fractions, °C.	Products isolated, mg.	
1	55–85	30	Pyridine picrate
2	85–95		
3	95–100		
4	100–107	300	2-Methylpyridine picrate
5	107–109		
6	109–115	450	Mixed picrates
7	115–122		
8	122–124		
9	124–138	10	2,6-Dimethylpyridine picrate
Residue			

Each fraction was extracted twice with an equal volume of 6 *N* sulfuric acid, the bases were liberated from the extracts with sodium hydroxide and steam distilled, and finally precipitated with aqueous picric acid.

Pyridine.—The combined picrates from cuts 1 and 2 were recrystallized from water, ethyl acetate and isopropyl alcohol. The product, m. p. 167.7–168°, proved to be pyridine picrate through a mixed melting point with an authentic sample.

Anal. Calcd. for $C_{11}H_8O_7N_4$: N, 18.19. Found: N, 18.30.

2-Methylpyridine.—After similar treatment of the picrates from cuts 4 and 5, a salt melting at 166° was identified as 2-methylpyridine through a mixed melting point.

Anal. Calcd. for $C_{12}H_{10}O_7N_4$: N, 17.40. Found: N, 17.62.

2,6-Dimethylpyridine.—Fraction 9 yielded a picrate melting at 163° after recrystallization from water and isopropyl alcohol. It was identified as 2,6-dimethylpyridine by a mixed melting point.

Investigation of O-I-A Fractions 135–170°

BY C. L. GUTZEIT

3-Methyl-, 4-Methyl- and 2,6-Dimethylpyridine.—These bases boiling at 144, 145.3 and 144.6°, respectively, were suspected in the 140–145° fractions, and, after their separation through picrates proved tedious and unsatisfactory, the following procedure was employed: a solution of 10 cc. of crude bases in 500 cc. of saturated mercuric chloride and 10 cc. of concentrated hydrochloric acid was evaporated to 150 cc. The precipitate was recrystallized from alcohol and then dissolved in 1000 cc. of a hot saturated solution of mercuric chloride containing 100 cc. of concentrated hydrochloric acid. On cooling, the 2,6-dimethylpyridine double salt of the composition $C_7H_9N \cdot HCl \cdot 2HgCl_2$ separated in granular crystals melting at 167°.[11] The picrate prepared from this salt melted at 162° as reported by Eguchi. In final identification of these salts, they were prepared from 2,6-dimethylpyridine, synthesized from 2-methylpyridine methiodide according to the general method of Ladenburg.[12] Mixed melting points carried out in the usual way showed no depression.

Anal. of picrate. Calcd. for $C_{13}H_{12}O_7N_4$: C, 46.42; H, 3.57; N, 16.67. Found: C, 46.35; H, 3.58; N, 16.52.

Anal. of base. Calcd. for C_7H_9N: C, 78.50; H, 8.41; N, 13.08. Found: C, 78.42; H, 8.43; N, 13.29.

For the separation of 4-methylpyridine, the filtrate from the mercuric chloride salt of 2,6-dimethylpyridine was neutralized with sodium hydroxide and then made just acid to methyl orange. After twelve hours, a salt separated which was recrystallized from water in long slender needles melting at 128–129°, as found by Ladenburg for the mercuric chloride salt, $C_6H_7N \cdot HCl \cdot 2HgCl_2$, of 4-methylpyridine[12] (p. 13). Final identification was effected through a mixed melting point with a sample of picrate made from 4-methylpyridine synthesized from pyridine methiodide.[13]

Anal. Calcd. for $C_{12}H_{10}O_7N_4$: C, 44.72; H, 3.11; N, 17.39. Found: C, 44.66; H, 3.15; N, 17.49.

Anal. of base. Calcd. for C_6H_7N: C, 77.42; H, 7.53; N, 15.09. Found: C, 77.36; H, 7.51; N, 15.12.

In isolation of 3-methylpyridine, the low melting picrates from purification of 4-methyl- and 2,6-dimethylpyridine were used. After it was found impractical to segregate this picoline through the picrate, mercuric chloride salt[12] (p. 8) or the zinc chloride salt,[14] advantage was taken of the non-reactivity of 3-methylpyridine with benzaldehyde in contrast to the ease with which condensation takes place with the associated pyridine homologs.[15]

The bases recovered from the low melting picrates were mixed with twice their volume of benzaldehyde, a small piece of zinc chloride was added and the mixture was heated at 225° for six hours. The unchanged 3-methylpyridine was extracted with benzene from the reaction mixture made alkaline with sodium hydroxide. The dried extract was distilled and the 140–145° fraction was treated with a benzene solution of picric acid. The third recrystallization from alcohol gave a pure product in the form of long glistening needles melting at 149°, as reported for 3-methylpyridine picrate[11] (pp. 229, 241).

Anal. Calcd. for $C_{12}H_{10}O_7N_4$: C, 44.72; H, 3.11; N, 17.39. Found: C, 44.64; H, 2.93; N, 17.50.

Identification was further confirmed by a mixed melting point with the picrate prepared from the synthetic base.[16]

The 135–140° fraction of bases was investigated in a fruitless search for methylpyrazine. Since only 8 cc. of material was available, amplified distillation was resorted to in fractionation. A small amount of 3-methyl- and 2,6-dimethylpyridine was isolated, but none of the 4-methylpyridine.

3,5-Dimethylpyridine.—This base is easy to isolate and identify because of the difficult solubility and high melting point of its picrate. Three fractions of bases in the 165–170° range were picrated in two volumes of alcohol to one

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[11] *Cf.* Takashi Eguchi, *Bull. Chem. Soc. Japan*, **3**, 181, 241 (1928); *Chem. Zentr.*, **100**, 331 (1929).

[12] A. Ladenburg, *Ann.*, **247**, 2 (1888).

[13] Otto Lange, *Ber.*, **18**, 3439 (1885); ref. 12, p. 12.

[14] J. G. Heap, W. J. Jones and J. B. Speakman, THIS JOURNAL, **43**, 1936 (1921).

[15] Paul Schwarz, *Ber.*, **24**, 1676 (1891); Fr. Schuster, *ibid.*, **25**, 2398 (1892); A. Marcuse and R. Wolffenstein, *ibid.*, **32**, 2526 (1899).

[16] Ludwig Storch, *ibid.*, **19**, 2456 (1866).

volume of bases, picric acid solution being added to where no further separation of picrates resulted. The crude material melted at 234–236°. After two recrystallizations from acetone, the most satisfactory solvent for this salt, the melting point was raised to 242.5–243.5°.[17]

Anal. of picrate. Calcd. for $C_{13}H_{12}O_7N_4$: C, 46.43; H, 3.57; N, 16.67. Found: C, 46.61; H, 3.59; N, 16.54.

Anal. of base. Calcd. for C_7H_9N: C, 78.50; H, 8.41; N, 13.08. Found: C, 78.44; H, 8.36; N, 13.35.

The identity of the picrate was confirmed further by a mixed melting point with a sample made from synthetic 3,5-dimethylpyridine.[18]

3-Ethylpyridine.—From the 165–167.5° fraction of bases oily picrates admixed with crystalline 3,5-dimethylpyridine picrate were obtained. After removal of the latter, long yellow needles followed in about two weeks and, after several recrystallizations from alcohol, the melting point 129° agreed with that of 3-ethylpyridine picrate.[19]

Anal. Calcd. for $C_{13}H_{12}O_7N_4$: C, 46.43; H, 3.57; N, 16.67. Found: C, 46.32; H, 3.54; N, 16.56.

In further structural proof, 0.3 g. of the base in 100 cc. of water containing 2 g. of potassium permanganate was allowed to stand three days when the colorless solution was filtered hot and neutralized with acetic acid. On addition of copper acetate, followed by concentration of the solution to a small volume, a deep blue copper salt precipitated. After removal of the copper with hydrogen sulfide and evaporation of the filtered solution, the residue, recrystallized several times from alcohol, melted at 229° in agreement with nicotinic acid.[20]

2,4,6-Trimethylpyridine.—This pyridine was isolated from the 167.5–170° fraction of bases through the following procedure. The mixed bases (20 cc.) in 100 cc. of a saturated alcoholic solution of mercuric chloride containing 10 cc. of concentrated hydrochloric acid were allowed to stand for twelve hours, oily impurities were removed and the residue was dissolved in a small volume of hot alcohol. After twenty-four hours a dense crystalline precipitate separated. On one recrystallization from a saturated solution of mercuric chloride containing 5% hydrochloric acid,[21] and three recrystallizations from very dilute acid, the characteristic needles of the double salt of 2,4,6-trimethylpyridine, $C_8H_{11}N\cdot HCl\cdot 2HgCl$, melting at 156° were obtained.

The picrate melting at 155° was prepared and compared in the usual way with a sample made from the synthetic base.[22]

Anal. Calcd. for $C_{14}H_{14}O_7N_4$: N, 16.00. Found: N, 15.89.

2,4-Dimethylpyridine.—The 155–157.5° fraction of bases was treated with mercuric chloride in the way described under 2,4,6-trimethylpyridine. The more soluble mercuric chloride salts thus obtained were recrystallized three times from a mercuric chloride solution containing 5% hydrochloric acid. Since a pure product was not obtained, the bases were liberated in the usual way and converted to picrates. After four recrystallizations, a pure product melting at 182° in agreement with 2,4-dimethylpyridine picrate[11] (pp. 232, 241) was obtained. A mixed melting point with the picrate of the synthetic base[23,12] showed no depression.

Anal. Calcd. for $C_{13}H_{12}O_7N_4$: N, 16.67. Found: N, 16.56.

Investigation of Base Fractions in the 236–280° Boiling Range of O-II and III-A

By Ivy Parker

Quinoline and Isoquinoline.—The combined 236, 238 and 240° fractions (50 cc.) were dissolved in 75 cc. of 6 *N* hydrochloric acid and extracted with eight successive portions of chloroform. From the aqueous layer 27 cc. of bases was recovered. This material, extracted with 10 cc. of 3.5 *N* sulfuric acid, left undissolved 19 cc., which was treated with an excess of picric acid in alcoholic solution. The precipitate, after extraction with boiling benzene and next with boiling alcohol, was recrystallized from glacial acetic acid, yielding 2.5 g. of a picrate in the form of needles melting at 203°. Identification of this product was effected by a mixed melting point with an authentic sample of quinoline picrate.

Anal. Calcd. for $C_{15}H_{10}O_7N_4$: C, 50.28; H, 2.79; N, 15.64. Found: C, 50.21; H, 2.68; N, 15.74.

For the isolation of isoquinoline, 3 cc. of bases, recovered from the quinoline picrate washings above, was dissolved in 3 cc. of alcohol and fractionally precipitated in 11 stages with successive 3-cc. portions of a saturated solution of picric acid in alcohol. To induce crystallization, it was necessary to seed with a small crystal of isoquinoline picrate. The first eight isoquinoline picrate precipitates, leached out with boiling alcohol, yielded on recrystallization from glacial acetic acid 0.25 g. of light yellow needles melting at 221–222°. The identity of the product was established by a mixed melting point with an authentic sample of isoquinoline picrate.

Anal. Calcd. for $C_{15}H_{10}O_7N_4$: N, 15.64. Found: N, 15.92.

Quinaldine.—After it was found that the 246° fraction, unlike the lower boiling bases, showed phthalone formation, 5 cc. was heated for four hours at 200° with 2 g. of phthalic anhydride and the reaction mixture, after being dissolved in 17 cc. of concentrated sulfuric acid, was poured into 400 cc. of water. From the crude phthalone, admixed phthalic anhydride was sublimed at reduced pressure and the residue, after a leaching out with boiling alcohol, was dissolved in glacial acetic acid and poured into a large volume of water. From the impure product (0.22 g.) which precipitated, a pure phthalone was sublimed[24] in the form of

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(17) This determination is in agreement with 244° reported by Eguchi, ref. 11, pp. 231, 241. Beilstein, 4th ed., Vol. XX, p. 246, gives 228–230°.

(18) E. Durkoff and H. Göttsch, *Ber.*, **23**, 685, 1113 (1890).

(19) C. Stoehr, *J. prakt. Chem.*, [2] **45**, 38 (1892).

(20) A. Ladenburg, *Ann.*, **301**, 152 (1898).

(21) With water the solvent at this stage, an amorphous insoluble salt with an indeterminate decomposition point around 200° also separates and interferes with further purification. This type of salt, encountered in connection with all fractions of bases investigated, is very soluble in dilute acid, even with a high concentration of mercuric chloride, and cannot be converted to a crystalline picrate.

(22) Gattermann, "Die Praxis des organischen Chemikers," 1927, p. 332.

(23) The 2,4-dimethylpyridine used here was obtained as a by-product in the synthesis of 2,6-dimethylpyridine.

(24) E. Jacobson and C. L. Reimer, *Ber.*, **16**, 1082 (1883).

glistening yellow needles melting at 235°. A mixed melting point with an authentic sample of quinphthalone (m. p. 234–235°) showed no depression.

For hydrolysis of the phthalone a 0.5-g. sample was heated in a sealed tube for twenty-four hours with 2 cc. of concentrated hydrochloric acid and from the solution, made alkaline with caustic, an oil was distilled in steam. From the base a picrate was prepared which crystallized from alcohol in rosets of short slender needles melting at 189°. A mixed melting point of 190–191° was obtained with an authentic sample of quinaldine picrate (m. p. 190–192°).

Anal. Calcd. for $C_{16}H_{12}O_7N_4$: N, 15.05. Found: N, 15.18.

Lepidine.—Four fractions of bases (190 cc.) of b. p. 260–270° and with $n^{30}D$ 1.5770–1.5817, were separately fractionated through a Podbielniak column, 4-cc. cuts being collected. The fractions (50 cc.) of b. p. 257–262° and with $n^{25}D$ 1.5785–1.5806 were combined in 68 cc. of 6 *N* hydrochloric acid and carried through cumulative extraction by four successive extractions with 50-cc. portions of chloroform. The bases (32 cc.) from the acid layer were fractionated under reflux at 25 mm. pressure into nine 3-cc. cuts, with a 5-cc. residue. Cuts 1 and 2 were combined, as were also cuts 7, 8 and 9.

Amplified distillation of these fractions with 10 volumes of hydrocarbon oil was carried out under reflux at 20 mm. pressure, a total of 61 4-cc. fractions being collected. The bases were extracted from the hydrocarbon oil with sulfurous acid and directly converted to picrates. Where smears appeared, they were leached out with cold acetic ether. Then the crystalline material was recrystallized successively from alcohol, glacial acetic acid and 50% acetic acid. Nine of the 32 cuts from original fractions 1–2, 3 and 4 yielded a total of only 0.2 g. of a pure picrate melting at 212–213°. This product was identified as lepidine picrate in the usual way by a mixed melting point determination. Lepidine (b. p. 263°) appeared only in the 225–242° (atmospheric pressure) fractions of hydrocarbon fractions from amplified distillation.

Anal. Calcd. for $C_{16}H_{12}O_7N_4$: N, 15.05. Found: N, 15.25.

2,3,8-Trimethylquinoline.[25]—Here a procedure, involving cumulative extraction and amplified distillation, and similar to that employed in search of lepidine was employed on six fractions of bases (45 cc., b. p. 274–279°, $n^{30}D$ 1.5815). In the hydrocarbon fractions of b. p. 259–283°, 2,3,8-trimethylquinoline (b. p. 280°) was suspected. The mixture of picrates obtained was leached out with boiling alcohol and recrystallized from glacial acetic acid. In this way there resulted an apparently pure product crystallizing in characteristic short rods and melting with decomposition at 242–243°. A mixed melting point with an authentic sample of 2,3,8-trimethylquinoline picrate showed no depression.

Anal. Calcd. for $C_{18}H_{16}O_7N_4$: N, 14.00. Found: N, 13.81, 13.98.

Isolation of $C_{11}H_{14}N_2$ Base.—In processing Fractions O-II and O-III, there was encountered in very small amount among the aromatic, petroleum ether soluble bases a product easy to isolate through its difficultly soluble picrate. This picrate of the composition $C_{11}H_{14}N_2 \cdot C_9H_3O_7N_3$ (*cf.* Fig. 3) remained in the residue, after leaching out with benzene, alcohol and glacial acetic acid the complex mixture of picrates obtained in this boiling range. In final purification, it was recrystallized from diacetone alcohol in characteristic glistening plates which darkened at 259° and melted with decomposition at 261–263°.

Anal. Calcd. for $C_{17}H_{17}O_7N_5$: C, 50.62; H, 4.22; N, 17.37. Found: C, 50.38; H, 4.05; N, 17.60.

The base was liberated from the picrate with ammonium hydroxide and extracted with ether. For purification, it was distilled between 187–192° at 34 mm. pressure. It boils at 283° (750 mm.) and has an $n^{30}D$ value of 1.5790. The free base has an unpleasant odor, and on standing in contact with air is converted in part to a white solid which dissolves in potassium hydroxide but is insoluble in ether. Nitrous acid and both alkaline and acid permanganate react with the base in the cold. The analysis along with the decided amphoteric character of this substance is in agreement with an alkylated dihydroquinazoline. The small amount of material available precluded its further study.

Anal. Calcd. for $C_{11}H_{14}N_2$: C, 75.86; H, 8.05; N, 16.09; mol. wt., 174. Found: C, 75.5; H, 7.66; N, 16.33; mol. wt. 167.

Mercuric Chloride Salt.—The base in a slight excess of dilute hydrochloric acid gave with a saturated solution of mercuric chloride a precipitate which was recrystallized from water in rosets of needles. This salt sintered at 153° and melted at 173–174°.

Anal. Calcd. for $C_{11}H_{14}N_2 \cdot HCl \cdot HgCl_2$: N, 5.81. Found: N, 5.84.

Summary

The present investigation was undertaken in order to determine whether in low temperature pyrolysis of a natural product, containing proteins, carbohydrates and fats, products of the same structural types as the *non-aromatic* bases from petroleum distillates would be encountered. Although only negative results, so far as the main objective of this research is concerned, were obtained, it was found that cottonseed meal, in contrast to pure proteins, like egg albumin, casein and serine, yields on destructive distillation basic nitrogen compounds in preponderant amount which are different in three main respects from bases previously obtained from a natural source: *these properties are petroleum ether insolubility, an exceptional tendency to tar formation and an abnormally high nitrogen content.*

From the low boiling fractions pyridine, and seven pyridine homologs, identical with coal tar for shale oil bases, were isolated and in the higher fractions quinoline, isoquinoline, quinaldine, lepidine, the kero base, 2,3,8-trimethylquinoline and

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[25] Originally obtained from California asphalt base petroleum, W. A. King and J. R. Bailey, THIS JOURNAL, **52**, 1245 (1930).

a diazine, $C_{11}H_{14}N_2$, of undetermined structure were isolated.

This research will be concluded with an investigation now in progress on 18 fractions in the boiling range of 172.5–215°, in an effort to explain the abnormally high nitrogen content of these bases, coupled with a progressive exaltation of densities and refractivities from $d^{25}{}_4$ 0.9514 and $n^{25}{}_D$ 1.5025 to $d^{25}{}_4$ 1.0189 and $n^{25}{}_D$ 1.5375, respectively.

AUSTIN, TEXAS RECEIVED APRIL 13, 1936

[CONTRIBUTION FROM DIVISION OF CHEMISTRY, NEW YORK STATE AGRICULTURAL EXPERIMENT STATION]

A Phase Rule Study of the Calcium Arsenates[1]

BY G. W. PEARCE AND L. B. NORTON

Calcium arsenate is a product of uncertain composition and variable properties, both in the form of the commercial insecticide and of the so-called pure salt. Although commercial preparations are generally assumed to consist essentially of tricalcium arsenate and an excess of hydrated lime, recent work[2,3,4] has shown that this assumption is inadequate to account for the variations in properties among products of similar gross composition. These variations suggest that other arsenates of calcium are probably present in the products prepared by the usual methods. Since data concerning the identity and the ranges of stability of the calcium arsenates are at present incomplete, a study of the equilibrium conditions in the system $CaO-As_2O_5-H_2O$ has been carried out.

A number of calcium arsenates have been reported in the literature. Smith,[5] in a study of the equilibrium conditions in the more soluble portion of the system, established the existence of two acid salts: monocalcium arsenate, $CaH_4(AsO_4)_2$, and dicalcium arsenate, $CaHAsO_4$. The dicalcium salt has also been prepared and studied by a number of other workers, and is known in the form of the minerals Haidingerite and Pharmacolite. Robinson[6] has reported the preparation of pure tricalcium arsenate, $Ca_3(AsO_4)_2$, from calcium chloride and sodium arsenate. Tartar *et al.*[7] obtained a basic product having the composition $[Ca_3(AsO_4)_2]_3 \cdot Ca(OH)_2$, by the repeated hydrolysis of calcium ammonium arsenate and of tricalcium arsenate prepared by Robinson's method.[6] Smith and Murray[8] concluded from complete analyses of a number of commercial preparations, that these products consist mostly of a compound more basic than tricalcium arsenate. Clifford and Cameron,[9] however, considered that some of the calcium arsenates reported were merely solid solutions of calcium oxide and arsenic oxide incidentally having the composition of possible compounds.

Experimental

The experiments were confined to the ranges of compounds more basic than dicalcium arsenate, since the work of Smith[5] on the acid compounds appears quite conclusive. Smith was unable to reach complete equilibrium in a reasonable time in the more basic region of the system at 35°, so a higher temperature was chosen for the present work. Preliminary experiments showed that changes in the system tend to occur more rapidly at higher temperatures, in spite of the decreased solubility of most of the compounds involved. Accordingly, a bath of petroleum oil maintained at 90 ± 0.1° was used for all of the work.

The calcium oxide was prepared by precipitating calcium carbonate from calcium chloride with ammonium carbonate, and igniting the product in an electric muffle furnace. It was found to be free from appreciable amounts of magnesium. Baker C. P. arsenic acid was used without further purification.

All analyses for calcium were made by the precipitation of calcium oxalate and titration with permanganate. Arsenic was determined by distillation as the trichloride and titration with bromate solution.[10] Application of these procedures to samples of pure calcite and of Bureau

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[1] Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 136, April 8, 1936.

[2] Pearce, Norton and Chapman, N. Y. Agr. Expt. Sta. Tech. Bull. 234 (1935).

[3] Chapman, Pearce, Dean and Hammer, *J. Econ. Entomol.*, **27**, No. 2, 421 (1934).

[4] Howard and Fletcher, U. S. Bur. Entomol. Paper E-304, mimeographed (1933).

[5] Smith, THIS JOURNAL, **42**, 259 (1920).

[6] Robinson, *J. Agr. Research*, **13**, 281 (1918).

[7] Tartar, Wood and Hiner, THIS JOURNAL, **46**, 809 (1924).

[8] Smith and Murray, *Ind. Eng. Chem.*, **23**, 207 (1931).

[9] Clifford and Cameron, *ibid.*, **21**, 69 (1929).

[10] The bromate method for arsenic in foods [*J. Assoc. Official Agr. Chem.*, **16**, 75 (1933)] was modified by using hydrazine sulfate instead of the ferrous sulfate–sodium bromide mixture as reducing agent.

of Standards arsenious oxide, respectively, showed that the maximum errors of the analysis were less than 0.1 mg. of calcium oxide and 0.05 mg. of arsenic oxide. In the analyses of the unknown samples, such quantities were taken that the analytical error was less than 1% except for the four most dilute solutions, in which it rose to about 3%.

Preliminary experiments, in which solid lime was shaken with arsenic acid of various concentrations, showed that equilibrium was not attained in six weeks, even at 90°. It appeared that penetration of the particles of lime by the dilute arsenic acid and the subsequent conversion to the proper compound is a process difficult to complete in a reasonable length of time. Further experiments in which the lime was added in solution showed more promise, but the solid in all cases showed a great reluctance to change, after once being precipitated, in contact with the extremely dilute solutions which characterize this portion of the system. These difficulties were finally avoided by precipitating the solid under such conditions that it had practically its final composition when it was first deposited. Both solution and solid then reached a constant and reproducible composition very quickly.

The procedure by which the final data were obtained was as follows. The solutions were made up in such proportions that small amounts of solid would precipitate at 90°, but the solutions would remain perfectly clear at room temperature. Such conditions were obtained when calculations from the preliminary data indicated that amounts of solid ranging from 50 mg. in the basic region to 500 mg. in the acid region should be deposited from 600 cc. of solution. Six hundred-cc. portions of the solutions were made up at room temperature in 1-liter wide-mouthed Pyrex Erlenmeyer flasks, using recently boiled distilled water and carefully standardized solutions of lime and of arsenic acid nearly saturated with lime. Each flask was closed with a rubber stopper through which extended a glass stirrer fitted with a mercury seal to protect the solution from evaporation and from contact with atmospheric carbon dioxide. The stopper also carried a small stoppered tube for withdrawal of samples for analysis during the course of the run. The flasks were immersed to the neck in the 90° bath, clamped in place, and the stirrers connected to a multiple stirring device which permitted the running of eight samples at one time. Most of the solids began to deposit only after the solutions had been held for some time at 90°. Under these conditions, equilibrium was established very quickly. Analyses of the solutions showed that no detectable changes occurred after the first few hours, but the samples were run for two to ten days before the final analysis. At the end of this period, most of the solids had begun to show a definite crystalline structure.

When the mixtures had reached a constant composition, they were removed from the bath and filtered rapidly by suction through a Büchner funnel. The filtration required about one minute, during which time the temperature of the solution dropped not more than 15–20°. No appreciable error was introduced by this procedure, since the composition of the filtered solutions checked within the

TABLE I

	Composition of solns. % by wt.			Composition of solids ratio CaO/As_2O_5		Max.	Compounds[a]	Mol. ratio
Expt.	As_2O_5	CaO	Mol. ratio CaO/As_2O_5	Wt.	Mol.	solid pptd., mg.	in solid phases	CaO/As_2O_5, calcd.
6	0.001	0.001	4.12	0.843	3.46	50	Basic + lime	
6	.003	.002	2.74	.814	3.34	50	Basic	3.33
5	.004	.002	2.05	.802	3.29	50	Basic	
6	.007	.003	1.76	.794	3.26	50	Basic	
2	.008	.004	2.05	.804	3.30	50	Basic	
4	.008	.003	1.54	.768	3.16	50	Basic + Tri	
6	.010	.004	1.64	.751	3.08	50	Tri	3.00
5	.012	.005	1.71	.746	3.06	50	Tri	
6	.013	.006	1.89	.743	3.05	50	Tri	
6	.018	.007	1.60	.731	3.00	100	Tri	
4	.021	.007	1.37	.717	2.94	100	Tri	
6	.025	.010	1.65	.731	3.00	100	Tri	
4	.031	.010	1.33	.729	2.99	100	Tri	
4	.038	.013	1.41	.704	2.89	100	Tri + Penta	
4	.042	.015	1.47	.604	2.48	100	Penta	2.50
3	.050	.018	1.48	.597	2.45	100	Penta	
4	.055	.018	1.34	.595	2.44	100	Penta	
4	.068	.022	1.33	.597	2.45	100	Penta	
3	.069	.022	1.31	.597	2.45	100	Penta	
3	.073	.023	1.29	.607	2.49	100	Penta	
1	.082	.026	1.30	.614	2.52	500	Penta	
1	.115	.034	1.22	.619	2.54	500	Penta	
1	.134	.038	1.17	.604	2.48	500	Penta	
1	.153	.044	1.18	.561	2.30	500	Penta + Di	
1	.156	.046	1.21	.497	2.04	500	Di	2.00
1	.177	.050	1.16	.492	2.02	500	Di	
1	.241	.065	1.11	.500	2.05	500	Di	

[a] Empirical formulas: basic = $[Ca_3(AsO_4)_2]_3 \cdot Ca(OH)_2$; tri = $Ca_3(AsO_4)_2$; penta = $Ca_5H_2(AsO_4)_4$; di = $CaHAsO_4$.

analytical error with samples of the same solutions previously pipetted directly from the flasks during the course of the run. Following the filtration, portions of the solution were cooled, weighed, and analyzed for calcium and arsenic. The solid was washed on the filter paper with small amounts of hot water, dissolved in 1:1 hydrochloric acid, made to volume, and suitable aliquots of this solution analyzed for calcium and arsenic. Because of the small quantity of the solid, no attempt was made to weigh it before analysis, but only the ratio of calcium oxide to arsenic oxide was determined.

Results and Discussion

The data obtained by the final procedure are presented in Table I, and plotted in Figs. 1 and 2.

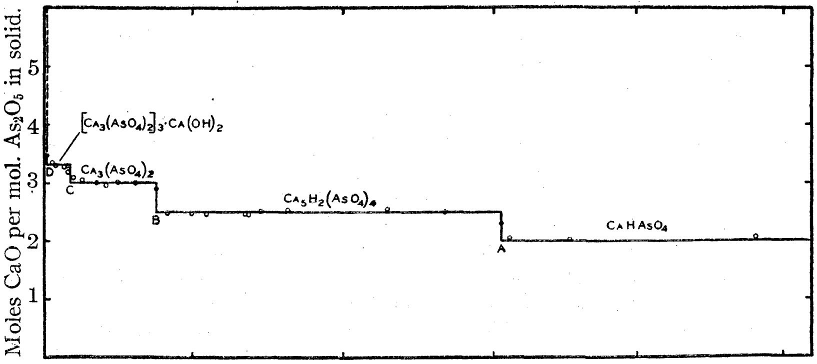


Fig. 1.

As shown in the table, the data are taken from the results of six different runs, only those samples being selected from each run which fulfilled the conditions of precipitating at 90° and not at room temperature. The reproducibility of the results is shown by the fact that the ranges of each of the three more basic compounds contain points from three different experiments.

The method of plotting used in Fig. 1 was employed for the identification of the compounds because the high dilution of all of the solutions made it impossible to plot the compositions of both solids and solutions to the same scale on a diagram such as that of Fig. 2.

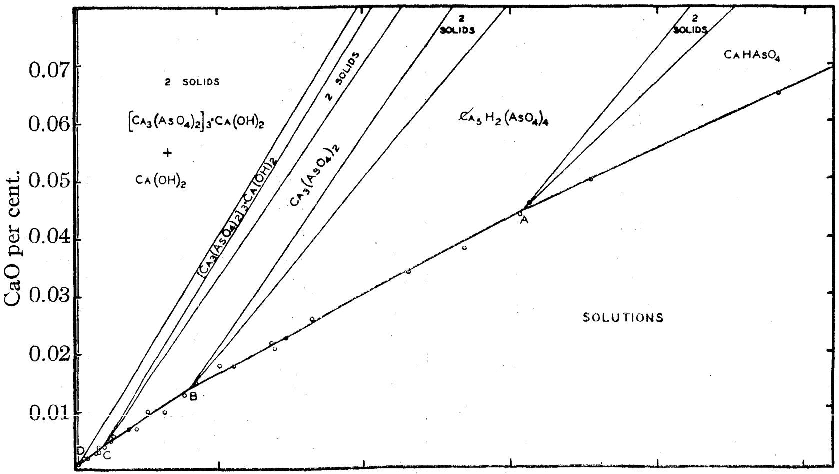


Fig. 2.

The flat portion of the curve in Fig. 1 from the extreme right to the point A shows the existence of a compound $2CaO:As_2O_5$. Although the data do not show the amount of water associated with any of the solid compounds, this composition corresponds to the dicalcium arsenate, $CaHAsO_4$. The curve as plotted shows only the extreme lower end of the range of this compound, which is stable in contact with solutions containing up to 27.5% arsenic oxide at 35°, according to Smith.[5] All of the solids in this group showed a definitely crystalline structure under the microscope.

The flat portion AB corresponds to a pentacalcium compound $5CaO:2As_2O_5$, which is another acid compound, the simplest empirical formula for which would be $Ca_5H_2(AsO_4)_4$. So far as the writers are aware, this compound has not previously been reported. An analogous compound is known among the calcium phosphates, however, in the form of the mineral Martinite, $Ca_5H_2(PO_4)_4$. The arsenate came out readily in the form of long, pointed needles, quite different in form from the crystals of dicalcium arsenate. The solid obtained in the sample, which falls on the vertical portion of the curve at A (Fig. 1), showed distinct crystals of both types.

The flat portion BC indicates the compound $3CaO:As_2O_5$, or tricalcium arsenate, $Ca_3(AsO_4)_2$. The very narrow range of this compound accounts for the difficulty experienced by other workers in preparing pure samples. The solids in this group were largely amorphous, although several showed a few crystals which were quite definitely not similar to those of either of the acid compounds.

The portion CD is somewhat more uncertain than the other three, being extremely short. There is very little question, however, from these results and from the results of preparations which are discussed later, that this portion represents a definite basic compound, $10CaO:3As_2O_5$, which is the same as the compound $[Ca_3(AsO_4)_2]_3 \cdot Ca(OH)_2$ reported by Tartar *et al.*[7] These solids appeared almost entirely amorphous, with a slight indication in one or two cases of the incipient formation of crystals.

The curve becomes vertical again at the point D, representing most probably a mixture of the basic compound with free lime. The points were not carried any farther up this curve, because the limitations of the analysis would not permit the identification of any further compounds if they existed, and because the etching of the flasks, which occurred in this region, would in any case make the results uncertain.

Figure 2 shows in more detail the general equilibrium conditions in the system. The curve ABCD represents the compositions of solutions in equilibrium with the various solid compounds. The letters A, B, C, and D represent the same points as in Fig. 1.

The diagram in Fig. 2 was used as the basis for a number of preparations of the different compounds, which were made in order to check the validity of the curve, and to furnish larger quantities of the pure compounds for a study of their properties. Small amounts of each of these preparations were made at 90°, but it was found more convenient for the larger amounts to be prepared at 100°, assuming that the curve would not be widely different at that temperature. Samples of two or three grams were prepared by making up solutions having a composition on the curve ABCD at about the center of the range of the compound sought, heating to boiling, and simultaneously adding lime and arsenic acid solutions in the proper proportions to form the compound, regulating the boiling and the rate of addition of the solutions so that the total volume of the mixture was kept constant. Little difficulty was experienced in obtaining products having the proper CaO/As_2O_5 ratios. Products were obtained having the following molecular ratios: basic, 3.30, 3.26; tri, 3.01, 3.00; penta, 2.49, 2.52; di, 2.00, 1.98. The actual percentages of the constituents varied somewhat, due to the fact that the products were rather amorphous in most cases, making it difficult to remove all of the mechanically combined water. Further attempts are being made to prepare completely crystalline samples of the compounds, on which accurate chemical and physical data can be obtained.

Figure 2 also furnishes an explanation of the fact that preparations made by adding concentrated arsenic acid to a suspension of lime are not consistent in properties. Even though the final composition of the mixture may lie in the region corresponding to a mixture of the basic compound with free lime, temporary local concentrations of the acid may make possible the formation of appreciable amounts of the other compounds. The conversion of these compounds being very slow, considerable amounts of them may be left unchanged in the final product. Thus commercial calcium arsenates probably contain a mixture of several compounds depending on the conditions of precipitation.

It is apparent from the fourth column in Table I that the basic compound is the only one which can dissolve in water at 90° without hydrolysis. All of the solutions in equilibrium with the other compounds have a lower ratio of lime to arsenic than the compounds themselves, as was noted by Smith[5] in the case of dicalcium arsenate. The data are in agreement with Tartar's[7] observation that the basic salt is formed by hydrolysis of the tricalcium salt, but is unchanged by further treatment with water. The di and penta salt should also be convertible to the basic by the same treatment.

Acknowledgment.—The authors wish to express their appreciation to Dr. A. W. Avens for his assistance in much of the analytical work.

Summary

1. A study of the system $CaO–As_2O_5–H_2O$ at 90° has been carried out.

2. A technique has been developed which permitted rapid attainment of equilibrium in the system.

3. Four compounds have been identified: dicalcium arsenate $CaHAsO_4$, pentacalcium arsenate $Ca_5H_2(AsO_4)_4$, tricalcium arsenate $Ca_3(AsO_4)_2$, basic calcium arsenate $[Ca_3(AsO_4)_2]_3 \cdot Ca(OH)_2$.

4. Application of the data to the preparation of pure and commercial calcium arsenates has been discussed.

GENEVA, N. Y. RECEIVED APRIL 11, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

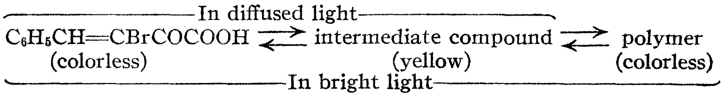
The Action of Light on Beta-Bromobenzalpyruvic Acid

BY MARIE REIMER

The action of sunlight on the methyl ester of benzalpyruvic acid results in polymerization of the ester to cyclobutane derivatives[1] as is the case with the cinnamic acids and many other ethylenic compounds. In a study of other unsaturated α-ketonic acids, in this Laboratory, it has been found[2] that benzalpyruvic acids in which methoxyl groups are substituted in the nucleus are less affected by light than the unsubstituted ester. The most active substance encountered is β-bromobenzalpyruvic acid which is extraordinarily sensitive to light. The present paper describes results so far obtained in the study of this light reaction.

When a colorless solution of β-bromobenzalpyruvic acid in benzene is allowed to stand in the diffused light of the laboratory it takes on a yellow color and, after two to three days, has become a brilliant lemon yellow. This color change does not take place in the dark.

On exposure of this yellow solution in thin layers to the direct sunlight the color fades quickly and the solution remains colorless for hours if kept in the direct rays of the sun. As soon as it is removed from the sunlight the yellow color reappears. The change from a yellow to a colorless solution in direct sunlight and from colorless to yellow in diffused light is rapid and can be repeated many times. The solution is so sensitive to the difference in intensity of the light that moving it a few cm. out of the direct rays is sufficient to bring back the yellow color and even the passing of a cloud over the sun has the same effect. After several hours of exposure a white crystalline substance begins to separate on the walls of the containing vessel. This is a dimeric form of β-bromobenzalpyruvic acid. The filtered solution, colorless after a day of exposure to the sunlight, becomes brilliantly yellow overnight. This yellow intermediate compound is, in all probability, a geometrical isomer of the original acid which forms an equilibrium mixture with that acid in diffused light. The effect of light on β-bromobenzalpyruvic acid is then, in part, as follows



$$\overbrace{\underbrace{\underset{\text{(colorless)}}{\mathrm{C_6H_5CH{=}CBrCOCOOH}} \rightleftarrows \underset{\text{(yellow)}}{\text{intermediate compound}} \rightleftarrows \underset{\text{(colorless)}}{\text{polymer}}}_{\text{In bright light}}}^{\text{In diffused light}}$$

The cause of the rapid change in color of the solution as it is moved into and out of the direct rays of the sun is evidently the difference in rate of polymerization in bright and in diffused light, the speed of polymerization outstripping that of isomerization in bright light but falling far behind it in diffused light, a sensitivity to difference of light intensity recalling that of lactoflavine, recently described.[3]

If the tubes used for exposure are tightly stoppered another effect of light becomes apparent in the formation of a volatile substance which, as soon as it has saturated the benzene solution, changes the course of the reaction. This substance was found to be hydrogen bromide formed evidently by photodecomposition of some of the bromine compounds present. In its presence there is no appearance of the yellow compound, the polymer is formed in but small quantity, much of the original acid being recovered unchanged. The solution slowly takes on a brown color due to formation of decomposition products. When the tubes are left open to the air, so that the hydrogen bromide escapes, there is no evidence of such products until the solution has been exposed for several weeks. The containers used were at first loosely stoppered to allow the escape of this gas but, as it was found that the solutions were sensitive to the oxygen of the air, later experiments were conducted in an atmosphere of nitrogen. The best yields of polymer were obtained in this way.

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(1) Reimer, THIS JOURNAL, **46**, 783 (1924).

(2) Reimer and Kamerling, *ibid.*, **55**, 4643 (1933); Reimer, Tobin and Schaffner, *ibid.*, **57**, 211 (1935).

(3) Karrer, Köbner, Salomon and Zehender, *Helv. Chim. Acta*, **18**, 270 (1935).

The yellow solutions, saturated with nitrogen and exposed to bright sunlight with a stream of nitrogen running through, rapidly lost their yellow color. The polymeric compound was deposited in yields of 75 to 80%. The characteristics of this compound are like those of the substance formed from the unsubstituted benzalpyruvic ester in the sunlight[1] which has been proved to be a cyclobutane derivative. If these two reactions are, indeed, analogous, exposure to the light of the unsaturated bromo acid without a solvent would be expected to give directly a polymeric product, without the intermediate formation of an isomer, which should then be different from the polymer obtained from benzene solution. This has been found to be the case. On exposure of bromobenzalpyruvic acid to the sunlight without solvent, there is no change in color. The crystalline acid slowly crumbles to a fine powder from which there can be separated, in small quantity, a crystalline dimeric compound isomeric with the one obtained in benzene solution. The space relation of these isomeric polymers is still under investigation.

When freshly prepared, colorless solutions of β-bromobenzalpyruvic acid were exposed to bright sunlight with a stream of dry oxygen running through the solution, they took on a brownish-yellow color almost at once, a color which did not fade at all in the light, and a pale brownish solid was deposited slowly. This is a mixture, the chief components of which are the dimer, obtained previously from benzene solution, melting at 201°, and a bromo acid melting at 109°. This acid has the formula $C_{10}H_8O_4Br_2$, differing from the original unsaturated bromo acid, $C_{10}H_7O_3Br$, by the elements of hypobromous acid. It is evidently formed in the oxidizing mixture by the addition of hypobromous acid to the unsaturated acid as it can be readily obtained by suspending β-bromobenzalpyruvic acid in water and drawing bromine vapor through the liquid. It is the presence of this bromo acid (109°) that gives the brownish-yellow color to the solution.

The most interesting product of the action of light on β-bromobenzalpyruvic acid appeared after the experiments had been in progress for some time when the solvent was benzene from another source than that previously used. The yellow solutions, in tubes open to the air, began to deposit colorless crystals with a brilliant pearly luster almost immediately on exposure to the sunlight. After several hours the solution became slightly cloudy and the polymeric compound (201°) was slowly deposited. In many repetitions of this experiment the separation of the shining solid began within a few seconds of exposure to the sunlight and stopped abruptly after several hours. The fact that this compound had not been obtained when benzene from another source was used as a solvent and that its formation stopped completely after a limited time suggested that it was a product of reaction of the unsaturated acid with some foreign substance in the benzene. On investigation the benzene was found to contain moisture; after its removal the reaction proceeded as previously described. The new compound is, therefore, a hydrolytic product. It is a saturated acid free from bromine, fairly soluble in cold water, melting with vigorous decomposition at 134°. It has the formula $C_{10}H_{10}O_6$. Oxidation of a dilute solution of the sodium salt of the acid with hydrogen peroxide gave two soluble products which were proved to be mandelic and oxalic acids. The properties of the substance and these two products of oxidation suggest that the compound $C_{10}H_{10}O_6$ is an hydroxy acid, $C_6H_5CHOHCOCOCOOH \cdot H_2O$. The acid, however, is colorless and it does not lose water on standing for many weeks over sulfuric acid. Because of these facts and because the ketone groups in such a compound would be highly activated, more probable structures would be $C_6H_5CHOHCOC(OH)_2COOH$ or $C_6H_5CHOHC(OH)_2COCOOH$. That there are two hydroxyl groups attached to neighboring carbon atoms and the second of these formulas therefore correct is shown by the behavior of the acid toward the Criegee[4] reagent; when treated with lead tetraacetate, benzaldehyde is formed immediately.

It is to be expected that an acid of this constitution could be obtained from β-bromobenzalpyruvic acid by oxidation and hydrolysis at the double linkage and subsequent hydrolysis of the bromine atom and it has, in fact, been found possible to reproduce the light reaction by use of potassium permanganate under carefully controlled conditions. The products of this reaction were the bromo acid (109°), mandelic and oxalic acids and a 35 to 40% yield of the hydroxy acid. The possibility of preparing from this acid compounds with several highly activated groups makes it of more than usual interest. These experiments are now in progress.

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(4) Criegee, *Ber.*, **64**, 260 (1931).

It is evident, from the foregoing account, that the products formed by action of light on β-bromobenzalpyruvic acid are determined by the conditions of the reaction. The acid, exposed to light in the solid condition, is very slowly polymerized to a dimeric form. In benzene solution it changes fairly rapidly to a yellow compound, probably a geometrical isomer, which in bright sunlight is transformed into a colorless, isomeric diamer. In the presence of oxygen the chief products obtained from the benzene solution are this same diamer and a bromo acid formed by addition of hypobromous acid to the original unsaturated acid. If moisture as well as oxygen is present, an hydroxy acid, $C_6H_5CHOHC(OH)_2$-COCOOH, separates rapidly from the benzene solution on exposure to the light. Such a light reaction, resulting in the addition of two hydroxyl groups to an ethylenic linkage, was postulated by Ciamician[5] to account for the final products obtained by him from the mixture of substances formed by action of light on methylheptenone but the compound was not isolated. A parallel behavior, "hydroxylation" at the double linkage, has recently been suggested[6] to account for the formation of azafrin in the escobedia plant and mentioned as a possible first step in the change of β-carotene to vitamin A. Certainly the compound here described is the result of photochemical "hydroxylation" in the presence of moisture and oxygen of the air.

Experimental Part

Beta-bromobenzalpyruvic acid was obtained as previously described[1] from benzalpyruvic acid prepared by a later method.[7] The pure bromo acid in saturated benzene solution was exposed to bright sunlight in quartz test-tubes or flasks fitted with grooved stoppers so that the hydrogen bromide, that had been found to block the reaction, could escape. The intermediate yellow compound, under these conditions, changed to the polymer as fast as it was formed. On moving the solution out of the direct rays of the sun, the yellow color became apparent. After several hours of exposure, fine crystals of the polymeric compound began to separate. These were filtered out at frequent intervals. After about two weeks of exposure there was no further separation of this compound. The benzene filtrates, now of a pale brownish color, contain a complex mixture of material from which benzoic and oxalic acids, an unidentified bromo acid and a tarry residue have been obtained. When dry nitrogen was passed through the solutions during exposure the yield of polymeric compound was increased from about 50 to nearly 80%.

The solid polymer, washed with benzene, separates slowly from methyl alcohol in large, brilliant, clear, rhombic crystals which rapidly become opaque on exposure to the air. The pure substance melts with vigorous decomposition at 201°. It is readily soluble in acetone, fairly soluble in ether and in boiling methyl alcohol, insoluble in benzene, chloroform and ligroin.

Anal. Clear crystals: Calcd. for $C_{20}H_{14}O_6Br_2 \cdot 2CH_3OH$: C, 45.99; H, 3.83. Found: C, 45.51; H, 3.66. Opaque crystals: Calcd. for $C_{20}H_{14}O_6Br_2$: C, 47.06; H, 2.74. Found: C, 47.03; H, 2.56.

The compound decomposes to give yellow solutions on long heating in organic solvents and, in the dry condition in the light, it takes on also a yellow color.

All attempts to replace the bromine atoms with hydrogen or to eliminate the bromine atoms so that the compound could then be reduced in the hope of obtaining one of the unsubstituted cyclobutane acids formerly prepared[1] have been unsuccessful. The acid is either not attacked at all by the reagents used or suffers deep-seated decomposition. It is interesting to find that Stoermer in his latest work on cyclobutane acids[8] has met with the same difficulty in the case of a brominated γ-truxillic acid.

The **methyl ester** of the acid could not be prepared by the action of methyl alcohol, saturated with hydrogen chloride, but was readily formed by action of diazomethane. The ester is very slightly soluble in ether and alcohols, more readily in acetone and benzene. It separates from boiling methyl alcohol in colorless prisms melting at 212° with slow decomposition above the melting point.

Anal. Calcd. for $C_{22}H_{18}O_6Br_2$: C, 49.07; H, 3.34; mol. wt., 538. Found: C, 49.08; H, 3.29; mol. wt. (Rast), 526.

The ester does not decompose on long boiling with methyl alcohol nor in the light but solutions in benzene turn yellow slowly on heating. It is extremely resistant to saponification. This same ester can be prepared by exposing methyl β-bromobenzalpyruvate to sunlight in benzene solution.[9]

When finely ground crystals of β-bromobenzalpyruvic acid were exposed to the sunlight without solvent they crumbled slowly to a fine powder, strongly triboelectric. After two to three months' exposure, the mass was extracted repeatedly with small quantities of boiling benzene from which the original unsaturated acid crystallized on cooling. The small amount of residue, not soluble in benzene, was a colorless acid which separated from boiling methyl alcohol in stocky needles melting with decomposition at 285°. The acid does not crystallize with methyl alcohol. It is readily soluble in boiling benzene and in ether.

Anal. Calcd. for $C_{20}H_{14}O_6Br_2$: C, 47.06; H, 2.74; mol. wt., 510. Found: C, 47.47; H, 3.17; mol. wt. (Rast), 468.

The *methyl ester* was prepared with diazomethane in the

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(5) Ciamician and Silber, *Ber.*, **46**, 3077 (1913).

(6) Kuhn and Brockmann, *Ann.*, **516**, 111 (1935).

(7) Reimer, This Journal, **53**, 3147 (1931).

(8) Stoermer and Stroh, *Ber.*, **68**, 2102 (1935).

(9) The methyl ester of bromobenzalpyruvic acid previously prepared[10] was described as an oil. The oil is evidently a mixture of isomers as the ester obtained by action of diazomethane on the monobromo acid crystallizes from diluted methyl alcohol in shining plates melting at 62°. *Anal.* Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.34. Found: C, 49.05; H, 3.19.

(10) Reimer, This Journal, **48**, 2454 (1926).

usual manner. It crystallizes from methyl alcohol in fine, shining colorless needles melting at 233–234°.

Anal. Calcd. for $C_{22}H_{18}O_6Br_2$: C, 49.06; H, 3.34. Found: C, 48.95; H, 3.60.

α-Keto-β,β,γ-trihydroxy-γ-phenylbutyric Acid, $C_6H_5CHOHC(OH)_2COCOOH$.—This acid, obtained when benzene containing a trace of moisture was used as solvent in the light reactions, separated from solution in small platelike crystals which are conspicuous because of their brilliant pearly luster. It was purified by repeated extraction with boiling benzene, the residue then dissolved in the smallest possible quantity of dioxane, in which it is readily soluble, and double the volume of benzene added. The acid separates in fine needles melting with vigorous decomposition at 134°. It is readily soluble in alcohols and acetone, fairly soluble in water.

Anal. Calcd. for $C_{10}H_{10}O_6$: C, 53.09; H, 4.42; mol. wt., 226. Found: C, 53.26; 53.38; H, 4.47; 4.42; mol. wt., 232.

Proof of Structure.—To one-half gram of the acid in the calculated quantity of dilute sodium carbonate solution, 10 cc. of hydrogen peroxide (13 vol.) was added. After twenty-four hours the solution was acidified, extracted with ether, the ether evaporated and the residue crystallized repeatedly from boiling benzene. Clear needles separated which rapidly became opaque in the air and then melted at 118°. These properties indicated mandelic acid and this was confirmed by a mixed melting point with an authentic sample. The crystals left from evaporation of the residual aqueous solution were identified as oxalic acid.

These two products proved that the groups C_6H_5CHOHC— and —COCOOH were present in the molecule. The proof that there are two hydroxyl groups attached to neighboring carbon atoms and that the formula of the acid is, therefore, $C_6H_5CHOHC(OH)_2COCOOH$, was obtained by oxidation with lead tetraacetate prepared according to the directions of Dimroth.[11] After half an hour, steam was passed through the reaction mixture which smelled strongly of benzaldehyde. *p*-Nitrophenylhydrazine added to the distillate gave a brick red solid which, after crystallization from glacial acetic acid, melted at 192–194° alone and when mixed with a sample of the *p*-nitrophenylhydrazone prepared from pure benzaldehyde.

As the yields of the hydroxy acid were small, rarely more than 5%, attempts were made to obtain it in larger quantity. The obvious procedure of adding more water to the benzene before exposure was not satisfactory; if but a small excess of water was added, the hydrate of bromobenzalpyruvic acid crystallized out and the reaction stopped. By passing moist oxygen through the benzene solution, however, the yields of hydroxy acid were increased to 10 to 12%. After this acid had crystallized out, a mixture of solids slowly formed from which have been separated the dimeric compound (201°), unchanged β-bromobenzalpyruvic acid, mandelic acid and the bromo acid (109°).

Synthesis.—Four grams of β-bromobenzalpyruvic acid was dissolved in a mixture of 130 cc. of acetone and 30 cc. of water and a few drops of sulfuric acid. A solution of 1 g. of potassium permanganate in 200 cc. of acetone was added slowly, the mixture mechanically stirred, and kept at a temperature of 0 to −3°. Small amounts of dilute sulfuric acid were added as needed to keep the solution faintly acid. The oxidation required two and one-half hours. After spontaneous evaporation of the acetone there remained about 12 cc. of water and a mixture of crystalline solids, which were washed with a very little cold water and dried over sulfuric acid for forty-eight hours. The mixture, 3.5 g., was then repeatedly extracted with 5-cc. portions of hot benzene. The shining residue, not soluble in benzene, was the pure hydroxy acid (134°). A further small amount was deposited from the benzene extracts as they cooled. The yield in all was 1.3 g. (36%). On standing the yellow benzene solutions deposited slowly clear shining crystals of the bromo acid, melting at 109°, described below. From the aqueous filtrate 0.34 g. of mandelic acid and 0.2 g. of oxalic acid were obtained, showing that about one-half of the unsaturated acid was oxidized and hydrolyzed to the hydroxy acid and that about one-fourth of this product was oxidized further to mandelic and oxalic acids.

The hydrogen bromide formed by the hydrolysis was evidently oxidized in the permanganate solution to hypobromous acid which formed an addition product with part of the unsaturated acid.

Hydrated Dibromohydroxybenzylpyruvic Acid, $C_6H_5CHBrCBrOHCOCOOH \cdot H_2O$ or $C_6H_5CHOHCBr_2COCOOH \cdot H_2O$.—This acid was synthesized in quantitative yield as follows: 5 g. of β-bromobenzalpyruvic acid was suspended in 400 cc. of water, the mixture cooled with ice and 3 g. of bromine vapor drawn through slowly with a current of air. The bromine was at first rapidly decolorized, then more slowly, and a pure white granular solid separated. The compound can also be prepared by dropping bromine into a cooled, aqueous suspension of the unsaturated acid. The substance crystallizes from benzene in clear fine needles melting to an opaque liquid at about 107°, to a clear liquid at 109°. It is readily dehydrated over sulfuric acid.

Anal. Calcd. for $C_{10}H_8O_4Br_2 \cdot H_2O$: C, 32.43; H, 2.70. Found: C, 32.58, 32.73; H, 2.78, 2.63. Calcd. for $C_{10}H_8O_4Br_2$: C, 34.09; H, 2.27. Found: C, 34.18; H, 2.61.

When benzene solutions of the acid are heated or left standing in the air they take on the deep brownish-yellow color characteristic of benzene solutions of β-bromobenzalpyruvic acid exposed to light in the presence of oxygen.

Summary

The action of light on β-bromobenzalpyruvic acid results in products differing according to the conditions of the reaction. Two isomeric diamers, a hydrated bromo acid and a trihydroxy ketonic acid are here described.

NEW YORK, N. Y.

RECEIVED APRIL 21, 1936

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[11] Dimroth, Friedemann and Kämmerer, *Ber.*, **53**, 485 (1920).

[CONTRIBUTION NO. 42 FROM COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Exhaustive Chlorination of a Bituminous Coal

BY J. F. WEILER

Further support of the concept that coal is essentially benzenoid[1] in character was sought by subjecting a bituminous coal from the Pittsburgh seam, Edenborn Mine, to exhaustive chlorination in antimony pentachloride, this reaction converting aliphatic substances to carbon tetrachloride and hexachloroethane while removing only the side chains of benzenoid substances, leaving the ring structures intact.[2]

The coal, suspended in carbon tetrachloride at 76°, in phosphorus oxychloride at 107°, stannic chloride at 114°, and antimony pentachloride at 100, 150, 200 and 400°, was treated with chlorine. The reaction in the first three media did not proceed so far as in the antimony pentachloride, and the data obtained are not reported herein. About 10% of the reaction product in antimony pentachloride at 200° was volatilized easily and consisted of carbon tetrachloride, hexachloroethane and hexachlorobenzene. The non-volatile residue was too complex for identification. Elementary balances were made of both the volatile and non-volatile products.

Experimental

A sample of 200 mesh coal, dried *in vacuo* at 105° to constant weight and weighing about 7 g., was placed in a reaction flask connected with a trap cooled with dry ice and 50 cc. of antimony pentachloride added. Chlorine was led through the apparatus at the rate of about 3 cc. per minute while the temperature was maintained at the desired point by a furnace with automatic temperature control. As the chlorination proceeded volatile products were condensed in the trap.

At the conclusion of the chlorination the apparatus was disconnected and the trap allowed to warm up to 10° so as to evaporate the chlorine that had condensed there. Water was then added slowly and with good cooling to hydrolyze the antimony pentachloride that had condensed in the trap.

The volatile contents of the trap were then swept through a combustion train by means of a current of oxygen. Cerium dioxide on silica gel served as the combustion catalyst; it was followed by a layer of silver wool to remove halogens.

The non-volatile portion of the reaction product was treated in a Soxhlet extractor with 20% hydrochloric acid for six days in order to remove antimony, and then dried *in vacuo* over phosphorus pentoxide at room temperature.

Microelementary analyses of these non-volatile residues were made. The samples still contained enough antimony to vitiate the carbon–hydrogen determinations when the usual combustion tube filling was used. It was found possible, however, to adapt the red lead filling used to retain arsenic in macrocombustions[3] so that correct analyses were obtained on organic compounds containing antimony.[4]

Results and Discussion

Data are summarized in Table I in the form of elementary balances for the various experiments performed.

The criteria for following the extent of chlorination with time and temperature were the values for non-volatile chlorinated residue, for the carbon content of the volatile products, and the chlorine and hydrogen contents of the residue. The amount of non-volatile residue showed no significant change in the various experiments but the carbon in the volatile products increased greatly as the temperature rose from 100 to 150 to 200°, then increased but slightly as the time at 200° increased from one to four to six days. The rate of increase of chlorine content and decrease of hydrogen content with time and temperature fell off abruptly at the four-day 200° chlorination. Apparently the coal was exhaustively chlorinated after four to six days' chlorination at 200°.

As a further test of the extent of the chlorination one-half of a sample of coal chlorinated for six days at 200° without driving off the volatile reaction products was reheated with antimony pentachloride in a sealed tube at 400° for four days. Both halves of the sample were then extracted for twelve hours each, successively, with ether, chloroform and chlorobenzene, in a Soxhlet. Both products showed practically the same solubility, indicating that the chlorination at 200° had been nearly complete. The ether removed 21%, the chloroform 22% and the chlorobenzene 18%, leaving an insoluble residue of 39%. Analyses and empirical formulas for the fractions from the material chlorinated at 200° only are given in Table II. The empirical formulas are calculated

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(1) W. A. Bone, L. Horton and A. Ward, *Proc. Roy. Soc.* (London), **127A**, 508 (1930).

(2) G. Ruoff, *Ber.*, **9**, 1483 (1876); V. Merz and W. Weith, *ibid.*, **16**, 2870 (1883); F. Hartmann, *ibid.*, **24**, 1025 (1891); A. Eckert and K. Steiner, *Monatsh.*, **36**, 175 (1915).

(3) M. Falkov and G. W. Raiziss, THIS JOURNAL, **45**, 998 (1923).

(4) F. C. Silbert, unpublished.

TABLE I

ELEMENTARY BALANCES OF CHLORINATED PRODUCTS

Grams per 100 Grams of Coal

In product from chlorination for	Non-volatile chlorinated residue per 100 g. coal, g.	C			H	O	N	S	Cl	Ash
		In residue	In volatile	Total						
(Original coal)	...	..	..	77.4	5.32	6.95	1.36	0.87	..	8.12
4 days—100° (2)[a]	176	71.2	0.86	72.1	2.92	21.1	1.48	1.02	71.9	6.44
4 days—150° (2)	185	71.6	2.1	73.7	2.32	19.7	1.70	0.87	81.2	6.98
1 day—200° (1)	172	69.6	3.6	73.2	2.08	13.1	1.60	0.29	78.8	6.55
4 days—200° (3)	177	66.3	3.8	70.1	1.86	15.6	1.65	0.64	86.1	4.96
6 days—200° (2)	181	67.2	4.0	71.2	2.54	11.1	2.00	1.05	88.7	6.29

[a] Figures in parentheses refer to number of experiments; the values given in the table are averages.

TABLE II

SOLVENT FRACTIONATION OF COAL CHLORINATED AT 200° FOR SIX DAYS

	C	H	Cl (ash free)	N	S	O	Empirical formula
Ether soluble	38.97	1.89	48.20	0.64	0.39	9.91	$C_6H_{2.4}Cl_{2.5}(OH)_{1.1}$
$CHCl_3$ soluble	38.76	0.89	50.94	.94	.37	8.10	$C_6H_{0.7}Cl_{2.7}(OH)_{0.9}$
C_6H_5Cl soluble	44.66	1.11	44.68	1.14	.63	7.78	$C_6H_{1.0}Cl_{2.1}(OH)_{0.8}$
Residue	43.65	1.46	36.61	1.10	.36	16.82	$C_6H_{0.8}Cl_{1.7}(OH)_{1.7}$

arbitrarily on the basis of six carbon atoms and the oxygen is assumed to be hydroxyl oxygen.

The mean molecular weights of these fractions were determined cryoscopically in catechol by the method of Smith and Howard[5] but the results were not sufficiently reproducible to indicate more than the order of magnitude. The three soluble fractions gave values from 130 to 190; the insoluble residue gave values from 230 to 270. These values were too low to be consistent with the physical behavior of the substances and it may have been that the substances underwent a dissociation similar to that reported by the above authors for humic acids.

The ether soluble fraction was light brown in color. When heated considerable amounts of hexachlorobenzene sublimed off and then the material charred with evolution of hydrogen chloride. The ratio of carbon to attached substituents was nearly one to one, indicating the absence of appreciable amounts of condensed ring structure in this fraction.

The chloroform and chlorobenzene soluble fractions and the residue were black and infusible, losing hydrogen chloride on heating. The ratio of carbon to attached substituents was approximately 6 to 4 in each fraction, indicating the presence of a preponderance of condensed ring structure.

The fraction of each of the constituent elements of the coal which make up the stable ring structures as represented by the non-volatile residues from the 200° chlorinations may be obtained from the elementary balances in Table I.

The carbon balances show that the non-volatile residue accounted for 85% of the carbon of the original coal. Approximately 5% was accounted for in the volatile reaction products which consisted wholly of carbon tetrachloride, hexachloroethane and hexachlorobenzene, while 10% was unaccounted for. The 10% was probably lost as carbon dioxide. The results indicate that approximately 85% of the carbon of this coal is present in a large, condensed ring structure not destroyed by chlorination, the other 15% being present in side chains or ring structures broken by chlorination.

The values for hydrogen were erratic; the non-volatile residue contained approximately 35–50% of the hydrogen present in the original coal. Assuming that the increase in the oxygen content of the residue was due to replacement of chlorine by hydroxyl during the hydrochloric acid extraction and correcting for the hydrogen thus introduced, the hydrogen content of the residue before extraction was approximately 25–40% of that of the original coal. The 60–75% hydrogen not accounted for in the non-volatile residue is probably not entirely peripheral hydrogen[6] but includes such nuclear hydrogen as has undergone reaction.

The nitrogen balances show that the chlorinated residues contained more nitrogen than the original coal, the excess having increased with increased chlorination until it amounted to 50%.

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(5) R. C. Smith and H. C. Howard, THIS JOURNAL, **57**, 512 (1935).

(6) A. Eccles, G. H. Kenyon and A. McCulloch, *Fuel*, **10**, 6 (1931).

The nitrogen could not be traced to the reagents or to the small amount (<0.5%) of antimony in the residue. It is possible that the chlorination alters the nature of the nitrogen bonds in the coal so that nitrogen, previously inert to the Kjeldahl reagents, becomes susceptible to conversion to ammonium sulfate. It was observed that the chlorinated residue went into solution during the Kjeldahl digestion much more readily than the original coal. The presence of the total original nitrogen of the coal in the non-volatile chlorinated residue is in agreement with the findings of Heathcoat and Wheeler[7] and would indicate that the nitrogen is an integral part of the stable ring structure of coal.

The sulfur balances, although the values are erratic, show a trend toward less sulfur in the more highly chlorinated residues. It is possible that the antimony in the residue caused some error in the microanalyses, which were done by combustion in oxygen.

The oxygen balances show that the residues from the mildest chlorinations contained threefold the amount of oxygen contained in the original coal. The oxygen content decreased uniformly as the time and temperature of chlorination increased, until it was only 1.5 times that of the original coal. The increase in oxygen is probably due to hydrolysis during the hydrochloric acid extraction. In the earlier stages of chlorination the amount of chlorine susceptible to hydrolysis would be greatest, diminishing with increased temperature and time of chlorination due to splitting out as hydrogen chloride.

The chlorine balances show that the non-volatile residues from the four- and six-day chlorinations at 200° contained approximately 50% chlorine.

The ash content of the coal has been lowered somewhat, probably as much the result of the hydrochloric acid extraction as of the chlorination.

Acknowledgments.—The author is indebted to F. C. Silbert and T. B. Smith for the microanalytical determinations, and to R. C. Smith for the molecular weight determinations.

Summary

Coal has been chlorinated exhaustively with chlorine and antimony pentachloride for six days at 200°. Additional chlorination at 400° for four days did not materially increase the breakdown of the coal substance. The volatile reaction products obtained at 200° consisted of carbon tetrachloride, hexachloroethane and hexachlorobenzene, and contained only about 5% of the carbon of the original coal. This 5% and an additional 10% unaccounted for were probably formed from the peripheral material of the coal substance.

The non-volatile residue is considered to originate from the stable nuclei of the coal substance. Elementary balances showed that the residue contained: (1) 85% of the carbon of the original coal, (2) 40% of the hydrogen of the original coal, (3) an excess of 50% nitrogen over that of the original coal, (4) approximately double the oxygen of the original coal due to hydrolysis of the more active chlorine atoms, and (5) a ratio of carbon to attached substituents that indicates a condensed ring structure.

The residue was separated into ether, chloroform and chlorobenzene soluble fractions; each showed a mean molecular weight (cryoscopic in catechol) of approximately 160; the insoluble residue which remained had a mean molecular weight of about 250.

From these data it may be concluded that approximately 85% of the carbon of a bituminous coal from the Pittsburgh seam is part of a large condensed ring system of which the nitrogen in the coal is probably an integral part.

PITTSBURGH, PA. RECEIVED FEBRUARY 12, 1936

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[7] F. Heathcoat and R. V. Wheeler, *J. Chem. Soc.*, 2839 (1932).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, ST. PETER'S COLLEGE]

The Catalytic Properties of Charcoal. I. "Peroxidase" Activity

BY CLAUDE SCHWOB

Active charcoal has been found to influence the oxidation of uracil by hydrogen peroxide in a peculiar way. In the absence of charcoal this pyrimidine is completely oxidized at 95°, in its presence the isolation of several intermediate products of biological importance is possible.[1] This action is not strictly analogous to the catalysis of some oxidative reactions by peroxidases, but it suggested an investigation of the behavior of active charcoal in some reactions commonly used to evaluate the activity of peroxidases.

The charcoal used in this investigation was one known to modify the uracil oxidation as above.[2] Although all charcoals tested in this Laboratory gave the usual qualitative tests for peroxidases, this one was chosen because of its neutrality, that is, it did not change the *p*H of buffer solutions in several hours, thus permitting work at constant *p*H.[2] However, there is no reason to suspect that, in other respects, the other charcoals would not behave very much as this one.

The first test used was the indophenol reaction, recently applied to peroxidases.[3] The indophenol produced was found to be strongly adsorbed by the charcoal, so that the latter and the filtrate were analyzed separately. Figure 1 shows the amount of indophenol formed in various times. For the present, we have no explanation to offer for the shape of the curves. The oxygen evolved during the reaction, due to the "catalase" action of the charcoal, was measured and gave a perfectly smooth curve when plotted against time. The behavior of the curve showing the amount of indophenol in the filtrate leads to interesting speculation. One of the hypotheses still under consideration, but still to receive experimental support, is that some of the charcoal had been reduced to colloidal size, and that, under the conditions of the experiments, this colloidal part underwent oxidation by the peroxide after one-half minute. We have observed the destruction of charcoal in colloidal solution at 60°, but not at room temperature with sufficient velocity to account for the rapidity of the disappearance of the indophenol from the filtrate. It may be, however, that the other components of the reaction mixture are a factor affecting this speed. The oxidation by hydrogen peroxide of indophenol adsorbed on charcoal has never been observed by us. It seems possible that the colloidal charcoal is destroyed and that the indophenol thus liberated by loss of its adsorbent is then adsorbed by the "massive" particles of charcoal. This transfer of indophenol would explain the fact that the additive curve shows no discontinuity at this point (curve 3, Fig. 1).

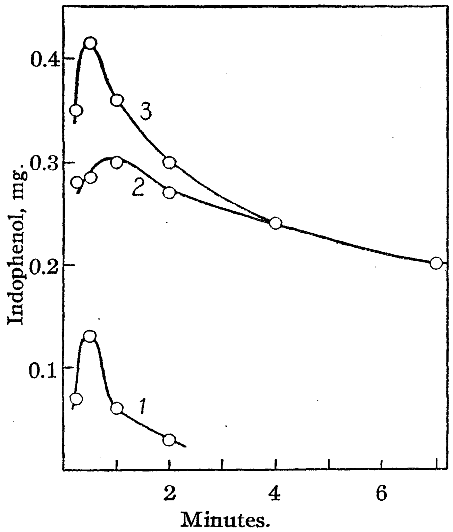

Fig. 1.—Curve 1, indophenol in the filtrate; curve 2, indophenol obtained from the charcoal. The amount remains constant at 0.20 ± 0.02 mg. from seven to at least forty minutes. Curve 3, total amount of indophenol obtained.

Colloidal charcoal was next tested by means of this same reaction. In the literature we were unable to find a method for the preparation of a colloidal solution of active charcoal. Von Weimarn's procedure[4] for obtaining sols of various substances by means of hand grinding with solid diluents was adapted to the problem in hand. We were aided in this preparation by the fact that charcoal sols, like some sulfur sols, seem to belong to the intermediate class of hydrosols, and are somewhat reversible. In fact, although the

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(1) Schwob and Cerecedo, THIS JOURNAL, **56**, 2771 (1934).

(2) Schwob, Dissertation, Fordham University, 1933.

(3) Guthrie, THIS JOURNAL, **53**, 242 (1931); Pack, *Ind. Eng. Chem.*, *Anal. Ed.*, **6**, 170 (1934).

(4) Alexander, "Colloid Chemistry," The Chemical Catalog Co., New York City, 1926, Vol. I, p. 660.

colloidal properties of the charcoal sols so obtained have not as yet been fully ascertained, they are apparently similar to those of sulfur sols.

The behavior of this charcoal sol in catalyzing the formation of indophenol is shown in Fig. 2.

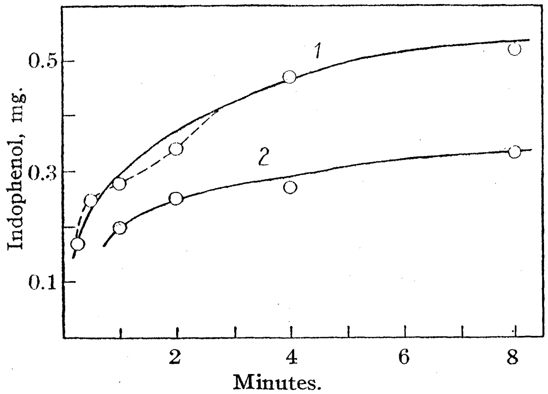

Fig. 2.—Curve 1, amount of indophenol obtained with charcoal hydrosol. For portion in dotted line see text. Curve 2, result obtained when the sol is replaced by distilled water.

No break in the curve, due perhaps to the destruction of the charcoal micelles, is apparent. A slight irregularity did show up in three of the five runs, the results of which have been averaged to give Fig. 2. These irregularities, however, were apt to cancel out in averaging, although if the average curve is redrawn as shown by the dotted line it assumes a form similar to, but less extreme than, each of the three "abnormal" curves. The point is still to be settled, however, since destruction of the charcoal would not necessarily lead to a great diminution in the indophenol yield.

An interesting fact observed was that the charcoal sol liberated no appreciable volume of oxygen from peroxide of the concentration used in these experiments over a period of several hours. Not only is this an added similarity of charcoal to natural purified peroxidase, since, until now, charcoal has been considered as having inherent "catalase" properties, but it tends to show that the suggested "peroxidase" activity is not due to a combined "catalase–oxidase" action. Accordingly, it seems untenable that the "catalase" activity serves to decompose the hydrogen peroxide to give oxygen which then forms indophenol under the influence of the "charcoal–oxidase."[5] Hence, it is probable that the charcoal activates the peroxide in some way. Ort and Bollman[6] have shown by electrometric means that some amino acids promote the oxidation of glucose by hydrogen peroxide. The effect of the charcoal sol on the voltage produced by hydrogen peroxide between a bright platinum electrode and an 0.1 *N* calomel electrode was therefore determined. While in the work of Ort and Bollman the activating effect of the amino acids may have been exercised on either the peroxide or the glucose, it seems that, in this case, it is the hydrogen peroxide that is activated. Figure 3 gives the curve obtained when there were added varying amounts of charcoal sol to peroxide solutions of fixed concentration (approximately 0.5%). By means of a blank run the effect of the small amount of gelatin used to stabilize the sol was found to be negligible for these rather qualitative results. It was thought interesting to find out whether a natural peroxidase gives a similar curve. The result for aqueous filtered potato extract (Fig. 3, curve 2) was found to have much in common with that obtained with charcoal, although the peroxide used in this case was not only from a different

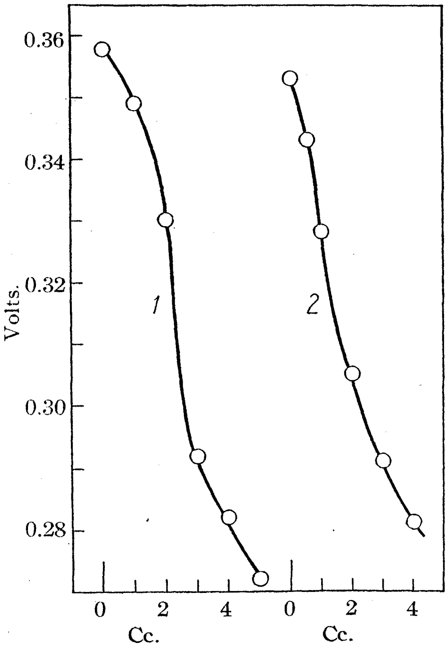

Fig. 3.—Curve 1, voltage obtained with hydrogen peroxide and varying amounts of charcoal hydrosol. Curve 2, result when diluted potato extract replaces the charcoal sol.

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(5) In fact, we were unable to oxidize uracil in the presence of charcoal with either air or oxygen, although this pyrimidine is strongly adsorbed by charcoal.[2]

(6) Ort and Bollman, THIS JOURNAL, **49**, 805 (1927).

batch, but was not of the same strength (about 0.6%). No attempt was made to obtain any but relative values, and no corrections have been applied to the voltages as read on the potentiometer. It is projected to elaborate on this method in order to attempt applying it to the determination of peroxidase activity.

Experimental

The charcoal was a commercial animal charcoal purified by refluxing with four times its weight of constant boiling hydrochloric acid for twenty hours. It was then washed with distilled water until free of chlorides. Twice its weight of hot 95% alcohol was then used to extract further impurities (mostly consisting of a greenish gum), followed by treatment with the same amount of ether. This process reduced the ash content from 45 to 1.67%, although the ash still gave a positive test for iron with thioglycolic acid.

Peroxidase Activity of "Massive" Charcoal.—A combination of the methods of Guthrie and of Pack[3] was used. A 0.500-g. sample of the charcoal was suspended in 10 cc. of distilled water, and 5.75 cc. of a solution of *p*-phenylenediamine hydrochloride containing 0.5265 g. per 100 cc. was added. To 8.75 cc. of citrate buffer of *p*H 4.5 in a 10-cc. graduate, 0.6 cc. of 4% alpha-naphthol in 50% alcohol was added carefully so as to float on top of the buffer. The contents of this cylinder were added to the flask containing the charcoal simultaneously with 10 cc. of 1% hydrogen peroxide (commercial, containing acetanilide). All chemicals were at about 25°. The flask was then shaken by hand or machine and, at the end of the required time, 2 cc. of a 2% potassium cyanide solution was added to slow up the reaction. The suspension was then filtered through a fluted filter paper and the charcoal washed with three 10-cc. portions of water, the last portion being used to force the charcoal to the bottom part of the filter. The wash-water was added to the filtrate and it was immediately extracted with 25 cc. of toluene in a separatory funnel for thirty seconds. The toluene layer was then compared with a standard indophenol solution in a colorimeter. The charcoal was dried on the filter paper in the funnel at 100° (higher temperatures tended to destroy part of the indophenol). Four 6-cc. portions of toluene were poured over the charcoal. The last drops filtering through were quite colorless. This solution was also analyzed colorimetrically. A concordance of results of 5 to 8% was usually obtained. Figure 1 represents the average of six such trials.

Preparation of the Charcoal Hydrosol.—One gram of the charcoal was ground by hand in a glass mortar with 9 g. of pure sodium chloride for twenty minutes. Two grams of the resulting mixture was ground with 18 g. of sodium chloride for a further twenty minutes. This was then dissolved in 500 cc. of distilled water. The high salt concentration precipitated the charcoal. This suspension was then filtered through asbestos in a Gooch crucible and washed with one liter of distilled water. The entire contents of the Gooch were then suspended in 500 cc. of water and, for the sol used in this investigation, 4 cc. of a 1% gelatin sol was added. The suspension was then filtered through ordinary filter paper after "aging" six to ten days at room temperature. A fine deposit formed overnight and was filtered off, after which the sol is stable for more than three months. The resulting sol contained approximately 0.003 mg. of charcoal per cc. and was brownish by transmitted light and grayish-black by reflected light. A sol of lesser concentration may be obtained without the use of gelatin.

"Peroxidase" Activity of the Charcoal Hydrosol.—These experiments were performed as with the "massive" charcoal, except that 15 cc. of the sol was used instead of the charcoal suspension. Of course, the resulting solution was extracted with toluene directly. For the blank 15 cc. of distilled water was used instead of the sol.

Electrometric Measurements.—A 15-cc. weighing bottle was used as the cell. The voltage was measured between an uncoiled bright platinum wire immersed 2 cm. and an 0.1 *N* calomel electrode. In order to obtain reproducible results, the wire was heated in a Bunsen flame before each reading. Equilibrium seemed to be reached in five to ten minutes, the calomel electrode being negative. A total volume of 10 cc. was used in each case. Five cc. of 1% hydrogen peroxide was placed in the bottle and, if necessary, water so that when either the charcoal sol or the potato extract was added the resulting solution had a volume of 10 cc. The results were duplicable to 2–3 millivolts.

Summary

1. The "peroxidase" activity of charcoal in the indophenol reaction has been measured at room temperature and *p*H 4.5. The yield of indophenol is at a maximum at one-half minute.

2. A hydrosol of charcoal has been prepared.

3. This charcoal sol has been found to exhibit "peroxidase" activity in the formation of indophenol. No "catalase" activity has been observed.

4. The charcoal sol affects the voltage of the Pt, H_2O_2 || KCl (0.1 *N*), Hg_2Cl_2, Hg cell in a manner similar to that of potato peroxidase.

JERSEY CITY, N. J.

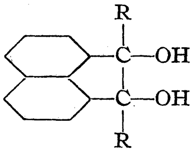
RECEIVED MARCH 20, 1936

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

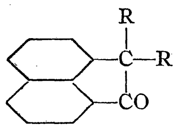
The Pinacol–Pinacolone Rearrangement. VIII. The Rearrangement of 7,8-Diarylacenaphthenediols

BY W. E. BACHMANN AND EDITH JU-HWA CHU[1]

Recently[2] we reported the results obtained on the rearrangement of a number of 9,10-diaryldihydrophenanthrenediols; in these compounds the simple aryl groups migrated exclusively and 9,9-diarylphenanthrones were formed. We have now turned our attention to the rearrangement of another class of cyclic pinacols, the 7,8-diarylacenaphthenediols (I).



I

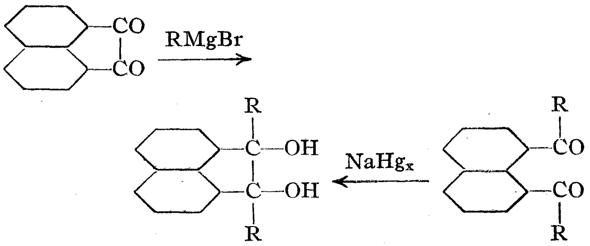


II

Acree[3] prepared 7,8-diphenylacenaphthenediol (I, R = phenyl) and reported that the compound remained unchanged when it was heated with acetyl chloride. Later, Beschke[4] obtained 7,7-diphenylacenaphthenone (II, R = phenyl) by heating the pinacol with acetic acid containing a small amount of hydrochloric acid.

We have now prepared seven new pinacols of this type in which the aryl groups, R, are *m*-tolyl, *p*-tolyl, *p*-biphenyl, *p*-anisyl, *p*-phenetyl, *p*-chlorophenyl and *p*-fluorophenyl. All of these pinacols were obtained from acenaphthenequinone through the Grignard reaction.

Since reduction of 2,2′-diacylbiphenyls by sodium amalgam gave 9,10-diaryldihydrophenanthrenediols which are diastereoisomers of the pinacols obtained by the Grignard reaction from phenanthrenequinone,[2] we have prepared several 7,8-diarylacenaphthenediols (I, R = phenyl, *p*-tolyl, *p*-chlorophenyl and *p*-fluorophenyl) by a similar reduction of 1,8-diacylnaphthalenes (III). Here, too, the pinacols prepared by reduction were diastereoisomers of those prepared by the Grignard reaction. It is of interest that solutions of the disodium salts of the diarylacenaphthenediols, like those of the diaryldihydrophenanthrenediols, are colorless, an indication that no appreciable dissociation into ketyl radicals takes place.[5]

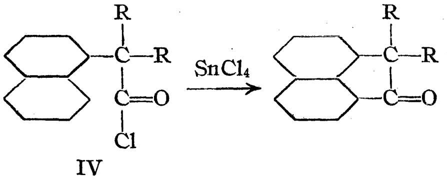


III

The yields and properties of the pinacols are shown in Table I.

Rearrangement of the Pinacols.—All of the pinacols were found to rearrange when they were heated with a solution of iodine in acetic acid. In every case the simple aryl group R was found to migrate exclusively with the formation of 7,7-diarylacenaphthenones (II). In the reaction the five-membered ring of the acenaphthene derivative was retained; no evidence of any tendency to form a four-membered ring was found. The stereoisomeric pinacols gave the same diarylacenaphthenone. The yields and the properties of the pinacolones are presented in Table II.

Two of the pinacolones, 7,7-diphenylacenaphthenone and 7,7-di-*p*-biphenylacenaphthenone, were synthesized by ring closure of diphenyl-α-naphthylacetyl chloride (IV, R = phenyl) and di-*p*-biphenyl-α-naphthylacetyl chloride (IV, R = *p*-biphenyl), respectively, by means of stannic chloride.



IV

7,8-Diarylacenaphthylenes.—The low yields of diarylacenaphthenones from the *p*-chlorophenyl and *p*-fluorophenyl pinacols were due to the formation of diarylacenaphthylenes (VI) through a side reaction. These compounds probably resulted through the action of hydrogen iodide present in the mixture of iodine and acetic acid; the pinacol is converted to the intermediate iodide (V) which yields the acenaphthylene (VI) by loss of a molecule of iodine.

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[1] From part of the Ph.D. dissertation of Edith Ju-Hwa Chu.

[2] Bachmann and Chu, THIS JOURNAL, **57**, 1095 (1935).

[3] Acree, *Am. Chem. J.*, **33**, 186 (1905).

[4] Beschke, *Ann.*, **369**, 200 (1909).

[5] Compare Bachmann, THIS JOURNAL, **55**, 1179 (1933).

TABLE I

7,8-DIARYLACENAPHTHENEDIOLS (I)

All of the compounds are colorless

-Acenaphthenediol	Recryst. solvent	Cryst. form	Yields, % Grignard reaction	Yields, % NaHg$_x$ reduction	M. p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
Diphenyl	Acet. + alc.	Fine needles	43		154.3–155.3			[a]	
Diphenyl	Alcohol	Needles		10	173.5–175.6			[b]	
Di-*p*-biphenyl	Acetone	Fine needles	49		220	88.2	5.3	87.7	5.4
Di-*p*-tolyl	Acet. + alc.	Prisms	45		182–182.5	85.2	6.0	85.1	6.0
Di-*p*-tolyl	Acetone	Fine needles		52	154.3–155.3	85.2	6.0	84.6	5.8
Di-*m*-tolyl	Acet. + bz.	Fine needles	36.5		152.3–153.3	85.2	6.0	85.4	5.8
Dianisyl	Acetone	Prisms	34		168–169	78.4	5.5	77.8	5.2
Diphenetyl	Acetone	Needles	24		144.5–145.5	78.9	6.1	78.5	6.1
Di-*p*-chlorophenyl	Bz. + acet.	Plates	29		222–223	Cl	17.4		16.9
Di-*p*-chlorophenyl	Acetone	Hexagonal plates		37	78–79.5				17.5
Di-*p*-fluorophenyl	Acet. + bz.	Prisms	38		220–221	F	10.2		10.0
Di-*p*-fluorophenyl	Acet. + alc.	Tetragonal plates		86	153.5–154.5				10.4

[a] Acree, *Am. Chem. J.*, **33**, 186 (1905). [b] Wittig, Leo and Wiemer [*Ber.*, **64**, 2405 (1931)] reported 171–173° for the melting point of 7,8-diphenylacenaphthenediol which they obtained by interaction of 1,8-dibenzoylnaphthalene and phenylmagnesium bromide.

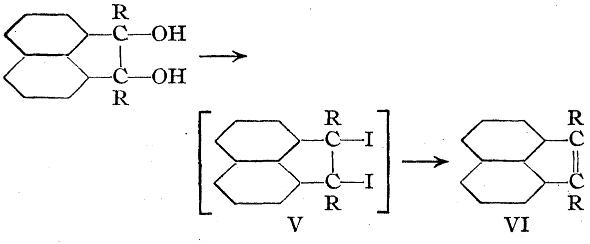
TABLE II

7,7-DIARYLACENAPHTHENONES (II)

All of the compounds are colorless

-Acenaphthenone	Recryst. solvent	Cryst. form	Yield, %	M. p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
Diphenyl	Acet. + alc.	Needles	94	171.3–172.4			[a]	
Di-*p*-biphenyl	Acet. + bz.	Prisms	99	248–249	91.	5.15	91.0	5.2
Di-*p*-tolyl	Acetone	Plates	99	128.5–129.5	89.7	5.7	89.9	5.8
Di-*m*-tolyl	Acetone	Tetragonal plates	100	147.5–148.5	89.7	5.7	89.5	5.7
Dianisyl	Acetone	Needles	100	151.5–152.5	82.1	5.3	81.5	4.9
Diphenetyl	Acet. + alc.	Prisms	100	122.8–123	OC_2H_5	22.1		22.0
Di-*p*-chlorophenyl	Acetone	Prisms	62	145.5	Cl	18.2		18.1
Di-*p*-fluorophenyl	Acetone	Prisms	68	127.5–128.5	F	10.7		10.7

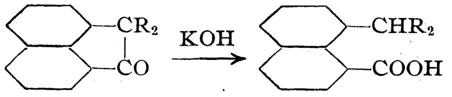
[a] Beschke, *Ann.*, **369**, 200 (1909).



V VI

The structures of the acenaphthylenes were established by synthesis. The pinacols were converted to the corresponding dichlorides by reaction with hydrogen chloride; when the dichlorides were heated with an acetone solution of sodium iodide the diarylacenaphthylenes were formed. In this manner we prepared five diarylacenaphthylenes (R = phenyl, *p*-biphenyl, *p*-tolyl, *p*-chlorophenyl and *p*-fluorophenyl) as shown in Table III. Usually some pinacolone as well as the dichloride was formed by interaction of the pinacol with hydrogen chloride and in the case of dianisylacenaphthenediol and diphenetylacenaphthenediol the pinacolones were the sole products.

Scission of 7,7-Diarylacenaphthenones to 8-(Diarylmethyl)-1-naphthoic Acids.—The 7,7-diarylacenaphthenones were transformed into 8-(diarylmethyl)-1-naphthoic acids (VII) either by fusion with potassium hydroxide or by refluxing with 25% potassium hydroxide solution in methanol. Their yields and properties are listed in Table IV.



VII

Oxidation of 7,8-Diarylacenaphthenediols to 1,8 - Diacylnaphthalenes.—The 7,8 - diarylacenaphthenediols were oxidized to 1,8-diacylacenaphthalenes (III) by a hot solution of chromic acid in acetic acid. The yields and the properties of these diketones are presented in Table V.

TABLE III

7,8-DIARYLACENAPHTHYLENES (VI)

All of these hydrocarbons are deep-orange in color

-Acenaphthylene	Recryst. solvent	Cryst. form	Yield, %	M. p., °C.	Analyses, % Calcd. C	H	Found C	H
Diphenyl	Acetone	Needles or prisms	95	161.3			[a]	
Di-*p*-biphenyl	Benzene	Needles	45	189.5–190.5	94.7	5.3	94.3	5.2
Di-*p*-tolyl	Acet. + alc.	Prisms	44	137.2–137.7	94.0	6.0	93.8	5.9
Di-*p*-chlorophenyl	Acetone	Needles	29	204.5–205.5	Cl, 19.0		18.8	
Di-*p*-fluorophenyl	Acetone	Needles	36	153.5–154.5	F, 11.2		11.1	

[a] See reference *b* under Table I.

TABLE IV

8-(DIARYLMETHYL)-1-NAPHTHOIC ACIDS (VII)

All of the compounds are colorless

-Methyl-naphthoic acid	Recryst. solvent	Cryst. form	Fusion temp., °C.	Time, min.	Yields, % Fusion	25% KOH	M. p., °C.	Analyses, % Calcd. C	H	Found C	H
Diphenyl	Bz. + acet.	Needles	250	10	74	74	226			[a]	
Di-*p*-biphenyl	Bz. + acet.	Needles	320	10	52	59	247–248	88.2	5.3	87.7	5.1
Di-*p*-tolyl	Acetone	Prisms	250	20	15	45	159.3–160.3	85.2	6.0	85.1	5.8
Di-*m*-tolyl	Acetone	Rect. prisms	250	20	30	65	189.5–190.5	85.2	6.0	84.9	6.0
Dianisyl	Acetone	Prisms	250	10	39	56	173.5–174.5	78.4	5.5	78.3	5.2
Diphenetyl	Acetone	Needles	250	10	34	54	170–171	OC_2H_5		21.1	20.9
Di-*p*-chlorophenyl	Acetone	Hex. heavy plates	250	20	10	3.5	225–226	Cl		17.4	17.2
Di-*p*-fluorophenyl	Acet. + alc.	Hex. plates	250	10	16	23	221–222	F		10.2	10.2

[a] See reference *a* under Table II.

TABLE V

1,8-DIACYLNAPHTHALENES (III)

All of the diketones are colorless

-Naphthalene	Recryst. solvent	Cryst. form	Yield, %	M. p., °C.	Analyses, % Calcd. C	H	Found C	H
Dibenzoyl	Acet. + alc.	Heavy plates	72	186.5			[a]	
Di-(*p*-phenylbenzoyl)	Acetic acid	Fine needles	75	219–220	88.5	4.9	88.1	5.0
Di-*p*-toluyl	Acet. + bz.	Plates	64	181.5–182.5	85.7	5.5	85.3	5.5
Di-*m*-toluyl	Acetic acid	Feather-like crys.	57	157.3–158.3	85.7	5.5	85.3	5.5
Dianisoyl	Acetone	Prisms	65	215–216	OCH_3	15.4		15.6
Diphenetoyl	Bz. + acet.	Plates	75	197–197.5	79.3	5.7	79.2	5.8
Di-*p*-chlorobenzoyl	Acetone	Prisms	54	188	Cl	17.5		17.4
Di-*p*-fluorobenzoyl	Acet. + alc.	Diamonds	64	166.5–167.5	F	10.2		10.2

[a] See reference *a* under Table II.

Experimental

Preparation of 7,8-Diarylacenaphthenediols. (a) **Grignard Reaction.**—To the Grignard reagent prepared from 0.14 mole of aryl bromide (bromobenzene, *p*-bromobiphenyl, *p*-bromotoluene, etc.) in 50 cc. of anhydrous ether was added a benzene solution of 10 g. of acenaphthenequinone. The mixture was refluxed on a steam-bath for twenty-four hours except in the case of diphenylacenaphthenediol for which only four hours were allowed. By hydrolysis of the reaction mixture with dilute acetic acid and recrystallization of the product, the pinacols were obtained as colorless crystals.

(b) Reduction by Sodium Amalgam.—One gram of 1,8-diacylnaphthalene (obtained by oxidation of the pinacols prepared by the Grignard reaction) in a mixture of ether and benzene was shaken with 114 g. of 1% sodium amalgam at room temperature for twenty days, the mixture was filtered and the filtrate was treated with dilute acetic acid in order to hydrolyze the disodium salts of the pinacols. The product was a mixture of the pinacol and some unreacted diacylnaphthalene from which the pinacol was obtained by repeated recrystallization.

Rearrangement of the Pinacols.—A mixture of 0.0045 mole of pinacol, 1 g. of iodine and 100 cc. of acetic acid was refluxed for thirty minutes. The diarylacenaphthenones, which were precipitated by pouring the solution into an aqueous solution of sulfur dioxide, were purified by recrystallization, forming colorless crystals.

In order to detect if any of the isomeric pinacolone, $C_{10}H_6C(R)COR$ was formed, 1 g. of the crude pinacolone was refluxed with a solution of 25 g. of potassium hydroxide in 100 cc. of methanol for three days. After removal of the solvent by distillation under reduced pressure, the residue was stirred with cold water and filtered. In the filtrate no trace of acids (benzoic, *p*-toluic, etc.) could be detected. By washing with dilute hydrochloric acid, purification through the ammonium salts and then recrystallization the residue gave colorless crystals of 8-(diarylmethyl)-1-naphthoic acids.

Synthesis of 7,7-Diphenylacenaphthenone.—A mixture of 0.50 g. of diphenyl-α-naphthylacetic acid[6] and 1 g. of thionyl chloride was refluxed for an hour. After removal of the excess of thionyl chloride, the acid chloride was dissolved in carbon disulfide and treated with 5 cc. of stannic chloride and heated on a steam-bath. From the products of hydrolysis there was isolated a solid which after repeated recrystallization from benzene and acetone gave crystals of 7,7-diphenylacenaphthenone, which proved to be identical with the pinacolone obtained by rearrangement.

Di-*p*-biphenyl-α-naphthyl-acetic Acid.—A mixture of 1.5 g. of di-*p*-biphenyl-α-naphthylchloromethane[7] and 5.1 g. of 45% sodium amalgam was shaken in 20 cc. of ether and 30 cc. of benzene for two hours. A stream of dry carbon dioxide was passed through the intensely colored solution of the triarylmethylsodium compound until the color disappeared completely. The di-*p*-biphenyl-α-naphthylacetic acid crystallized from benzene in colorless prisms; yield, 66%; m. p. 216–217° with decomposition.

Anal. Calcd. for $C_{36}H_{26}O_2$: C, 88.2; H, 5.3. Found: C, 88.1; H, 5.0.

Synthesis of 7,7-Di-*p*-biphenylacenaphthenone.—This compound was obtained by cyclization of di-*p*-biphenyl-α-naphthylacetyl chloride (prepared by means of thionyl chloride) in the same method that was used for the phenyl analog. The 7,7-di-*p*-biphenylacenaphthenone was identical with the pinacolone obtained by rearrangement.

Scission of 7,7-Diarylacenaphthenones by Potassium Hydroxide.—One-tenth gram of pinacolone was fused with 1 g. of potassium hydroxide in a metal bath at the temperature shown in Table V. After the mass had been dissolved in acetone and water, the 8-(diarylmethyl)-1-naphthoic acid was precipitated by dilute hydrochloric acid. For purification the acid was dissolved in ammonium hydroxide, precipitated again by dilute hydrochloric acid and then recrystallized.

Oxidation of the Pinacols.—A mixture of 0.003 mole of pinacol, 0.25 g. of chromic acid anhydride in 12 cc. of acetic acid was heated on a steam-bath for thirty minutes. The 1,8-diacylnaphthalene was precipitated by addition of cold water and then purified by recrystallization.

Synthesis of 7,8-Diarylacenaphthylenes.—A stream of dry hydrogen chloride was passed through an ice-cold solution of 0.001 mole of pinacol in chloroform for thirty minutes. After the solvent had been removed, the dichloride crystallized when it was stirred with a little acetone and petroleum ether.

A mixture of 0.0003 mole of the dichloride and 0.12 g. of sodium iodide in a few cc. of acetone was refluxed for thirty minutes. The solution became yellow and then dark red due to the liberation of iodine during the reaction. The mixture was poured into an aqueous solution of sulfur dioxide and the orange-colored solid was refluxed with 25% potassium hydroxide solution in methanol for two days in order to destroy the pinacolone which was present. The product after this treatment was digested with dilute ammonium hydroxide in order to dissolve the diarylmethylnaphthoic acid and the residue of diarylacenaphthylene was filtered, washed with water and recrystallized.

By treating 7,8-di-*p*-chlorophenylacenaphthylene dichloride with sodium iodide, 1,8-di-*p*-chlorobenzoylnaphthalene was formed instead of 7,8-di-*p*-chlorophenylacenaphthylene. However, by refluxing a mixture of 0.001 mole of the dichloride, 10 cc. of hydrogen iodide (d. 1.7) and 20 cc. of acetic acid for two hours the acenaphthylene was obtained mixed with a small amount of pinacolone. The compound was also obtained in 27% yield by refluxing an ether solution of the dichloride with zinc dust.

Summary

Seven new 7,8-diarylacenaphthenediols have been synthesized and subjected to rearrangement. It was found that in each case the simple aryl group migrates exclusively with respect to the acenaphthyl group; the products of the rearrangement are 7,7-diarylacenaphthenones.

The 7,7-diarylacenaphthenones are cleaved into 8-(diarylmethyl)-1-naphthoic acids either by treatment with 25% potassium hydroxide solution in methanol or by fusion with potassium hydroxide.

The 7,8-diarylacenaphthenediols are oxidized to 1,8-diacylnaphthalenes by chromic acid.

Four new 7,8-diarylacenaphthylenes have been synthesized from the 7,8-diarylacenaphthenediols.

ANN ARBOR, MICH. RECEIVED APRIL 25, 1936

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[6] Conant and Wheland, THIS JOURNAL, **54**, 1219 (1932).

[7] Schlenk and Bomhardt, *Ber.*, **46**, 1482 (1913).

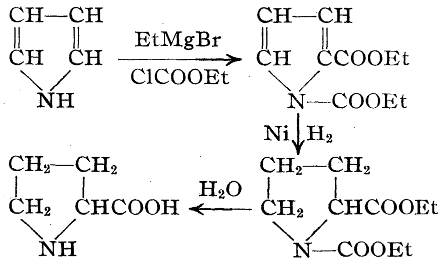
[A CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

A Synthesis of *dl*-Proline from Pyrrole[1]

BY FRANK K. SIGNAIGO AND HOMER ADKINS

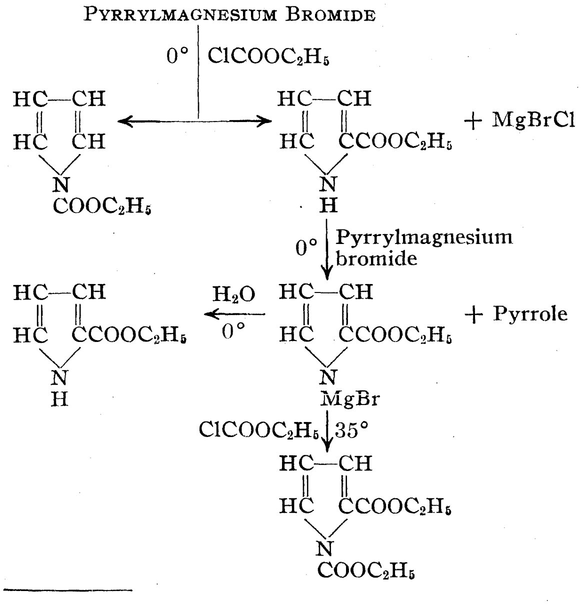
Several syntheses of *dl*-proline have been reported but none of them is very satisfactory from a preparational standpoint. The best methods are apparently those of Heymons,[2] who obtained the copper salt of *dl*-proline in three operations from piperidone-2, and that of Sørensen and Andersen,[3] who prepared the copper salt in five operations from malonic ester. The first method is said to give an over-all yield of 28%. The yield by the second method is not given, but is apparently somewhat greater. Several authors have suggested the desirability of developing a synthesis of proline from pyrrole through 2-carbethoxypyrrole as by Putokhin.[4] A difficulty in this process lies in the hydrogenation of the pyrrole ring in a carboxy- or carbethoxypyrrole. Putokhin used a high ratio of Adams platinum catalyst with 1 g. of pyrrole-2-carboxylic acid and as a result of repeated treatments with hydrogen and catalyst and change of solvent, obtained a 23% yield of the copper salt of *dl*-proline from the pyrrole acid.

While the hydrogenation of a 2-carboxy- or carbethoxypyrrole seems an impractical process with the catalysts now available, it appeared feasible to prepare *dl*-proline through the formation of 1,2-dicarbethoxypyrrole and the hydrogenation of the latter, *i. e.*



The hydrogenation may be carried out easily and almost quantitatively as a result of work recently reported.[5] The hydrolysis step is also a simple process but the preparation of the 1,2-dicarbethoxypyrrole in a good yield required study. However, by this process crystalline *dl*-proline has been obtained in an over-all yield of 57% from pyrrole.

Oddo[6] prepared 2-carbethoxypyrrole in over 90% yield from pyrrylmagnesium bromide and ethyl chlorocarbonate. In attempting to follow his method, but on a larger scale, we recovered 42% of the pyrrole and obtained 7% of 1-carbethoxypyrrole, 22% of 2-carbethoxypyrrole and 2% of 1,2-dicarbethoxypyrrole. When the conditions were modified by heating the reaction mixture for four hours at 35° before hydrolysis, instead of keeping it near 0°, then the yield of 1,2-dicarbethoxypyrrole was much greater, *i. e.*, 26%, accompanied by 13% of 1-carbethoxypyrrole and 3% of 2-carbethoxypyrrole. However, 50% of the pyrrole was recovered. These results suggested that pyrrylmagnesium bromide reacts with ethyl chlorocarbonate to give both 1- and 2-carbethoxypyrrole and that the latter but not the former reacts with pyrrylmagnesium bromide to give pyrrole and 2-carbethoxypyrrylmagnesium bromide. The last mentioned compound may then react, especially at higher temperatures, with ethyl chlorocarbonate to give 1,2-dicarbethoxypyrrole. These transformations are indicated below.



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(1) The Wisconsin Alumni Research Foundation allotted funds for a research assistantship held by F. K. S. in the period Sept., 1933 to Sept., 1935.

(2) Heymons, *Ber.*, **66**, 846 (1933).

(3) Sørensen and Andersen, *Z. physiol. Chem.*, **56**, 240 (1908).

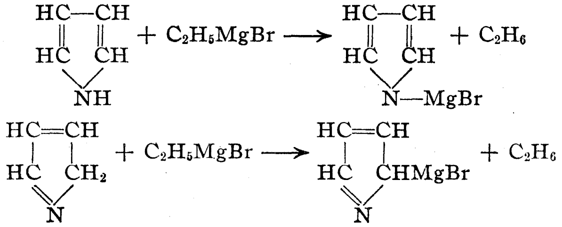
(4) N. Putokhin, *J. Russ. Phys.-Chem. Soc.*, **62**, 2216 (1930); *C. A.*, **25**, 3995 (1931).

(5) Signaigo and Adkins, THIS JOURNAL, **58**, 709 (1936).

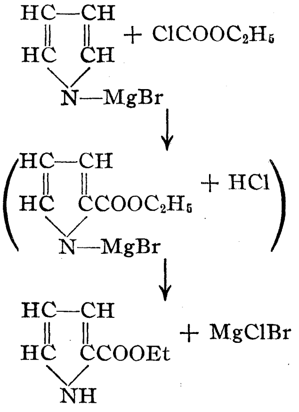
(6) Oddo, *Gazz. chim. ital.*, **39**, I, 649 (1909); **42**, II, 252 (1912).

Upon the basis of this scheme it seemed desirable to treat one mole of ethylmagnesium bromide with one mole of pyrrole and then to add *alternately* in *portions*, one mole each of ethyl chlorocarbonate and ethylmagnesium bromide and finally a second mole of ethyl chlorocarbonate. By such a process the reaction of all of the pyrrole was brought about and at the same time excessive reaction between the ethyl chlorocarbonate and the ethylmagnesium bromide was avoided. Such a procedure as described in the experimental part gave a 65% yield of 1,2-dicarbethoxypyrrole.

There seem to be two rather reasonable explanations of the fact that 1- and 2-carbethoxypyrroles are formed simultaneously. Tschelinzew and Karmanov[7] suggested that the isomerism of the pyrrole nucleus makes possible the formation of two "pyrrylmagnesium bromides," *i. e.*



The formation of a Grignard reagent in the second case would be analogous to the behavior of a methylene group in cyclopentadiene, indene and fluorene. The formulation is in accord with the fact that only pyrroles which may tautomerize form Grignard reagents.[8] If the above is accepted then the relative proportions of 1- and 2-carbethoxypyrroles formed are a function of the proportion of the tautomers and (or) of the relative rates of reaction of ethyl chlorocarbonate with the two Grignard reagents.



However, it is not necessary to assume the existence of tautomeric pyrroles in order to explain the formation of 2-carbethoxypyrrole, for the ethyl chlorocarbonate may condense with the hydrogen on the 2-carbon atom.

Such a scheme finds support in the fact that 1-methylpyrrole does not form a Grignard reagent yet condenses with acid chlorides in the presence of an alkylmagnesium halide to yield 1-methyl-2-acylpyrroles.[8] However 1-carbethoxypyrrole apparently did not react with ethyl chlorocarbonate in the presence of a Grignard reagent.

Experimental Part

The apparatus for the preparation of 1,2-dicarbethoxypyrrole consisted of a 1-liter, 4-necked flask fitted with a mercury-sealed stirrer, a reflux condenser, the upper end of which was connected to a drying tube containing calcium chloride, and two dropping funnels. One of these dropping funnels was of the usual type, and the other was a 500-cc. flask with a stopcock sealed on the bottom and so fitted that a Grignard reagent could be prepared in it. Both of the funnels were graduated.

Ethylmagnesium bromide (approximately 0.25 mole) was prepared in the reaction flask from 32.7 g. (0.30 mole) of ethyl bromide, 7.2 g. (0.30 mole) of magnesium turnings and 150 cc. of ether. A like amount also was prepared in the 500-cc. dropping funnel. The reaction flask was cooled with a mixture of ice and salt to below 0° and 17 g. (0.25 mole) of pyrrole in 35 cc. of ether was added dropwise through the smaller dropping funnel. The reaction mixture was stirred during this and subsequent operations.

Into the smaller dropping funnel was placed 75 cc. of an ether solution containing 28 g. (0.25 mole) of ethyl chlorocarbonate. The Grignard reagent in the larger dropping funnel was diluted with ether to a volume of 200 cc. These two reagents were then added to the reaction flask drop by drop in the following fashion. One-half of the ethyl chlorocarbonate solution (37 cc.) was first added. This was followed by one-half of the Grignard solution (100 cc.). Again half of the remaining ethyl chlorocarbonate solution (19 cc.) was added and followed by half of the remaining Grignard solution (50 cc.). This process was repeated, each time adding one-half of the solution remaining in the dropping funnel until only 5–10 cc. of each reagent remained. This last small amount of each solution was then added and 37 g. (0.35 mole) of ethyl chlorocarbonate was poured into the reaction mixture through the smaller dropping funnel. These addition processes were completed in two hours. The reaction mixture was allowed to warm up to room temperature and then refluxed on a steam-bath for four hours. The contents of the reaction flask were then poured onto ice and the mixture made slightly acid by the addition of dilute sulfuric acid. The ether layer was separated and the aqueous layer was extracted twice with ether. The combined ether solutions were then washed once with a small quantity of sodium bicarbonate solution and dried for eight hours over anhydrous sodium sulfate. The ether was distilled off and the liquid residue was fractionated at reduced pressure as indi-

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(7) (a) Tschelinzew and Karmanov, *J. Russ. Phys.-Chem. Soc.*, **47**, 161 (1915); (b) *cf.* Oddo, *Gazz. chim. ital.*, **64**, 584 (1934).

(8) Oddo, *ibid.*, **44**, I, 706 (1914).

cated in the table. The recovery of ethyl chlorocarbonate as well as the amount of 1-carbethoxypyrrole obtained, indicate that 1.75 mole each of the Grignard reagent and the ethyl chlorocarbonate per mole of pyrrole would give as good a yield as did the proportion of reactants used above.

Table I

Products of Reaction

Fraction	Compound	Boiling range, °C.	Weight, g.	Yield, %
1	Ethyl chlorocarbonate	Up to 55° (65 mm.)	10	..
2	1-Carbethoxypyrrole	60– 65° (7 mm.)	9.2	26.4
3	2-Carbethoxypyrrole	100–110° (7 mm.)	0.5	1.5
4	1,2-Dicarbethoxypyrrole	125–135° (7 mm.)	34.2	65.0
	Residue		1.8	
			Total	92.9

The fourth fraction was found to be nearly pure 1,2-dicarbethoxypyrrole[5] since on refractionation 98% of the material distilled at 132–134° at 8 mm. The 1-carbethoxypyrrole had a b. p. of 57–58° at 7 mm., and 178–180° at 740 mm., and d^{25} 1.037, n^{25}_{D} 1.4698. The boiling point of this compound checks with that reported by other investigators. Only one author has reported the density and refractive index of this compound and these values do not check with those given above. However, the compound seems to be sufficiently characterized by the fact that it takes up 4 atoms of hydrogen to give a non-basic compound having the correct analysis for a carbethoxypyrrolidine, indicating that the carbethoxy group is on the nitrogen atom. The 1-carbethoxypyrrole is better prepared from potassium pyrrole and ethyl chlorocarbonate.[7a,9]

The 2-carbethoxypyrrole had a m. p. of 41–42° when crystallized from low-boiling petroleum ether and a b. p. of 102–104° at 7 mm.

The 1,2-dicarbethoxypyrrole so obtained was hydrogenated rapidly and quantitatively over Raney nickel.[5] In a typical experiment 1,2-dicarbethoxypyrrolidine b. p. 133–134° (8 mm.) was obtained in 98% yield by the hydrogenation of 0.2 mole of the pyrrole ester over 5 g. of Raney nickel under 100 to 200 atm. of hydrogen at 50 to 85° in less than one hour.

The 1,2-dicarbethoxypyrrolidine (10.6 g. or 0.05 mole), was refluxed with 25 cc. of concentrated hydrochloric acid for three hours; 10 cc. more of hydrochloric acid was then added and the refluxing continued for two hours. The mixture was then evaporated on a steam-bath. The partially crystallized residue was dissolved in 100 cc. of water and treated with 0.10 mole of freshly precipitated silver carbonate. After filtration, the filtrate was treated with hydrogen sulfide. The solution was heated with 1 g. of activated charcoal and this together with the silver sulfide was removed by filtration. Upon evaporation of the filtrate on a steam-bath, there was obtained 5.7 g. of a gummy crystalline mass. This was dissolved in 25 cc. of hot ethanol and 50 cc. of hot dioxane was added. After cooling the solution with ice, the crystalline proline was filtered off and dried in a desiccator. The yield was 5.2 g. (90%), m. p. 204°. The picrate was prepared by dissolving 1 g. of proline and 2 g. of picric acid in 2 cc. of hot acetic acid, followed by addition of 7 cc. of ether and cooling. The picrate was recrystallized from ethanol and showed a m. p. of 136°.

Summary

Crystalline *dl*-proline may be prepared in yields of 55 to 60% from pyrrole through the intermediate formation of 1,2-dicarbethoxypyrrole and 1,2-dicarbethoxypyrrolidine. A method for the synthesis of 1,2-dicarbethoxypyrrole has been devised and developed.

Madison, Wisconsin Received March 13, 1936

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[9] Ciamician and Dennstedt, *Ber.*, **15**, 2579 (1882); *Ber.*, **60**, 196 (1927).

[Contribution from the Converse Memorial Laboratory of Harvard University]

A Further Study of Extremely Weak Acids

By W. K. McEwen

The purpose of this paper is to report the new methods used and the results obtained in the study of extremely weak acids.

It has been shown by Conant and Wheland[1] that reactions of the type

$$R_1H + R_2^- \rightleftarrows R_1^- + R_2H$$

may be used to determine the relative acid strength of very weak acids such as the aromatic and aliphatic derivatives of water, ammonia and methane. The determination of the relative amounts of the different substances present at the point of equilibrium is a measure of the relative strength of the two acids. This can be determined in either of two ways.

The first method used was to observe the change in color. Since many compounds of the type R^- are colored, it is only necessary to mix the reactants and observe whether or not a change in color results. As a check the products of the reaction are also mixed. From such observations the compounds can be arranged in a series of de-

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[1] Conant and Wheland, This Journal, **54**, 1212 (1932).

creasing acid strength. Using equivalent quantities, and assuming that apparent complete reaction corresponds to at least 90% reaction, a minimum difference in *pK* for the acids may be taken as 2 *pK* units.

A second method used by Conant and Wheland was to introduce carbon dioxide into the equilibrium mixture, isolate the acids and from their analysis draw similar conclusions regarding the equilibrium and the relative strengths of the acids.

Three methods have been used in the present paper to extend the series of weak acids.

I. Colorimetric Method

Essentially the same method as devised by Conant and Wheland was used to measure acids having colored sodium or potassium salts. Twenty-five acids were investigated by this method. These results, with the results of the two following methods, are summarized in Table II.

Each compound that has a colorless metallic salt was measured against the nearest colored compound appearing in the table, and was found to differ from it in acidity by at least 2 *pK* units. Every compound having a colored metallic salt was measured against as many compounds as necessary to determine its position in the table. However, alpha-naphthylfluorene could not be measured against phenylfluorene as the metallic salts of both compounds have approximately the same color. For this same reason, phenylxanthane could not be measured against xanthane. The last four compounds in Table II had been measured by Conant and Wheland using a five-fold quantity of the hydrocarbon, so that they were found to differ by only a minimum of 0.4 *pK* unit. By using equivalent quantities, the minimum difference was extended. It was found that etioporphyrin I[2] had an acidity approximately that of the alcohols. The formation of the sodium salt of the porphyrin is accompanied by a striking spectroscopic change. Etioporphyrin I forms a disodium salt[3,4] but no difference in acidity could be found between its first and second dissociation constant.

Other compounds were measured colorimetrically but the data obtained were insufficient to warrant placing them definitely in Table II. Diethylcarbinol, diphenyl-alpha-naphthylcarbinol, phenylxanthydrol, acetanilide, tricarbomethoxymethane, 2,4-dimethylpyrrole and pyrrole were found to be 2 *pK* units stronger than phenylfluorene, while tertiary butylfluorene seemed to be weaker than triphenylmethane.

II. Spectroscopic Method

This method is strictly analogous to the ordinary water system of acid–base titration. That is, the acid to be measured is titrated with sodium triphenylmethyl, a strong base, in the presence of a minute amount of etioporphyrin I as an indicator, in an inert atmosphere. The change in the indicator is apparent when the shift in the absorption bands is observed with a small hand spectroscope. If the porphyrin is at least 2 *pK* units stronger than the acid, it will take the sodium from the first few drops of sodium triphenylmethyl. Likewise, if both the acid and the porphyrin are the same strength, the porphyrin will be partially converted into its basic form at the start, but will not be completely converted until the end of the titration. The results of this method are also summarized in Table II. This method was useful in showing that of the alcohols measured, all were at least 2 *pK* units weaker than etioporphyrin except methyl alcohol which has an acidity very close to that of etioporphyrin. Standard pyrrole (2,4-dimethyl-3,5-dicarbethoxypyrrole) was only slightly weaker. Experiments with other porphyrins and porphyrin-like compounds showed that they were at least 2 *pK* units stronger than etioporphyrin I. However, N-methyletioporphyrin I[4] is only about 1 *pK* unit stronger than etioporphyrin itself. This compound is interesting in that one of the imino hydrogens of the porphyrin ring is replaced with a methyl group, making the compound a monobasic acid. According to Hammett and Deyrup,[5] it is thus better suited for an indicator.

III. Polarimetric Method

The third method is useful in dealing with colorless compounds and permits in some cases more exact values for the relative acid strength of the compounds studied. In this method an optically active acid is used and the position of equilibrium determined with the aid of a polarimeter. The optical activity of the equilibrium mixture together with the values for the optical activity of the acid and salt allow one to calculate

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(2) Fischer, Baumann and Riedl, *Ann.*, **475**, 205 (1929).

(3) Fischer and Neumann, *ibid.*, **494**, 225 (1932).

(4) Work to be published.

(5) Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932).

Table I

Acid	Cc. of soln.	Total concn. moles/liter	Menthylate, %	Moles of acid	α	pK
CH_3OH	43	0.119	27	0.0002	−1.41	−1.0 (min.)
	43	.119	27	.0004	−1.44	−0.2 (min.)
$(C_6H_5)CH_2OH$	10	.100	95.3	.000385	−1.40	−1.4
	34.1	.119	9			
$(C_6H_5)_2CHOH$	43	.071	88	.00286	−0.84	−0.86
	43	.071	88	.00298	− .86	− .92
	30	.100	95.3		− .80	− .86
	(14			.215 *M* C_6H_6 soln.)		
	43.6	.119	27	.0006	−1.47	−1.2
$(CH_3)_2CHOH$	10	.100	95.3	.00092	−1.47	−1.1 (max.)
	33.4	.119	9			
	43.1	.119	27	.00053	−1.45	−0.9
	43.1	.119	27	.00053	−1.44	− .7
$(CH_3)_3COH$	17.5	.100	95.3	.0010	−0.36	− .31
	25.3 C_6H_6					
	18.5	.100	95.3	.0010	− .38	− .43
	24.6 C_6H_6					
$(C_2H_5)(CH_3)_2COH$	23.9	.100	95.3	.00203	− .50	+ .12
	19.3 C_6H_6					
	24.4	.100	95.3	.00184	− .51	− .12
	19.3 C_6H_6					
$(C_6H_5)COCH_3$	43.6	.119	27	.0006	−1.39	+ .2
Phenylfluorene	43	.100	95.3	.00186	−0.53	+1.8 (max.)
	43	.100	95.3	.00130	− .54	+1.5 (max.)

$[\alpha]^{23}_D$ sodium *l*-menthylate −12.2°. $[\alpha]^{23}_D$ *l*-menthol −45.6°.

the extent to which the reaction has gone. Thus, if a weak acid is allowed to react with sodium menthylate,[6,7] the amount of free menthol produced can be measured and the strength of the weak acid, relative to menthol, can be calculated. This was done with six alcohols, one enol and one hydrocarbon. The data are shown in Table I.

It should be noted that the *pK* values, given in the table above, are relative to menthol, a negative value indicating that an acid is stronger than menthol. A precipitate formed in the reaction with those acids whose value is followed by the abbreviation "max." The consequent shift in the point of equilibrium results in a maximum value. That is, the acid is no stronger than the value given, and may be weaker. In attempting to measure the acidity of methyl alcohol, it was found that the reaction went substantially to completion with the formation of a precipitate. It was then necessary to determine the solubility of sodium methylate in benzene in order to obtain the minimum value given in the table above. The order of magnitude of the solubility was necessary, rather than its precise value.

There are too few alcohols from which to draw definite conclusions, but it is apparent that the acidities fall into three groups corresponding to the primary, secondary and tertiary structures of the alcohols, with the acidity decreasing in that order. Evidently the determining factor in the acid strength of the alcohols resides in the functional group being of primary, secondary or tertiary character, and the substituents whether aliphatic or aromatic are of secondary influence.

From the position of acetophenone in the table, one can make a rough calculation of the fraction of the material which is present as enol. This is so small as not to be measurable by analytical means. The structure of the enolic form (a double bond alpha-beta to an hydroxyl group) is similar to phenol, and should have an approximate *pK* value of 10. This is probably fairly close, as the value for ethylacetoacetic ester has been found to be 12. Assuming the *pK* value of the pure enolic form of acetophenone is 10, the equilib-

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(6) F. H. Yorston of the Forest Products Laboratories of Canada stated that "I obtained a definite though small positive rotation in a toluene solution of the laevo alcohol [octenol-2] on adding potassium." (Private communication to J. B. Conant.)

(7) Professor E. P. Kohler suggested optically active menthol.

rium constant for the reaction keto $\rightleftharpoons$ enol would have to be 10^{-9}.

IV. Summary

In order to relate all the acids, it is necessary to choose some arbitrary standard to which to relate them. The standard chosen in this work is methyl alcohol whose acidic dissociation constant has been measured accurately by A. Unmack[8] and found to be 10^{-16}, giving it therefore a pK value of 16.

Since the values obtained by the three methods are transferred directly to Table II with no correction for solvent effects, or for changes of solvent or of concentration, the values should be considered as accurate to about one power of ten.

TABLE II

pK	Compound	Method used		
14–15	N-Methyletioporphyrin[1]		s[2]	
16	Etioporphyrin I		s	
16	Methyl alcohol (standard)	c	s	p
16.5	Standard pyrrole	c	s	
18[3]	Benzyl alcohol	c	s	p
	Ethyl alcohol	c	s	
	Benzhydrol	c	s	p
	Isopropyl alcohol	c		p
19	Triphenylcarbinol	c	s	
	Tertiary butyl alcohol	c		p
	Tertiary amyl alcohol	c	s	p
	Menthol			p
	Acetophenone	c	s	p
21	*Phenylfluorene* (C)	c		p
	α-Naphthylfluorene (C)	c		
	Phenylacetylene			
	Indene (C)			
23	Diphenylamine[4]	c		
25	*Fluorene* (C)	c		
27	Aniline[5]	c		
	p-Toluidine	c		
	p-Anisidine	c		
29	*Xanthane* (C)	c		
	Phenylxanthane (C)	c		
31	*Diphenylbiphenylmethane* (C)	c		
33	*Triphenylmethane* (C)	c		
34	*Diphenyl-alpha-naphthylmethane* (C)			
35	*Diphenylmethane* (C)	c		
36	*Diphenylmethylethylene* (C)			
37	*Cumene* (C)	c		

Compounds italicized appeared in the table of Conant and Wheland.

(C) = compounds having colored metallic salts
s = measured spectroscopically, using etioporphyrin as an indicator
c = measured colorimetrically
p = measured polarimetrically
1 = work to be published concerning this compound
2 = measured spectroscopically against methyl alcohol
3 = pK values 18–37 are minimum pK values
4 = equilibrium approached from both ends when measuring against fluorene and phenylfluorene
5 = acidity determined by Conant and Wheland, but not included in their table

Where feasible compounds were measured by two or more methods in order to check their positions in the table.

The author wishes to express his gratitude and appreciation to both former Professor James Bryant Conant who directed the research on the colorimetric and spectroscopic methods and Professor Henry Edward Bent who directed the research on the polarimetric method.

Experimental Part

Treatment of Compounds.—All liquid alcohols were carefully fractionated from their sodium salts and kept in sealed bottles in a desiccator over phosphorus pentoxide. Different samples of the same alcohol were used in various runs to guard against any one sample being contaminated.

The liquid amines were distilled from potassium hydroxide and kept in sealed bottles in a desiccator over potassium hydroxide.

All solids were recrystallized until pure by melting point and other tests, and dried in a drying pistol.

The nitrogen was passed through Fieser's solution, lead acetate solution, sulfuric acid, phosphorus pentoxide towers and finally through a xylene solution of sodium benzophenone ketyl. When a piece of apparatus is filled with nitrogen, it is done so by evacuating with an oil pump and then filling with nitrogen, the apparatus being flamed over with a micro-burner during the process. This procedure is carried out three times. The apparatus is of course allowed to cool before a solution is added so as not to evaporate any solvent. When the apparatus is cleaned, cleaning solution, soap and water, distilled water, alcohol, ether and dry, distilled ether are used in the order named.

Colorimetric Method.—The storage flask for the metal-alkyl solution was similar to that used by Conant and Wheland[1] for the storage of their metal-alkyl solutions, except that a calibrated Pyrex buret of 25-cc. capacity was used in place of the roughly calibrated side-arm, and two slant-bore stopcocks in series were used instead of the mercury seal stopcock. The lower stopcock bears the brunt of the frequent evacuations and fillings of the reaction flask, and thus protects the upper stopcock. As there is little or no difference in pressure on either side of it, there is no tendency for the ether to make channelings in the ether-soluble grease. The lower stopcock can be regreased, without danger of changing the titer of the solution, if the key is only taken from the socket when there is a strong positive pressure of nitrogen so as to prevent back diffusion. The upper stopcock need only be regreased at very infrequent intervals, and this is done in the same manner as the lower stopcock, except that the solution is again standardized to be sure that there has been no change.

A different reaction flask was developed. This was a small flask of 100 cc. capacity which was joined to the

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(8) A. Unmack, *Z. physik. Chem.*, **133**, 45 (1928).

lower terminal of the stopcocks on the storage flask by means of a ground glass joint. The nitrogen train was also attached to this flask with a ground glass joint. The substance to be measured, if a solid, is weighed into a short length of glass tubing which is then capped on each end with two pieces of glass tubing sealed at one end and fitting smoothly over the tube, forming a capsule. This capsule is then placed in a short length of 15-mm. tubing bent at an angle of 45°, sealed off at one end and carrying at the other end a 15-mm. male standard taper ground glass joint, which in turn fits into the female joint attached to the reaction flask. The tube containing the capsule is turned downward while the system is being filled with nitrogen. To introduce the compound, the tube is rotated, allowing the capsule to descend. Usually the capsule slips apart on hitting the bottom of the flask, but if this does not happen the apparatus is either gently shaken to break it open, or the capsule is covered with a layer of solution, and a vacuum is applied. The gas inside the capsule bursts it apart on expanding. The compound may then be measured directly against the metal-alkyl solution in the reservoir, by adding an equivalent amount and observing the color change. When the solution is standardized against benzoic acid, this method is used.

If the substance to be measured is a liquid, a somewhat different procedure is used. The entire apparatus is connected using, however, a little longer crooked tube. The system is evacuated and filled with nitrogen several times. The liquid is pipetted into one of the caps of the capsule, the crooked tube is disconnected from the apparatus, the cap is placed in it and it is filled with benzene, and reconnected to the reaction flask. The benzene is then frozen with a salt and ice mixture placed around the outside of the tube. When the benzene has frozen, the system is evacuated and again filled with nitrogen in order to get rid of any air that may have entered the apparatus when the crooked tube was temporarily removed. When it is desired to introduce the sample, the benzene is melted, the tube rotated and the contents run into the flask.

There was a certain amount of difficulty involved in the handling of volatile amines like *n*-butylamine and di-*n*-butylamine. For this reason, an attempt was made to use the amine hydrochlorides, and to treat them with one equivalent of sodium triphenylmethyl in order to liberate the free amine directly in the reaction flask. The amine hydrochlorides were so insoluble in ether that the reaction took place too slowly and did not seem to go to completion within a reasonable length of time. Although aniline hydrochloride worked fairly satisfactorily, and gave the same results as with aniline itself, the method was abandoned as it was too slow with the other amines.

Tertiary Butylfluorene.—2.38 grams (0.01 mole) of tertiary butylfluorenol,[9] 10 cc. of glacial acetic acid, 2 cc. of hydrogen iodide (sp. gr. 1.7) and 1. g. of red phosphorus were refluxed for four hours in a 50-cc. Erlenmeyer flask under a return condenser. The solution was filtered while hot and water added to precipitate the hydrocarbon, which was slightly pinkish. It was recrystallized from methyl alcohol to a melting point of 98–99° and a yield of 1.6 g. (73%) of fine white needles that gave no color in sulfuric acid. This product was further dried in a drying pistol at 61°.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.89; H, 8.11. Found: C, 91.68; H, 8.11.

Spectroscopic Method.—When using this method, the same apparatus is used as in the colorimetric method. The acid to be measured and a few specks of etioporphyrin were frozen in benzene in the long crooked tube of the apparatus. When the flask is ready, the benzene is melted, providing a homogeneous solution on which the effect of the sodium triphenylmethyl readily may be determined by viewing the solution through a small hand spectroscope. As to the efficiency of the indicator, dilution experiments showed that the basic form in the presence of the acidic form could be detected if 50% or greater. The acidic form could be detected in the presence of its basic form in as low an amount as 10%. This range, 50–90%, compares favorably with the range of the usual color indicators.

Polarimetric Method.—The storage flask for the sodium menthylate solutions was the same as used in the other methods for the storage of metal-alkyl solutions. The polarimeter cell was made from approximately 21-mm. Pyrex tubing with Pyrex windows sealed on the ends, and a slant-bore stopcock sealed to the middle of the tube. The length of the cell was 1.995 dec., and it had a capacity of about 43 cc. There was little or no strain noticeable in the windows. This cell was connected to the storage flask by a ground glass joint. The nitrogen train was attached between the junction of the cell and the storage flask. All the ground glass joints were standard taper.

Experiments were tried with fusel oil as a possible alcohol for the polarimetric method, but the difficulty of separating the active component and the inadvisability of using a mixture made its usefulness doubtful.

Difficulties arose in the preparation of pure sodium menthylate. It had been found in previous work on the preparation of alcoholates that they often turned yellow This yellow coloration was thought to be due to side reactions caused by the relatively high reaction temperatures. To prevent this, 40% sodium amalgam was used instead of sodium wire, and the mixture of amalgam, alcohol and benzene was shaken at room temperature under nitrogen until no more hydrogen was given off. This procedure formed a colorless solution of sodium *l*-menthylate. However, if air is present, the yellow color develops. Benzene was used as a solvent because it would dissolve sodium *l*-menthylate at least up to concentrations of 0.1 mole per liter. The sodium *l*-menthylate appeared very insoluble in ether. All polarimetric reactions were carried out using benzene (dried over sodium) as the solvent, under an atmosphere of dry, oxygen-free nitrogen. The polarimeter was readable to 0.01°. The light source was a General Electric sodium vapor lamp. The light from this lamp was about 99% monochromatic, by spectroscopic examination.

In order to obtain the specific rotation of pure sodium *l*-menthylate, the solution of menthylate, obtained by shaking with 40% sodium amalgam, was titrated with sodium triphenylmethyl just until the formation of a permanent end-point. The reaction between *l*-menthol and 40% sodium amalgam did not go to completion, so to be sure that all the *l*-menthol was finally converted to sodium

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[9] H. W. Scherp, "Rate of Autoxidation of Di-aryl-di-fluoryls," Thesis, Harvard University, 1931, p. 105.

l-menthylate, it was titrated with sodium triphenylmethyl. This solution was then measured in the polarimeter and the specific rotation for sodium *l*-menthylate was found to be $[\alpha]^{23}\mathrm{D}$ -12.2 ± 0.6. Patterson and Taylor[10] give the specific rotation of menthol as $[\alpha]^{23}\mathrm{D}$ -45.57.

An ethereal solution of menthol was successively diluted from 1 to 0.0125 *M*, and no change was observable in the specific rotation.

Patterson and Taylor[10] have shown that *l*-menthol in benzene is "practically insensitive to temperature change." With the menthylate solution, a 0.003° change in rotation was observed for every degree change in temperature. In the same way, the temperature effect on the equilibrium of a reaction is from 0.001 to 0.003° change in rotation per degree temperature change. Since the polarimetric room was thermostatted to 24.5 ± 1.5°, the maximum change in rotation due to temperature change is less than the experimental error.

Since the specific rotation of both pure menthylate and menthol is known, it is only necessary to know, in a given solution, the total concentration of menthol, either as menthol or menthylate, and a measurement of the rotation gives the concentrations of both. The total concentration was found by weighing the amount of pure menthol used and measuring the benzene volumetrically.

The rates of these metathetical reactions were all practically instantaneous. In the measurement of benzhydrol, three to five minutes after adding the benzhydrol, the reaction had reached a value that did not change after one and one-half hours. A second reading after at least one-half hour had elapsed was taken on tertiary amyl alcohol, tertiary butyl alcohol, isopropyl alcohol and acetophenone, and no change was observed. Of the remaining compounds, precipitates appeared with methyl alcohol and phenylfluorene which took quite a while to settle (one to two hours) and only on benzyl alcohol was no second reading taken after some time had elapsed. So with no alcohol was a shift in the rotation observed. The rate of the reaction was faster than could be detected.

Since most of the sodium salts of the alcohols are fairly insoluble in benzene, it was necessary to prevent their formation as much as possible. This was done by using smaller and smaller amounts of alcohol and menthylate and larger and larger quantities of menthol, until no precipitate formed. This was not always successful, and the accuracy of the readings was reduced. When the menthol was used in solution to partially block the reaction, a small amount of menthylate was also present in the solution in order to be sure that there was no contaminating substance present.

Solubility of Sodium Methylate in Benzene.—A 100-cc. flask was filled with benzene under nitrogen and a large amount of sodium wire was added. One-half cc. of methyl alcohol was added against a current of nitrogen. A rapid reaction occurred. The flask was left for two days, after which three samples were removed and titrated with 0.01 *N* hydrochloric acid, using phenolphthalein as an indicator. The value for the solubility was found to be 0.3 to 0.9 of a millimole per liter. A correction was then made for the dissolved sodium hydroxide. The solubility was determined by sealing sodium hydroxide, sodium and benzene in a small flask and shaking overnight. The solution was titrated and found to contain 0.1 millimole of sodium hydroxide per liter of benzene.

Summary

1. Fifteen weak acids have been measured colorimetrically and inserted in a table of acids of decreasing strength. Eight other weak acids have been investigated by this method.

2. Ten weak acids have been measured spectroscopically by an indicator method that is described.

3. The acidity of six alcohols, one enol and one hydrocarbon have been determined by a polarimetric method that is described.

CAMBRIDGE, MASS. RECEIVED FEBRUARY 25, 1936

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[10] Patterson and Taylor, *J. Chem. Soc.*, **87**, 122 (1905).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, McGILL UNIVERSITY]

The Diffraction of X-Rays by the Higher Polyethylene Glycols and by Polymerized Ethylene Oxides[1]

BY W. H. BARNES AND SYDNEY ROSS

In recent studies[2] Hibbert, Perry and Pullman have obtained very strong evidence in support of the suggestion[3] that polymerized ethylene oxides probably have the same composition as the polyethylene glycols (*i. e.*, $HOCH_2CH_2(OCH_2CH_2)_xOCH_2CH_2OH$). Since the former already have been subjected to x-ray examination,[4] and since specimens of polymerized ethylene oxides and polyethylene glycols of comparable molecular weights[5] were available, an opportunity was presented for a comparison of the diffraction

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[1] This paper constitutes No. LI in the series of "Studies on Reactions Relating to Carbohydrates and Polysaccharides," by Dr. Harold Hibbert and co-workers.

[2] Hibbert and Perry, *Can. J. Research*, **8**, 102 (1933); Perry and Hibbert, *ibid.*, **B14**, 77 (1936). The method of preparation, the constitution and the physical and chemical properties of the higher polyethylene glycols and polymerized ethylene oxides will be discussed in forthcoming articles by Pullman and Hibbert.

[3] (a) Staudinger and Schweitzer, *Ber.*, **62**, 2395 (1929); (b) Carothers, *Chem. Rev.*, **8**, 391 (1931); (c) Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932, p. 287.

[4] Sauter, *Z. physik. Chem.*, **B21**, 161–185 (1933).

[5] Molecular weights stated throughout this paper refer to values in solution as determined by Staudinger's viscosity methods,[3c] p. 56 *et seq.*

of x-rays by the polymerized ethylene oxides and polyethylene glycols prepared by Pullman and Hibbert[2] and a comparison of these data with those for the polymerized ethylene oxides examined by Sauter.[4]

Sauter[4,6] has studied polymerized ethylene oxides of molecular weights 2400, 3100, 8000, 13,000, 16,000, 33,000, 55,000 and 100,000, respectively. The last, which is reported[4] to be a rubber-like substance, enabled him to obtain fiber diagrams by stretching the specimen, so that most of his work was confined to this polymer. Powder diagrams of all specimens, however, were identical (at least without photometric or ionization measurements) both as to positions of haloes and relative intensities.

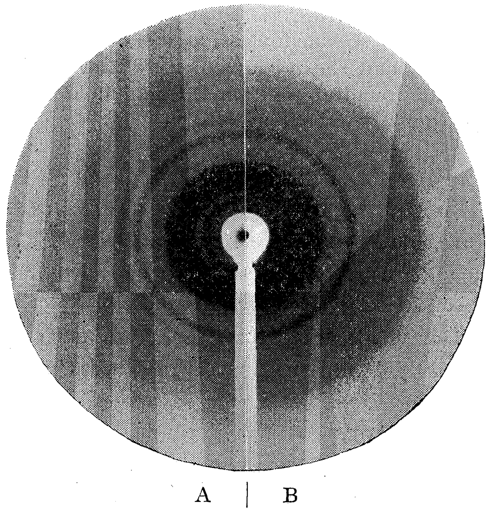

Fig. 1.—A, Polymerized ethylene oxide; B, polyethylene glycol.

As none of the polymers available for the present investigation were high enough to possess any appreciable elasticity the present paper is concerned solely with powder diagrams. Copper radiation (λ = 1.54 Å.), filtered through nickel foil to remove the K_β line, was employed with a crystal-to-plate distance of 2.25 cm.

The specimens of Pullman and Hibbert[2] selected for study were the 54 and 162-membered polyethylene glycols and the corresponding polymerized ethylene oxides (mol. wts. 3000 and 6500). Preliminary photographs having given essentially identical diagrams for all four specimens, and shown that very long exposure times would be necessary for accurate identification and measurement of the weaker haloes, a detailed examination of the 162-membered polyethylene glycol and the polymerized ethylene oxide of molecular weight 3000 (corresponding to the 54-membered polyethylene glycol) was undertaken.

A typical composite negative for these two specimens is reproduced in Fig. 1. Due to the pronounced background fogging (particularly in the case of the glycol) and to the excessive range of densities in the original negatives some difficulty was experienced in obtaining reproducible prints. The authors are indebted to Mr. H. Rudoff, graduate student in the Department of Chemistry, McGill University, for technical assistance in this connection.

The detailed results of the x-ray examination are summarized in Table I. The first and second columns give the numbers of the diffraction effects and the corresponding values of sin θ, respectively, from Table I of Sauter's paper.[4] Corresponding values of sin θ for the polymerized ethylene oxide of molecular weight 3000 and for

TABLE I

SUMMARY OF RESULTS

No.	sin θ (λ = 1.54 Å.)			I		
(S)	(S)	(O)	(G)	(S)	(O)	(G)
1	0.106	..	..	v.w.	...	..
2	.117	..	..	w.	...	..
3	.121	..	..	v.w.	...	..
4	.133	0.131	0.131	w.	w.	w.
5	.138	..	..	v.w.	...	..
6	.163	.166	.166	v.w.	v.s.	v.s.
7	.169			v.s.		
8	.196	.202	.202	w.	v.s.	v.s.
9	.205			m.		
10	.208			v.s.		
11	.221	.231	.233	w.	s.	s.
12	.229			m.		
13	.234			m.		
14	.237			w.m.		
15	.243			w.		
16	.270	.270	.270	w.m.	w.	w.
17	.283	.284	.284	m.	v.w.	v.w.
18	.308	.309	.309	m.	s.	s.
19	.308			m.		
20	.308			m.		
21	.316			m.w.		
22	.344	.342	.340	m.	m.	w.
23	.358	..	.355	w.	..	v.w.
24	.372	.369	.369	w.	w.	w.
25	.372			w.		
26	.390	.388	.388	w.	w.	w.
27	.407	.417	.418	v.w.	w.	w.
28	.418			v.w.		
29	.428			v.w.		
30	.460	.454	.454	v.w.	v.w.	v.w.
31	.460			v.w.		
32	.482	.483	..	v.w.	v.v.w.	..

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(6) See Staudinger,[3c] p. 294.

the 162-membered polyethylene glycol are shown in columns three and four, respectively. Visually estimated intensities[7] are recorded in columns five (from Sauter's paper[4]), six (for the oxide), and seven (for the glycol), respectively.

In connection with the foregoing table the following remarks may be noted. Sauter's lines 1 and 2 apparently are present in traces on the best negatives for the oxide and glycol obtained in the present study but are too weak in intensity for measurement. Lines 3 and 5 would fall within about 0.2 mm. of the inner and outer edges of line 4 so that they would practically be unresolvable for the crystal-to-plate distance employed. The remainder of the data, however, appeared to be conclusive enough not to warrant the long exposure times necessary to bring out lines 1, 2, 3 and 5 at a longer crystal-to-plate distance. Certain groups of diffraction effects in Sauter's table appear as bands in the powder diagrams. In Table I these have been bracketed and the mean position of the observed band is given in columns 3 and 4. For example, Sauter's numbers 11, 12, 13, 14, 15 have sin θ values which would result in haloes falling within the inner and outer edges of the band on the present oxide negative whose mean position is given by a sin θ value of 0.231. Finally the very weak halo at sin $\theta = 0.482$ (Sauter's No. 32) is present in the best negative for the glycol but is not included in Table I because it is too weak in intensity for accurate measurement.

The general agreement among Sauter's data for polymerized ethylene oxides, and the present data for the polymerized ethylene oxides and polyethylene glycols prepared by Pullman and Hibbert is very satisfactory. The only anomalous features are the absence of line 23 from the present polymerized ethylene oxide negatives, and the definitely stronger relative intensity of line 22 in the oxide compared with the glycol photographs. In this connection, however, it should be noted that line 23 is of weak intensity and is, moreover, clearly present on the glycol negatives. These features may be purely fortuitous or may have something to do with the relative physical characteristics of the samples. In general the glycols are more hygroscopic than the corresponding oxides, probably because the former comprise only one polymeric species while the latter probably contain appreciable fractions of higher (less hygroscopic) polymers. In comparing the relative intensities of Sauter with those observed in the present investigation it must also be borne in mind that the former were estimated on fiber diagrams whereas the latter were obtained from powder diagrams.

A consideration of the data presented in Table I, and a comparison between Fig. 1 of this paper and Fig. 2 of that of Sauter,[4] leads to the conclusion that, in so far as the diffraction of x-rays is concerned, there is no essential difference either between the polymerized ethylene oxides and the polyethylene glycols prepared by Pullman and Hibbert or between these and the polymerized ethylene oxides prepared by Lohmann for Sauter's investigation.

Montreal, Canada

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[7] m. = medium; s. = strong; v. = very; w. = weak.

[Contribution from the Baker Laboratory of Chemistry at Cornell University]

A New Reagent for Structure Determination

By Ralph Connor[1] and John H. Van Campen

In the identification of organic compounds those tests are especially valuable which can be carried out quickly on small amounts of material and which show, by the production of a color or precipitate, the presence of a specific group or structure. In work with active methylene compounds it has often been desirable to have a reliable *general* test for such substances. The production of colors with ferric chloride solution is limited in usefulness because many active methylene compounds (for example, the malonic esters) do not react with this reagent. The present paper describes a test which has frequently been of value and which, under the conditions specified later, is general for substances which contain hydrogen on a carbon atom bearing at least *one* acyl group or *two* other activating groups.

The test consists of the addition of an alcoholic solution of mercuric chloride to a solution of the unknown in alcohol containing sodium ethoxide.

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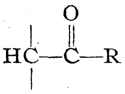
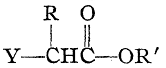
The formation of a *white* (or occasionally, cream-colored) precipitate is a *positive* test. The negative test is the formation of a deep yellow precipitate similar to that obtained when the sodium ethoxide and mercuric chloride solutions are mixed in the absence of an additional reactant.

Over two hundred organic compounds have been tested with this reagent and *it seems advisable to limit the test to neutral compounds which do not contain elements other than carbon, hydrogen and oxygen.* Considering this limitation, the classes of compounds with which the test will be concerned include ketones, aldehydes, esters, hydrocarbons, ethers, acetals, alcohols, quinones and anhydrides. Of these, the last five types fail to give a positive test. Aldehydes and ketones with hydrogen on the carbon atom bearing the carbonyl group give a positive test. The only esters which give a positive test are those which have both hydrogen and a labilizing group on the carbon bearing the carboxyl group. While acetylenes have not been investigated thoroughly, they apparently give a positive test and are certainly the only hydrocarbons to do so.

A few substances (such as anthrone) give colors with sodium ethoxide solution and others (such as ethyl formate) give white precipitates with sodium ethoxide; in such cases the results of the test are not significant. Likewise, the formation of reduction products of mercuric chloride should not be considered as either positive or negative, but merely as indicating the presence of a structure susceptible to oxidation.

The limitation of this test to neutral compounds containing no elements other than carbon, hydrogen and oxygen is imposed because the results of the test are anomalous when it is applied to other compounds. This is not a serious limitation, however, since many tests are available for acidic and basic compounds and for those containing elements in addition to carbon, hydrogen and oxygen. The test in its present form is specific for the structures  $\mathrm{H}\overset{|}{\underset{|}{\mathrm{C}}}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}$ and  $\mathrm{Y}-\overset{\overset{\mathrm{R}}{|}}{\mathrm{C}}\mathrm{H}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{OR'}$ (where Y is a labilizing group and R may be hydrogen, alkyl or aryl); few tests are available for such structures. This is a quick and satisfactory method, for example, of distinguishing between mono- and di-substituted malonic esters and for detecting the presence of a monosubstituted product in a disubstituted malonic ester.

From the types of compounds which undergo the reaction and from the efficiency of sodium ethoxide as a catalyst, it seems probable that the reaction is one of the enol form. The mechanism of the mercuration may then involve addition to the double bond of the enol[2] or the formation of intramolecular chelation products similar to those proposed by Johnson[3] and by Carothers[4] for other reactions of similar systems.

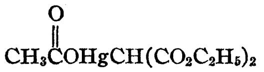
The reaction upon which this test is based is probably similar to that obtained by other workers[5] with mercuric compounds, but apparently sodium ethoxide is a more efficient catalyst and permits the omission of the periods of reflux previously used. As applied in this test, the reaction usually occurs instantly and always within a few minutes.

The compounds obtained from these reactions have been assigned various structures.[5] With malonic ester and mercuric chloride or mercuric acetate the possibilities suggested include the following

$\mathrm{Hg{=}C(CO_2C_2H_5)_2}$ $\mathrm{HOHgCH(CO_2C_2H_5)_2}$

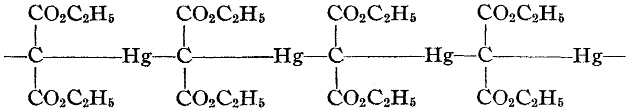
$\mathrm{(C_2H_5O_2C)_2CHHgCH(CO_2C_2H_5)_2}$

$\mathrm{(ClHg)_2C(CO_2C_2H_5)_2}$



$\mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OHgCH(CO_2C_2H_5)_2}$

For the present purpose a discussion of the structures of the products is not pertinent. However, the possibility of the formation of structures similar to the following should be pointed out



$$-\underset{\underset{\mathrm{CO_2C_2H_5}}{|}}{\overset{\overset{\mathrm{CO_2C_2H_5}}{|}}{\mathrm{C}}}-\mathrm{Hg}-\underset{\underset{\mathrm{CO_2C_2H_5}}{|}}{\overset{\overset{\mathrm{CO_2C_2H_5}}{|}}{\mathrm{C}}}-\mathrm{Hg}-\underset{\underset{\mathrm{CO_2C_2H_5}}{|}}{\overset{\overset{\mathrm{CO_2C_2H_5}}{|}}{\mathrm{C}}}-\mathrm{Hg}-\underset{\underset{\mathrm{CO_2C_2H_5}}{|}}{\overset{\overset{\mathrm{CO_2C_2H_5}}{|}}{\mathrm{C}}}-\mathrm{Hg}-$$

Although we have no definite evidence for such structures, the intractable nature of the products leads us to believe that linear polymers of this type may be formed.

Experimental Part

Procedure.—The mercuric chloride solution was prepared by dissolving 10 g. of mercuric chloride in 100 ml. of commercial absolute ethanol. The sodium ethoxide solution was prepared by dissolving 1.0 g. of sodium in 100 ml. of commercial absolute ethanol. For use by students it has been convenient to keep these solutions in indicator

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[2] Sandborn and Marvel, This Journal, **48**, 1409 (1926); Griffith and Marvel, *ibid.*, **53**, 789 (1931); Wright, *ibid.*, **57**, 1993 (1935).

[3] Johnson, *ibid.*, **55**, 3029 (1933).

[4] Carothers and Berchet, *ibid.*, **55**, 2807 (1933).

[5] Hoffmann, *Ber.*, **31**, 2215 (1898); Biilmann, *ibid.*, **35**, 2571 (1902); Schoeller and Schrauth, *ibid.*, **42**, 777 (1909); Schrauth and Schoeller, *ibid.*, **41**, 2087 (1908); Naik and Patel, *J. Indian Chem. Soc.*, **9**, 185 (1932); *ibid.*, **9**, 533 (1932).

bottles fitted with medicine droppers. To 1 ml. of sodium ethoxide solution was added 2 drops of the unknown, followed by 5 drops of the mercuric chloride solution. The mixture was shaken vigorously and the result observed after one minute.

Influence of Conditions upon the Reaction.—The relative amounts of reactants indicated above were selected after a series of tests with acetophenone, using varying amounts of the mercuric chloride and sodium ethoxide solutions. An excess of mercuric chloride over that necessary for reaction with acetophenone gave a yellow-orange precipitate which masked the white. Mercuric acetate seemed to be fully as satisfactory as the chloride and gave the same type of products. Mercuric nitrate, however, was reduced by sodium ethoxide and was unsatisfactory. Mercuric sulfate was too insoluble for use in alcohol solution. Dilute aqueous potassium hydroxide solution could be used to replace the sodium ethoxide but the formation of the white product was very slow and it was necessary to allow the test to stand for some time before judging the results.

The results are summarized below. In the lists of compounds tested, compounds with more than one functional group are given with the last-discussed series; thus, ketonic esters are given with the esters, cyano esters with the nitriles, etc. In each series the compounds giving a white precipitate are listed under "positive," those giving a yellow or orange precipitate under "negative," and compounds which give other results are listed under "special reactions."

Neutral Compounds Containing no Elements Other than Carbon, Hydrogen and Oxygen

HYDROCARBONS

Positive—Phenylacetylene.

Negative—Benzene, 2-pentene.

ALCOHOLS

Negative—Allyl alcohol, ethyl alcohol, ethylene glycol, isoamyl alcohol, triphenylcarbinol.

ETHERS

Negative—Acetal, anisole, *n*-butyl ether, ethyl ether.

ALDEHYDES

Positive—Acetaldehyde, heptaldehyde.

Negative—Anisaldehyde, benzaldehyde, piperonal, *p*-tolualdehyde.

Special Reactions—Formaldehyde reduced the mercuric chloride and paraldehyde first gave a yellow precipitate which turned lighter on standing.

ANHYDRIDES

Negative—Acetic, benzoic, *n*-butyric, cinnamic and isobutyric anhydrides.

KETONES

Positive—Acetone, acetophenone, benzalacetophenone, benzylacetophenone, 2-butanone, *n*-butyrophenone, desoxybenzoin, dibenzoylmethane, 2-heptanone, *p*-methylacetophenone, 2-octanone, α,γ-dibenzoyl-β-phenylpropane, pinacolone, propiophenone, 2-undecanone.

Negative—Benzalpinacolone, benzophenone, xanthone.

Special Reactions—Anthrone, benzoin, furfuralacetophenone, mesityl oxide and phenanthraquinone gave such deep colors with sodium ethoxide solution that the color of the precipitate was obscured. Some of these also apparently caused reduction of the mercuric chloride. Carvone, cyclohexanone and 1,1-dibenzoylethane also gave slight colors with the sodium ethoxide solution but the precipitate formed when the mercuric chloride was added was distinctly white.

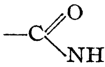
ESTERS

Positive—Ethyl acetoacetate, ethyl α-benzoylisovalerate, ethyl α-benzylacetoacetate, ethyl benzylmalonate, ethyl *n*-butylmalonate, ethyl α,γ-dibenzoyl-β-phenylbutyrate, ethyl α-ethylacetoacetate, ethyl ethylmalonate, ethyl malonate, ethyl α-methylacetoacetate, ethyl methylmalonate, ethyl phenylacetate, ethyl phenylmalonate, methyl phenylacetate.

Negative—Benzyl acetate, benzyl propionate, *n*-butyl acetate, ethyl acetate, ethyl benzoate, ethyl α-benzoylcinnamate, ethyl *n*-butyrate, ethyl cinnamate, ethyl crotonate, ethyl diethylmalonate, ethyl α-ethyl-β-hydroxybutyrate, ethyl isobutyrate, ethyl isovalerate, ethyl myristate, ethyl β-phenylpropionate, ethyl propionate, ethyl sebacate, ethyl succinate, isoamyl acetate, isoamyl benzoate, methyl benzoate, methyl cinnamate, methyl oxalate, phenyl acetate, triacetin.

Special Reactions—Ethyl α-acetyl-β-phenyl-γ-benzoylbutyrate and ethyl α-benzalacetoacetate gave colors with sodium ethoxide solution and the color of the precipitate formed when mercuric chloride was added could not be determined. Ethyl benzalmalonate and ethyl formate gave white precipitates with sodium ethoxide solution; however, the final reaction products were yellow.

Compounds Acidic or Basic or/and Containing Elements Other than Carbon, Hydrogen and Oxygen

Many *phenols* gave bright colors with sodium ethoxide solution and some reduced the mercuric chloride; only guaiacol gave a positive test. *Nitro compounds* gave negative tests in which the colors varied, depending upon the influence of sodium ethoxide on the nitro compound. Nitromethane, the only aliphatic nitro compound tested, gave a white precipitate with sodium ethoxide solution, but this became yellow when the mercuric chloride solution was added. No generalizations can be made concerning the behavior of *amines*—some gave positive tests, some negative tests and some reduced the mercuric chloride. The test may prove of some value with *amides*. It was found that the grouping  $—C\begin{smallmatrix}\nearrow O\\ \searrow NH_2\end{smallmatrix}$ gave a positive test. The only exceptions were *o*-acetotoluide, which gave a positive test, and thiourea, which gave a black precipitate (mercuric sulfide). *Sulfonamides* ($—SO_2NH_2$), gave a negative test. All the *nitriles* tested (except ethyl cyanoacetate) gave a negative test. *Acids, salts of acids* and *quaternary ammonium salts* formed the yellow precipitate only. The specific compounds tested are listed below.

PHENOLS

Positive—Guaiacol.

Negative—*o*-Chlorophenol, *m*-cresol, *o*-cresol, *p*-cresol, β-

naphthol, phenol, phenyl salicylate, phloroglucinol, vanillin.

Special Reactions—Catechol, hydroquinone, orcinol and resorcinol monomethyl ether all gave colored solutions with sodium ethoxide. The first three of these also reduced the mercuric chloride. A color was also formed with sodium ethoxide and α-naphthol, but the precipitate formed with mercuric chloride was distinctly yellow. Resorcinol gave a negative test but the precipitate darkened on standing. Salicylaldehyde gave a white precipitate with sodium ethoxide; the addition of mercuric chloride solution gave a yellow solution but the white precipitate apparently remained.

AMINES

Positive—*n*-Butylethylamine, diethylamine, isoamylamine, methyl anthranilate, *o*-toluidine.

Negative—1-Amino-2,4-dimethylaniline, aniline, *o*-anisidine, *m*-bromoaniline, *o*-bromoaniline, *p*-bromoaniline, di-*n*-butylamine, tri-*n*-butylamine, *p*-chloroaniline, N,N-diethylaniline, diphenylamine, N-ethylaniline, ethyl *p*-aminobenzoate, ethyl anthranilate, α-naphthylamine, nicotine, *m*-toluidine, *p*-toluidine.

Special Reactions—β-Naphthylamine and benzidine reduced the mercuric chloride. *p*-Aminoazobenzene, *p*-aminophenol and *p*-anisidine gave colors with sodium ethoxide solution and apparently reduced the mercuric chloride as well.

NITRILES

Positive—Ethyl cyanoacetate.

Negative—Acetonitrile, benzonitrile, isocapronitrile, phenylacetonitrile, *o*-tolunitrile, *p*-tolunitrile, *n*-valeronitrile.

ACIDS

Negative—Acetic acid, *m*-aminobenzoic acid, anthranilic acid, *p*-hydroxybenzoic acid, salicylic acid.

Special Reactions—Malonic acid formed a white precipitate when treated with the sodium ethoxide solution. Acids will give only a clear solution when the test is applied to them, unless an excess of sodium ethoxide is present. In the case of acetic acid, for example, it was necessary to add an additional portion of sodium ethoxide in order to obtain a precipitate.

NITRO COMPOUNDS

Negative—*o*-Bromonitrobenzene, *p*-bromonitrobenzene, *p*-chloronitrobenzene, *m*-dinitrobenzene, *o*-dinitrobenzene, methyl *m*-nitrobenzoate, *m*-nitroaniline, *p*-nitroaniline, *o*-nitroanisole, *p*-nitroanisole, *m*-nitrobenzaldehyde, *o*-nitrobenzaldehyde, nitrobenzene, *m*-nitrobenzoic acid, *o*-nitrobenzoic acid, *p*-nitrobenzoic acid, *p*-nitrobenzyl acetate, *p*-nitrophenol, *m*-nitrotoluene, *o*-nitrotoluene, *p*-nitrotoluene.

Special Reactions—2,4-Dinitrobenzaldehyde, *o*-nitroaniline, *o*-nitrophenol, picric acid and 1,3,5-trinitrobenzene gave colors with sodium ethoxide solution. Nitromethane gave a white precipitate with the sodium ethoxide solution but when a mercuric chloride solution was added, a yellow precipitate, characteristic of the negative test, was obtained.

AMIDES

Positive—Acetamide, *o*-acetotoluide, benzamide, α-bromopropionamide, urethan.

Negative—Acetanilide, β-acetonaphthalide, *p*-acetotoluide, benzanilide, N-methylacetanilide, phenacetin, phthalimide.

Special Reactions—*p*-Nitroacetanilide gave a colored solution with sodium ethoxide solution, but a typical negative test was obtained when the mercuric chloride solution was added. Succinamide was apparently quite insoluble in the sodium ethoxide solution and the addition of mercuric chloride solution gave a yellow precipitate; upon standing, however, a white precipitate was formed. Thiourea gave a negative test but the precipitate quickly became dark.

SALTS

Negative—Ammonium benzoate, tetraethylammonium bromide, tetramethylammonium chloride, tetramethylammonium iodide.

MISCELLANEOUS

Positive—Benzal-*p*-bromoacetophenone.

Negative—Benzenesulfonamide, *p*-bromobenzaldehyde, carbazole, *o*-chlorobenzaldehyde, *p*-chlorobenzyl acetate, dicresyl-*o*-sulfobenzoate.

Summary

A mercuric chloride test for structure determination has been described. It is recommended for use with neutral compounds which contain no elements other than carbon, hydrogen and oxygen; it gives a positive test with ketones and aldehydes which have hydrogen on the alpha carbon atom and with esters having at least one hydrogen and one labilizing group on the alpha carbon atom. The behaviors of over two hundred organic compounds with this reagent have been described.

ITHACA, NEW YORK

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[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

The Nature of the Hydrogen Bond. I. Association in Carboxylic Acids

BY R. H. GILLETTE AND ALBERT SHERMAN

Introduction

It has long been known that many organic compounds, especially those containing hydroxyl groups, are associated at ordinary temperatures, both in the gaseous state and in solution in nonpolar solvents.[1] The equilibrium was investigated by Auwers,[2] who was able to distinguish two classes of associating substances, those in which the molecular weight increases in proportion to the concentration and those in which the molecular weight approaches a limiting value corresponding to dimer formation. Examples of the former class are alcohols, phenols and amides; of the latter class the carboxylic acids constitute the best example. Much later work using many different methods has yielded discordant results but has largely verified the above conclusions. The present work is concerned with assuming a structure for the dimeric carboxylic acid, and calculating its energy with respect to unassociated molecules. It is mainly for these substances that experimental values for the heat of the association reaction are available. For formic acid Coolidge[3a] obtained the value 14,125 cal., and Fenton and Garner[3b] found 13,790 cal. for acetic acids. The fact that consistent values for the heat of association over a considerable range of temperature and pressure were obtained lends considerable credence to the view that these acids are associated only to dimers, as does also the work of Smyth and Rogers,[4] who showed that associated molecules of acetic acid and butyric acid have an electric moment of zero in benzene solution.

Several mechanisms have been postulated to explain this association, the simplest being that the interaction between two juxtaposed dipoles is responsible for the reaction. This, however, is unimportant in this case, and in general this interaction is insufficient to deal with polar molecules, as has been pointed out by Hildebrand.[5] Williams[6] remarks that the presence of a dipole movement may be a necessary condition for association in general, but it is not sufficient. Phenol and benzoic acid are generally regarded as associated, yet over a considerable range of concentration (benzene solution) these substances show no change in their molar polarizations.

Moore and Winmill[7] were probably the first to postulate a hydrogen bond, *i. e.*, two atoms or groups held together by a hydrogen atom or nucleus between them. Pfeiffer[8] used the idea to explain the weakness of *o*-hydroxyanthraquinone and Huggins[9] used the concept as a theory in regard to certain organic compounds. Latimer and Rodebush[10] were the first to recognize the hydrogen bond as a general phenomenon.

Pauling[11] has considered a hydrogen bond to be polar in nature while Sidgwick[12] as a result of his theory of the coördinate covalent link, postulated that organic acids would associate since an inner coördination would lead to a four-membered ring, which is unstable, whereas two molecules could join together, forming a stable configuration, with carboxyl groups facing one another, the hydroxyl hydrogens acting as acceptors for the formation of coördinate links. This view is, however, untenable, as Sidgwick himself has since stated,[13] since hydrogen cannot be divalent unless some of the electrons are promoted to the 2s state, which is unstable. This argument for the instability of divalent hydrogen assumes that the atomic quantum numbers for hydrogen essentially retain their significance in the molecule.

Sidgwick now regards the hydrogen as first attached to one atom and then to the other, this electronic resonance on a time average amounting to making hydrogen divalent, *i. e.*, the resonance phenomena of wave mechanics. Bell and Arnold[14] come to the same conclusion for dimer formation in the case of trichloroacetic acid molecules.

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(1) W. E. S. Turner, "Molecular Association," Longmans, Green & Co., N. Y., 1915, p. 33.

(2) Auwers, *Z. physik. Chem.*, **12**, 689 (1893); **23**, 449 (1897).

(3) (a) Coolidge, THIS JOURNAL, **50**, 2166 (1928); (b) Fenton and Garner, *J. Chem. Soc.*, 694 (1930).

(4) Smyth and Rogers, THIS JOURNAL, **52**, 1824 (1930).

(5) Hildebrand, *Science*, **83**, 21 (1936).

(6) Williams, *Proc. Nat. Acad. Sci.*, **14**, 932 (1928).

(7) Moore and Winmill, *J. Chem. Soc.*, **101**, 1675 (1912).

(8) Pfeiffer, *Ann.*, **398**, 137 (1913).

(9) Huggins, Undergraduate Thesis, Univ. of California, 1919.

(10) Latimer and Rodebush, THIS JOURNAL, **42**, 1419 (1920).

(11) Pauling, *Proc. Nat. Acad. Sci.*, **13**, 359 (1928).

(12) Sidgwick, "The Electronic Theory of Valence," Oxford University Press, 1929; *Chem. Soc. Ann. Rep.*, **30**, 115 (1934).

(13) Sidgwick, *ibid.*, **31**, 34 (1935).

(14) Bell and Arnold, *J. Chem. Soc.*, 1432 (1935).

W. D. Kumler[14a] discusses the hydrogen bond in relation to dielectric constants and boiling points of organic liquids.

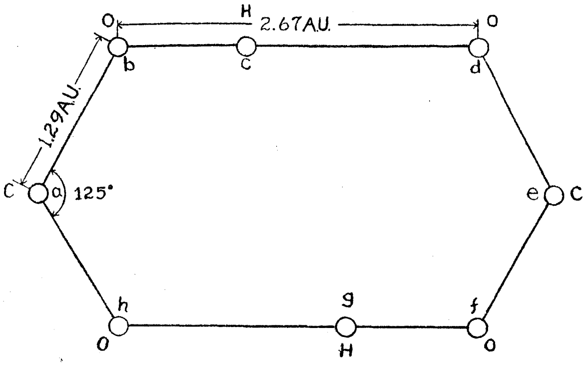


Fig. 1.—The model obtained from electron diffraction experiments for associated dimeric formic acid. The two carboxyl groups form an eight-membered plane ring.

In view of the above facts it is of interest to calculate the energy of the carboxylic acid complex with the aid of wave mechanics in order to throw some light upon the nature of the hydrogen bond, *i. e.*, to determine whether it is polar, homopolar or both.

We shall restrict our considerations for the present to formic acid, partly because it is the simplest acid and partly because accurate experimental data for the substance are available. In order to calculate the energy of the dimer we must assume some particular spacial configuration. The one chosen was that suggested by Latimer and Rodebush[10] and verified experimentally by Pauling and Brockway[15] by electron diffraction measurements. This structure places all the atoms in a plane with carboxyl groups opposite one another, as shown in Fig. 1. Zahn[16] has suggested an alternative model as a result of electric moment investigations, and based on the results of electron diffraction measurements by Hengstenberg and Brú.[17] However, Pauling and Brockway state the model postulated by the latter authors is not in agreement with their electron diffraction pattern and hence can be definitely excluded.

Procedure

All the electrons are considered uniquely paired except those in the ring and the problem is treated in the ordinary way as one of 8 electrons with spin degeneracy. There are in general 14 linearly independent bond wave functions for 8 electrons, a convenient set being the so-called canonical set[18] given below.

The energy of the complex is calculated as a function of the distance between carboxyl groups, *i. e.*, between atoms b and d. For every distance r_{bd} two cases were considered. In one case the hydrogen atoms are placed midway between the oxygen atoms, as shown in Fig. 1. In the other case the hydrogen atoms are at the normal O–H distance (0.97 Å.) from diagonally opposite oxygen atoms. It is of course immaterial where the hydrogen atoms are located as far as the 14 bond wave functions in Fig. 2 are concerned.

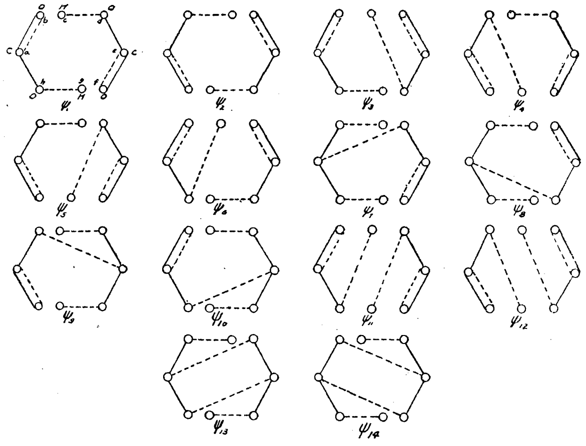


Fig. 2.—Fourteen linearly independent bond wave functions for eight electrons in the ring of dimeric acetic acid.

For the second case we give ψ_3 and ψ_4 the same coefficient in the wave function for the system, and similarly for ψ_5 and ψ_6 and ψ_7, ψ_8, ψ_9 and ψ_{10}. The functions ψ_{11}, ψ_{12}, ψ_{13} and ψ_{14} are neglected. They are what Pauling and Wheland[19] have called second excited structures, and it is evident that they will contribute little to the energy of the system and may be neglected in an approximate calculation. Thus, we define

$$\phi_1 = \psi_1,\ \phi_2 = \psi_2,\ \phi_3 = \psi_3 + \psi_4,\ \phi_4 = \psi_5 + \psi_6,$$
$$\phi_5 = \psi_7 + \psi_8 + \psi_9 + \psi_{10}$$

The matrix components between the ϕ's were computed by first calculating the components in terms of the ψ's, by either Pauling's[18] or Eyring and Kimball's method,[20] and then using the definition of the ϕ's.

In this case $ab = ah = de = ef$; $ac = eg$; $ad = af = be = eh$; $ag = ce$; $bc = fg$; $bd = fh$; $bf = dh$; $bg = df$; $cd = gh$; $dg = ch$ and $bh = df$.

(14a) W. D. Kumler, THIS JOURNAL, **57**, 600 (1935).

(15) Pauling and Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

(16) Zahn, *Phys. Rev.*, **37**, 1516 (1931); **35**, 1047 (1930).

(17) Hengstenberg and Brú, *Anal. soc. españ. fís. quím.*, **30**, 341 (1932).

(18) Pauling, *J. Chem. Phys.*, **1**, 280 (1933).

(19) Pauling and Wheland, *ibid.*, **1**, 362 (1933).

(20) Eyring and Kimball, *ibid.*, **1**, 626 (1933).

The components in terms of the ϕ's are given below.

$$H_{11} = Q + (ab - ac - ag - bc - bd - bf - bg - bh - dg) + 2(cd - ad) - {}^1/_2(ac + cg)$$
$$H_{22} = Q + (ab - ac - ag - bd - bf - cd - bg - bh - dg) + 2(bc - ad) - {}^1/_2(ac + ag)$$
$$H_{33} = 2{}^1/_2Q + 4(ab - ag - bh) - 2{}^1/_2(ac + bc + bd + bf + dg) + 2(bg + cd) - 1{}^1/_4(ac + cg) - 5ad$$
$$H_{44} = 7{}^1/_2Q + 3(ab + ad) + 6(cd + bc - bg - dg) - 4{}^1/_2cg - 7{}^1/_2ac - 10{}^1/_2(ac + ag) - 12(bd + bh) - 9bf$$
$$H_{55} = 2{}^1/_2Q + 4(ab - ac - bh) - 2{}^1/_2(ag + bd + bf + bg + cd) + 2(bc + dg) - 1{}^1/_4(ae + cg) - 5ad$$
$$H_{12} = {}^1/_8Q + {}^1/_2(ab + ad - ac - bd - ag - bh - bf) + {}^1/_4(bc + cd + bg + dg - ae - cg)$$
$$H_{13} = Q + 2{}^1/_2(ab - ag - bh) + 2(cd - ad) - (ac + bc + bd + bf + dg) + {}^1/_2(bg - ae - cg)$$
$$H_{14} = 1{}^1/_2Q + 2{}^1/_4(ab - ag - bf - bh) + {}^3/_4(ad + bc - cg - bg) + 3cd - 1\,{}^1/_2(ae + dg) - {}^{15}/_4(ac + bd)$$
$$H_{15} = {}^1/_2Q + 1{}^1/_4(ab - ac - bd - bf - bh - ag) + {}^1/_4(bc + bg - ad - ac) + cd + dg - cg$$
$$H_{23} = {}^1/_2Q + 1{}^1/_4(ab - ac - bd - bf - bh - ag) + {}^1/_4(cd + dg - ad - ae) + bc + bg - cg$$
$$H_{24} = 1{}^1/_2Q + 2{}^1/_4(ab - ac - bf - bh) + {}^3/_4(ad + cd - dg - cg) - {}^{15}/_4(bd + ag) + 3bc - 1{}^1/_2(ae + bg)$$
$$H_{25} = Q + 2{}^1/_2(ab - bh - ac) + 2(bc - ad) + {}^1/_2(dg - ae - cg) - ag - bd - bf - bg - cd$$
$$H_{34} = 2{}^1/_4Q + 4{}^1/_2(ab - bd - ag - bh) + 1{}^1/_2(ad + bc + bg) - 6(bf + ac) + 3cd - 2{}^1/_4(ae + cg)$$
$$H_{35} = 1{}^1/_4Q + 2(ab - ac - ag - bh - bf) - ad + bc + cd + bg + dg - ae - 2{}^1/_2cg - 3{}^1/_2bd$$
$$H_{45} = 2{}^1/_4Q + 4{}^1/_2(ab - ac - bd - bh) + 1{}^1/_2(ad + cd + dg) - 6(bf + ag) + 3bc - 2{}^1/_4(ae + cg)$$

Here Q is the Coulombic energy of the system, ab the exchange energy between electrons a and b, and similarly for ac, ad, etc.

The Coulombic and exchange energies were evaluated from the various Morse potential energy curves in question, and an approximate formula was used for correcting the Morse values for directed valence. It was assumed that $K'_{ab} = K'_{ab}\cos^2\alpha$ holds for a bond formed from one s and one p electron, where K_{ab} is the exchange energy of a bond determined from a Morse curve, α the angle through which the bond is distorted from its normal value (*i. e.*, from the angle for which the bond energy is a maximum), and K'_{ab} the directed valence exchange energy. The carbon wave functions were considered to be tetrahedral and orthogonal. The Coulombic energy was assumed to be 14% of the total bond value.[21]

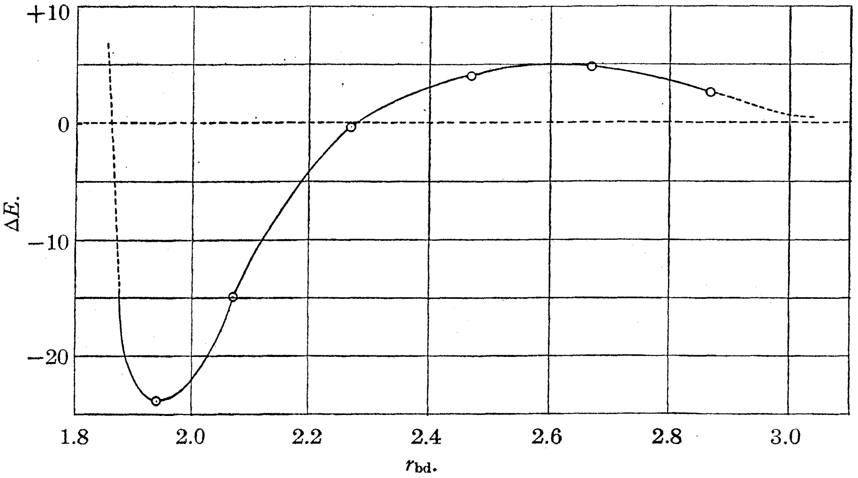


Fig. 3.—The heat of the association reaction of two carboxyl groups as a function of the distance between them. The minimum corresponds to the formation of a stable dimer.

The constants used for constructing Morse curves are given in Table I.

TABLE I

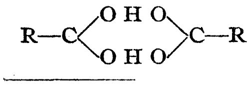
Bond	r_0(Å.)	ω(cm.$^{-1}$)	D(kcal.)
O–O	1.32	1304	34.3
C–H	1.12	2930	92.3
C–O	1.43	1030	81.8
H–H	0.74	4375	102.4
C–C	1.54	990	83.0
O–H	0.97	3660	113.1

Results

For every distance between oxygen atoms b and c or h and f the configuration where the hydrogen atoms are placed at the normal distance from diagonally opposite oxygen atoms turned out to be more stable than when they were placed midway between the oxygens. Hence only the matrix component for the more stable configuration was given in the preceding section, since it is the only one of interest for our present problem.[22]

The results of the calculation are shown in Fig. 3.

ΔE is the heat of the association reaction 2R—COOH ⟶



$$R{-}C\begin{matrix}\diagup O\ H\ O \diagdown \\ \diagdown O\ H\ O \diagup\end{matrix}C{-}R$$

, *i. e.*, $\Delta E = E_{\text{dimer}} - 2E_{\text{monomer}}$

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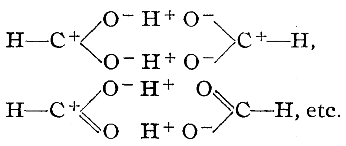
[21] This percentage is taken over from activation energy calculations. See Van Vleck and Sherman, *Rev. Modern Phys.*, **1**, 168 (1935).

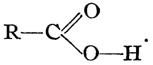
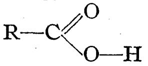
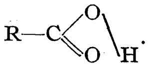
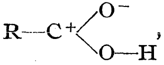
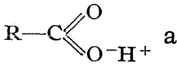
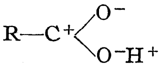
(22) The secular equation for the more unstable configuration was taken as a cubic, defined by the wave functions $\theta_1 = \psi_1 + \psi_2$, $\theta_2 = \psi_3 + \psi_4 + \psi_5 + \psi_6$, $\theta_3 = \psi_7 + \psi_8 + \psi_9 + \psi_{10}$.

Discussion

It is seen from Fig. 2 that the curve has the form to be expected and that for the reaction 2HCOOH $\longrightarrow$ $(HCOOH)_2$ we calculate an activation energy of 4.8 kcal., a minimum at $r_{bd} = 1.94$ Å., and a heat of reaction of 23.8 kcal. This is to be compared with the experimental values $r = 2.67$ Å., and ΔE at the minimum equal to 14.1 kcal.

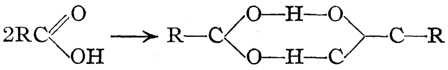
From theoretical considerations we know that a complete wave function for a system should include terms to allow for both polar and homopolar states. It is exceedingly difficult, however, to include polar states in the calculation in any practical way, but it was considered of interest to see to what extent homopolar states alone could account for the results in order to determine, if possible, the relative importance of each. The existence of such states as



are possible, and the most important cause of the discrepancy between calculated and experimental quantities is undoubtedly to be sought in the neglect of them. Pauling and J. Sherman[23] calculate from thermochemical data that the resonance energy of a carboxyl group is 1.2 v. e. relative to the structure . We have made additional calculations and find the resonance energy to be 0.8 v. e. if it arises from the two states  and . Accordingly other states must be involved, such as ,  and .

To the extent that polar states are important directed valence is unimportant. Since we neglected polar terms we consequently over-corrected for directed valence. This is the main reason why the calculated ΔE was not in numerical agreement with experiment.

Polar terms will come in to the energy expression in an additive way. Although it is not quite correct to infer that they will therefore effectively increase the Coulombic percentage above 14, nevertheless it is interesting to remark that if the importance of directed valence is decreased and the percentage of Coulombic energy slightly increased agreement with experiment is obtained. Thus if directed valence be decreased by 25% and the Coulombic percentage increased from 14 to 17.5 the calculated value of ΔE agrees with experiment.

Resonance between bond wave functions ψ_1 and ψ_2 may be considered to be the resonating hydrogen bond of Sidgwick, mentioned in the introduction. It is to be noticed, however, that if the functions ψ_1 and ψ_2 alone were involved ΔE would be $+5$ kcal. rather than -23.8 kcal. Thus we see that states ψ_3 through ψ_{10}, although not as important as ψ_1, and ψ_2, must also be considered since they contribute considerable energy to the complex. If all excited states[19] be neglected, both for the dimer and the monomers, the heat of the association reaction turns out to be approximately equal to that found by taking all states into account.[24] Hence it turns out that the ordinary chemical formulation of the reaction  happens to be fortuitously correct if the bonds drawn in the complex are interpreted to represent the functions ψ_1 and ψ_2.

Various assumptions concerning the value of a in the expression $K' = aK \cos^2 \alpha$, together with various choices of the Coulombic percentage all affect the value of ΔE and the activation energy of the association, but many detailed calculations show that the position of maximum stability always occurs at $r_{bd} = 1.94$ Å. The fact that r_{bd} (exptl.) $= 2.67$ Å. indicates polar states are important, but the discussion above indicates that homopolar states are also important.

Pauling,[11] after remarking that the hydrogen bond in HF_2^- is polar, *i. e.*, $F^-H^+F^-$, says the polar concept of the hydrogen bond explains why only atoms of high electron affinity such as fluorine, oxygen and nitrogen form such bonds. It is not clear, however, why from this viewpoint chlorine which is at least as electronegative as nitrogen[25] forms at best only very weak hydrogen bonds.[26]

We wish to thank Professor Farrington Daniels for his constant interest in this problem. One of us (A. S.) also acknowledges a profitable talk with Professor L. Pauling. He also wishes to thank

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(23) Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1936).

(24) Pauling and Wheland[19] used this general assumption.

(25) Pauling [This Journal, **54**, 3570 (1932)] gives for the coordinates of these elements on his electronegativity scale Cl = 0.94, N = 0.95, O = 1.40, F = 2.00.

(26) Pauling, *ibid.*, **58**, 92 (1936).

the Wisconsin Alumni Research Foundation for financial support.

Conclusions

From the preceding discussion we conclude that the wave function for a hydrogen bond should include both polar and homopolar terms.

Although we are not able to decide quantitatively the relative importance of each it seems safe to conclude that both are important. Most simply, therefore, the hydrogen bond must be considered as consisting of at least the three states $X^-H^+X^-$, X—H X and X H—X.

Madison, Wisconsin Received April 14, 1936

[Contribution from the Laboratory of Physical Chemistry, University of Wisconsin]

The Effect of Association on the Infra-red Absorption Spectrum of Acetic Acid

By R. H. Gillette and Farrington Daniels

The effect of interactions between various groups on the infra-red absorption of organic molecules has been investigated recently by a number of workers.[1] The work, however, has been confined chiefly to the study of the intensities of overtones of vibrations involving hydrogen linked to carbon, nitrogen or oxygen. Acetic acid is particularly interesting in this connection because one can observe the effect of association on the spectrum of the carboxyl group. It has, in fact, proved possible to measure a considerable portion of the spectrum of both the monomeric and dimeric acid and to interpret it so as to bring it into accord with the results of electron diffraction measurements and, perhaps less certainly, of electric moment measurements.

Several investigators have used Raman data to obtain such information.[2] Dadieu and Kohlrausch[3] have determined the Raman spectra of several binary liquid mixtures of acetic acid in different solvents and have found that only the lines associated with the C═O group are affected by the solvent. Leitman and Ukholin[4] have shown that the Raman line at 623 cm.$^{-1}$ in acetic acid becomes much weaker when the acid is dissolved in water, and finally, as the concentration is decreased, fades out entirely. They interpret this to mean that the association of acetic acid leads to molecules of quite definite configuration.

Experimental

The spectrometer of the Wadsworth type using a rock salt prism, Nerst glow lamp, and Paschen galvanometer has been described before.[5] The absorption cells were made by cementing polished rock salt windows onto both ends of Pyrex tubes 8 cm. long. Glyptol cement was found to be excellent for attaching the windows to the glass—much better than fish glue. The cells were heated electrically with a constancy of ±1°.

The acetic acid, obtained from the Niacet Chemical Company, was carefully purified by distillation *in vacuo*. Different samples always gave the same absorption spectrum.

Results

The vapor of acetic acid was studied at room temperature and at 172° from 1100 to 10,000 cm.$^{-1}$, the results being shown in Table I and Fig. 1 (to conserve space the high frequency region containing only the band ν_1 was omitted in Fig. 1). In both cases the acid was present at a partial pressure of 19 mm. in an atmosphere of air.

Table I

Band	25° C.	172° C.
ν_1	2985 cm.$^{-1}$	2985 cm.$^{-1}$
ν_2	1740 cm.$^{-1}$	1786 cm.$^{-1}$
ν_3	1435 cm.$^{-1}$	1398 cm.$^{-1}$
ν_4	1296 cm.$^{-1}$	1288 cm.$^{-1}$
ν_5	1190 cm.$^{-1}$	1185 cm.$^{-1}$

Five sharply defined bands occur in the region studied, their shape suggesting that the rotational fine structure is completely blotted out, as might be expected at the high pressure of foreign gas. Of these, three are not shifted by the increase in temperature although the band at 1190 cm.$^{-1}$ (ν_5) is greatly intensified. The remaining two bands, at 1740 cm.$^{-1}$ (ν_2) and 1435 cm.$^{-1}$ (ν_3) at room temperature, are shifted considerably fur-

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(1) Errera and Mollet, *J. Phys. Radium*, **6**, 281 (1935); Liddel and Wulf, This Journal, **55**, 3574 (1933); **57**, 1464 (1935); Hilbert, Wulf, Hendricks and Liddel, *Nature*, **135**, 147 (1935); Pauling, This Journal, **58**, 94 (1936).

(2) Mayer, *Physik. Z.*, **30**, 170 (1929); **32**, 293 (1931); Pringsheim and Schlivich, *Z. Physik*, **60**, 582 (1931).

(3) Dadieu and Kohlrausch, *Physik. Z.*, **31**, 514 (1930).

(4) Leitman and Ukholin, *J. Chem. Phys.*, **2**, 825 (1934).

(5) Cross and Daniels, *ibid.*, **2**, 6 (1934).

ther apart at 172°—occuring at this temperature at 1786 and 1398 cm.$^{-1}$, respectively.

Since the temperature shifts are appreciably larger than the shifts produced by substitutions in the acetic acid molecule itself,[6] it was felt that some type of chemical reaction must be involved which changes bonds between atoms. It is well known from the work of Ramsay and Young[7] and Fenton and Garner[8] that acetic acid is almost completely associated into double molecules even at the boiling point, and at 183° and 400 mm. pressure is still 9% associated. If this association is responsible for the observed shifts, it would be expected that at intermediate temperatures where both monomeric and dimeric forms are present both bands should appear. This is strikingly borne out in Fig. 2 where the absorption of the C=O group is shown at various temperatures. As is to be expected the weaker band drifts toward the stronger one due to the fact that the width of the spectrometer slit is finite and some overlapping occurs.

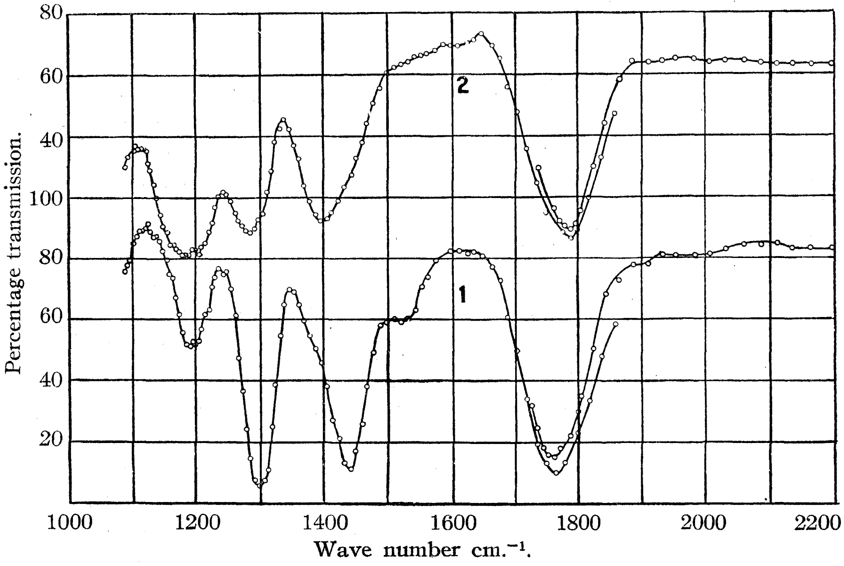

Fig. 1.—The infra-red absorption spectrum of acetic acid vapor. Curve 1 at 25°; Curve 2 at 172°.

Discussion

In order to assign the bands to definite vibrations within the molecule, it is necessary first to consider the nature of the single and double molecules. The former cannot vary greatly from the planar model assumed by Mecke[9] for formaldehyde. There is some arbitrariness in the choice of fundamental modes of vibration for this molecule, but since the molecule is completely unsymmetrical a possible set is shown in Fig. 3, where ω's are used to indicate modes of vibration of the model to be associated with the fundamental frequencies in the absorption spectrum (ν's) having the same subscript. The usual assumptions that interactions between bonds can be neglected and that only the valence vibrations will lie in this region are made.[10] It is apparent that these modes correspond essentially to the vibration of a C=O, a –C–O–, and a C–C bond. At 172° under the conditions of our experiments acetic acid is almost completely dissociated into single molecules and hence the spectrum at this temperature should correspond to that of the model of Fig. 3.

One of the most firmly established frequencies in infra-red spectroscopy is that of the C=O group which occurs in the same region in aldehydes, ketones, acyl halides, amides, esters and acids and has been investigated extensively[11] by both Raman and infra-red measurements. This is clearly to be associated with the ν_2 and ω_2 described here.

Bands occurring in the vicinity of 2960 cm.$^{-1}$ are well known to be produced principally by a valence vibration of the C–H bond.[12] In this region occur also bands due to overtone and combination vibrations of the carboxyl group as well as the fundamental of the O–H vibration. It is also well established that a deformation vibration of the C–H group occurs in the vicinity of 1300 cm.$^{-1}$. To these two vibrations we assign our ν_1 and ν_4, respectively.

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(6) Bennett and Daniels, THIS JOURNAL, **49**, 50 (1927); Gillette, **58**, 1143 (1936).

(7) Ramsay and Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910); see also Drucker and Ullman, *Z. physik. Chem.*, **74**, 604 (1910).

(8) Fenton and Garner, *J. Chem. Soc.*, 694 (1930).

(9) Mecke, "Leipziger Vorträge" (English Edition. Debye, "Structure of Molecules," Blackie and Son, London, 1932, p. 47.

(10) Bartholomé and Teller, *Z. physik. Chem.*, **B19**, 367 (1933).

(11) Roth, *Z. Physik.*, **87**, 192 (1934); Weniger, *Phys. Rev.*, **31**, 388 (1910); Kohlrausch and Pongratz, *Z. physik. Chem.*, **B27**, 176 (1935).

(12) Ref. 11; also Easly, Fenton and Spence, *Astrophys. J.*, **67**, 185 (1928); Morton, *Z. physik. Chem.*, **117**, 97 (1925).

The remaining two vibrations are assigned as shown in Fig. 3. This assignment is in qualitative agreement with the fact that the frequency of a C–O vibration is in general higher than that of a C–C frequency, and will be further justified by a consideration of the double molecule.

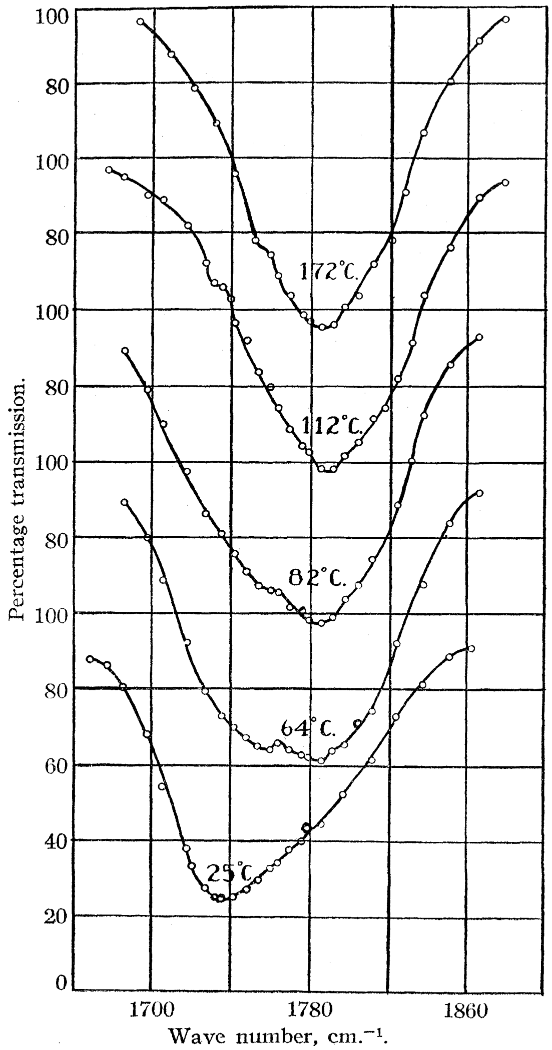
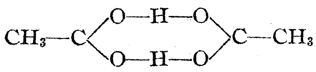


Fig. 2.—The infra-red absorption spectrum of the carbonyl group of acetic acid.

That the association of acetic acid involves hydrogen bonds was first suggested by Latimer and Rodebush.[13] This view was later verified by Pauling and Brockway[14] who determined the configuration of the double molecule of formic acid by electron diffraction measurements. It was found to be a monoplanar ring, the two molecules being joined by two hydrogen bonds



We shall assume that this same structure is also found in acetic acid.

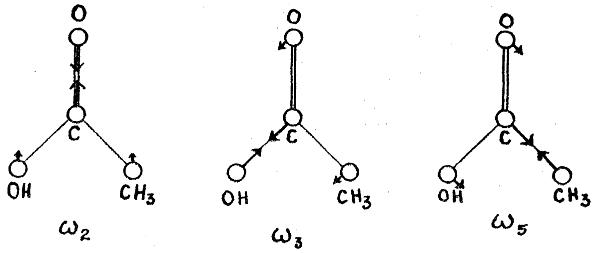


Fig. 3.—Fundamental modes of vibration of the single molecule of acetic acid. (The deformation vibrations have been omitted.)

In formulating the fundamental modes of vibration the hydrogen in the ring is neglected since the electric moment changes associated with its vibration are undoubtedly small as shown by the fact that the formation of hydrogen bonds blots out the characteristic O–H absorption. Again making the assumption that interaction between bonds is negligible we are able to separate the two vibrations of the methyl groups against the ring from vibrations of atoms in the ring itself.

The usual requirement that vibrations be symmetric or antisymmetric with respect to the symmetry elements present leads to the formulation for the double molecule shown in Fig. 4, where the primes are used to distinguish the vibrations of the dimer from those of the monomer. It may be seen that the frequencies in the first column are

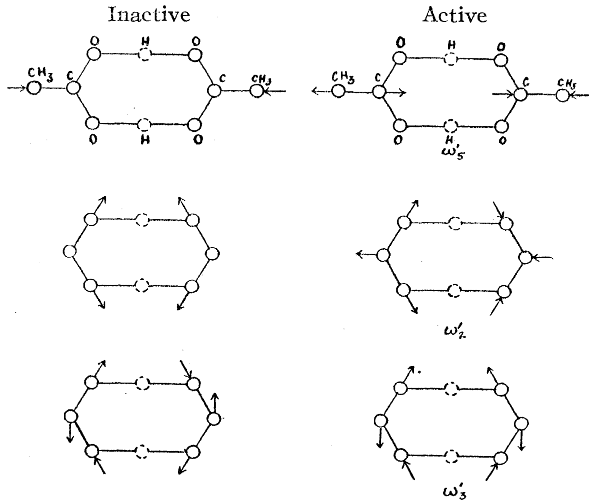


Fig. 4.—The fundamental valence vibrations of dimeric acetic acid.

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(13) Latimer and Rodebush, This Journal, **42**, 1419 (1920).

(14) Pauling and Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

inactive since they produce no change in the electric moment of the molecule.

It will now be shown that the active frequency ω_5' of the dimer should be the same as ω_5 of the single molecule. Denote by M the mass of the ring exclusive of the methyl groups and by m the mass of a methyl group. Then the reduced mass for the vibration ω_5' is

$$\mu = \frac{2m_1M}{2m + M} = \frac{2m}{1 + (2m/M)}$$

while that for ω_5 is

$$\mu_5 = \frac{m(M/2)}{m + (M/2)} = \frac{m}{1 + (2m/M)}$$

But since there are two methyl groups involved in the vibration ω_5' the force constant f_5' will be twice as large as f_5. Thus the frequency of vibration calculated from the relation $\nu = {}^1/_{2\pi} \sqrt{f/\mu}$ will be the same in both cases. This indicates that it is justifiable to assign the frequency at 1190 cm.$^{-1}$ to this vibration. The greater intensity of absorption in the single molecule may be correlated with the splitting of the band upon association into an active and an inactive vibration.

The frequencies ν_1 and ν_4 associated with carbon to hydrogen vibrations should not, of course, be affected by the increase in temperature. This is, in fact, found to be the case, although the band ν_4 is slightly displaced at 172°, probably because of overlapping with ν_5 which becomes much more intense.

The remaining two frequencies ν_2 and ν_3 are more difficult to attribute to the definite modes of vibration of the associated molecule. Qualitatively they should be closer together in this case than in the single molecules since their separation is merely the result of similar modes of vibration of the ring which cannot have greatly different force constants. Since it appears plausible that a greater electric moment change is to be associated with the active vibration ω_2' than with ω_3' (Fig. 4) it may be tentatively assigned to the more intense band at 1740 cm.$^{-1}$ (ν_2).

The Raman spectrum of acetic acid has been examined most accurately by Kohlrausch, Köppl and Pongratz.[15] The Raman lines occurring in this region are 1275, 1363, 1429, 1663 ± 7.5 cm.$^{-1}$. These are to be compared with the maxima of the infra-red absorption bands recorded here at room temperature: 1205, 1296, 1435, 1740 cm.$^{-1}$.

The findings of this investigation suggest that in the single molecule it is safe, at least as a good approximation, to assign a definite band in the spectrum to a definite bond in the molecule. In the double molecule, on the other hand, because of the highly symmetrical structure this approximation fails completely. A similar case is discussed by Cross and Van Vleck,[16] who show that because of mass symmetry in ethyl alcohol it is no longer possible to apply the approximation which was found to hold well for the ethyl halides.

In all the above reasoning it has been assumed that the association of acetic acid, and undoubtedly of carboxylic acids in general, takes place through the formation of hydrogen bonds. The fact that it has been possible to interpret the spectra on this assumption yields additional evidence that this is the actual mechanism of association. The fundamental nature of this hydrogen bond is discussed by Gillette and A. Sherman.[17]

Summary

1. The infra-red absorption spectrum of acetic acid has been obtained at 25 and at 172°—corresponding to the single and the associated molecule. At intermediate temperatures both spectra appear.

2. Three of the fundamental frequencies are the same in both molecules and two are shifted. These two must be intimately connected with the association process.

3. Modes of vibration of the two molecules are suggested, corresponding to the fundamental frequencies.

4. The results of this investigation suggest that the association of carboxylic acids to give dimers occurs through the formation of hydrogen bonds leading to ring structure which gives rise to different absorption frequencies.

Madison, Wisconsin Received April 14, 1936

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[15] Kohlrausch, Köppl and Pongratz, *Z. physik. Chem.*, **B21**, 242 (1933).

[16] Cross and Van Vleck, *J. Chem. Phys.*, **1**, 350 (1933).

[17] Gillette and A. Sherman, This Journal, **58**, 1135 (1936).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Effect of Substitution on the Infra-red Absorption Spectrum of Acetic Acid

BY R. H. GILLETTE

In an earlier publication[1] from this Laboratory it was shown that the substitution of hydrogen atoms by chlorine in acetic acid giving progressively stronger acids is reflected also in a corresponding shift of the infra-red absorption band at 1721 cm.$^{-1}$. A more recent interpretation[2] of the infra-red absorption spectrum of the single and double molecules of acetic acid made it seem useful to investigate this substitution more thoroughly.

Experimental

The apparatus and method were the same as used in the investigation reported in the preceding paper.[2] The absorption cells were made by cementing rock salt windows onto both sides of holes drilled in plate glass about 4 mm. thick. They were filled through narrow grooves sawed in the window and sealed with partially dried Glyptal cement. One cell was filled with the pure solvent and the others with solutions of the acids being investigated.

The absorption spectra of acetic acid and eight substituted acids are shown in Fig. 1 and Table I. In all cases the acids were dissolved in carbon tetrachloride to give 0.025 *M* solutions and the measurements were taken at 25°. It had been found previously that the change in the position of absorption bands with concentration was very small. In the last column of Table I are recorded the dissociation constants of the acids at 25° when dissolved in water.

TABLE I

SHIFTS IN THE ABSORPTION BANDS OF THE SUBSTITUTED ACETIC ACIDS IN 0.025 MOLAR SOLUTIONS OF CARBON TETRACHLORIDE

No. in Fig. 1	Acid	ν_1, cm.$^{-1}$	ν_2, cm.$^{-1}$	ν_3, cm.$^{-1}$	Dissociation constant
4	Acetic	2941	1721	1435	1.86×10^{-5}
9	Monochloroacetic	2950	1736	1433	155×10^{-5}
8	Dichloroacetic	3049	1751	1428	5000×10^{-5}
7	Trichloroacetic	3030	1764	1416	$30{,}000 \times 10^{-5}$
6	Monobromoacetic	2976	1730	1447	138×10^{-5}
5	Monoiodoacetic	2992	1721	1441	74×10^{-5}
3	Dimethylacetic	2907	1715	1433	1.4×10^{-5}
2	Trimethylacetic	2907	1704	1433	0.98×10^{-5}
1	Diethylacetic	2910	1706	1433	1.89×10^{-5}

Discussion

Before it is possible to make any interpretation of these results it is necessary to investigate the degree of association of the acids under the conditions of measurement. A search of cryoscopic measurements in the older literature[3] suggested that down to small concentrations (about 0.01 *M*) all carboxylic acids are nearly completely associated in non-polar solvents. This is confirmed by the recent accurate measurements of Bury and

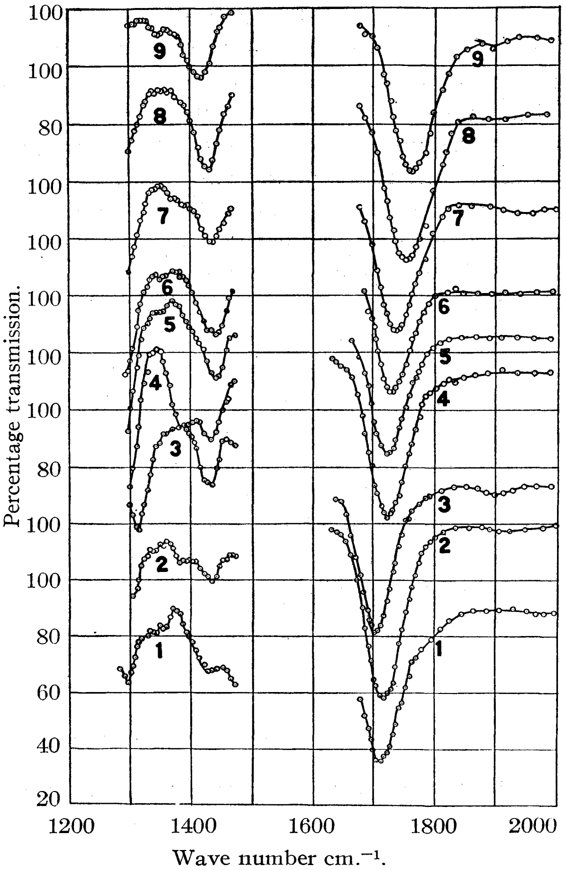

Fig. 1.—Displacements in the infra-red absorption spectrum produced by substituting various groups for hydrogen in acetic acid: 1, diethylacetic acid; 2, trimethylacetic acid; 3, isobutyric acid (dimethyl); 4, acetic acid; 5, iodoacetic acid; 6, bromoacetic acid; 7, chloroacetic acid; 8, dichloroacetic acid; 9, trichloroacetic acid.

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(1) Bennett and Daniels, THIS JOURNAL, **49**, 50 (1927).

(2) Gillette and Daniels, *ibid.*, **58**, 1139 (1936).

(3) Auwers, *Z. physik. Chem.*, **12**, 689 (1893); Raoult, *Ann. chim.*, [4] **2**, **66** (1884); Rozsa, *Z. Elektrochem.*, **109**, 685 (1911); Peddle and Turner, *J. Chem. Soc.*, **109**, 685 (1911).

Jenkins[4] and Bell and Arnold.[5] The latter authors have shown in benzene solutions of concentrations from $M = 0.01$ to $M = 1.5$ trichloroacetic acid is completely associated. We assume, therefore, that under the conditions of our measurements all the acids were entirely present as dimers.

The three infra-red absorption bands which can be investigated in this solvent correspond to the frequencies ν_1, ν_2 and ν_3 of the previous paper. The first of these (ν_1) (which has been omitted in Fig. 1 to conserve space) is mainly due to the C–H valence vibration, but is also in part made up of overtone and combination vibrations from other parts of the molecule. Thus it occurs even in trichloroacetic acid, but considerably displaced and much weaker. The remaining two bands are to be attributed to vibrations within the ring formed by the union of the two single molecules. Attempts to measure some of these bands in the single molecules at high temperatures were unsuccessful on account of decomposition.

It may be seen by reference to Table I that the band ν_2 is shifted toward higher frequencies by groups recognized by the organic chemist as electronegative, while it is shifted to lower frequencies by groups electropositive in the same sense. The uniform shift in the chloroacetic acids discovered by Bennett and Daniels is confirmed. The effect of the weight of the groups may be seen by considering the monohalogen acids. Here the shift in the band decreases as the weight of the halogen increases until in iodoacetic acid it occurs in the same position as acetic. This suggests that there may be two opposing factors operative, one a weight factor and the other perhaps connected with the electron affinity or polarizability of the substituted group. It is noticeable that there is a correlation between the strength of the acid in aqueous solution and the position of this band. This is perhaps to be associated with changes in the contribution of ionic states to the energy of the molecule.

The remaining band, ν_3, is shifted in each case in the opposite direction, but the displacement is smaller. This behavior was observed also in the investigation on the effect of association.[2] It does not seem possible in the light of our present knowledge to give an exact interpretation of these band shifts although they seem too uniform to be fortuitous.

The author is grateful to Dr. Farrington Daniels for helpful suggestions and for continued interest in this problem.

Summary

1. The infra-red absorption spectra of acetic acid and eight substituted acetic acids have been measured in carbon tetrachloride solution. Certain uniform shifts in the absorption bands have been observed and correlated with other measurements.

MADISON, WISCONSIN RECEIVED MAY 5, 1936

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[4] Bury and Jenkins, *J. Chem. Soc.*, 688 (1934).

[5] Bell and Arnold, *ibid.*, 1432 (1935).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Entropy of Water and the Third Law of Thermodynamics. The Heat Capacity of Ice from 15 to 273°K.

BY W. F. GIAUQUE AND J. W. STOUT

It has long been known to those interested in the accurate application of the third law of thermodynamics that measured entropy changes in reactions involving water did not agree with those calculated from low temperature heat capacity data. In early comparisons the inaccuracy of the available data seemed sufficient to explain the disagreement, but even after more accurate experiments were performed discrepancies still remained. The investigations of Wiebe, Johnston, Overstreet, and one of us[1] on the entropies of hydrogen chloride, hydrogen, oxygen and chlorine, combined with very accurate determinations of the heats of reactions

$$H_2 + {}^1/_2O_2 = H_2O$$
$$\text{and } 2HCl + {}^1/_2O_2 = H_2O + Cl_2$$

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[1] (a) Giauque and Wiebe, (HCl), THIS JOURNAL, **50**, 101 (1928); (b) Giauque and Johnston, (H_2), *ibid.*, **50**, 3221 (1928); (c) Giauque and Johnston, (O_2), *ibid.*, **51**, 2300 (1929); (d) Giauque, (H_2), *ibid.*, **52**, 4816 (1930); (e) Giauque and Overstreet, (HCl, Cl_2), *ibid.*, **54**, 1731 (1932).

made by Rossini[2] and various equilibrium data, including those relating to the reactions[3]

$$HgO + H_2 = Hg + H_2O$$
$$Hg + {}^1/_2O_2 = HgO$$

indicated that the $\int_0^T C_p d \ln T$ for water did not give the correct entropy. That this was so became a certainty when Giauque and Ashley[4] calculated the entropy of gaseous water from its band spectrum and showed that an entropy discrepancy of about one calorie per degree per mole existed. They presumed this to be due to false equilibrium in ice at low temperatures.

Water is a substance of such importance that we considered further experimental investigation to be desirable not only to check the above discrepancy but especially to see whether slow cooling or other conditions favorable to the attainment of equilibrium could alter the experimental result.

Apparatus.—In order to prevent strains in the resistance thermometer when the water was frozen a double-walled calorimeter, Fig. 1, was constructed. The outside wall was of copper, 0.5 mm. thick, 4.4 cm. o. d., and 9 cm. long. The inside copper wall, 0.5 mm. thick, was tapered, being 3.8 cm. o. d. at the bottom and 4.0 cm. o. d. at the upper end. The top of the inner container was made from a thin copper sheet, 0.2 mm. thick, which prevented the transmission of strains to the resistance thermometer. The neck for filling the calorimeter was in the center of this sheet. A series of thin circular slotted vanes of copper were soldered to the inner container, and the assembly forced inside the outer tube. A heavy copper plate, 1 mm. thick inside the inner wall, and 2 mm. thick between the walls, served as the bottom of both tubes. The thermocouple was soldered into tube D by means of Rose's metal.

A resistance thermometer-heater of No. 40 double silk covered gold wire containing about 0.1% silver was wound on the outside of the calorimeter. The resistance was 310 ohms at 290°K. and dropped to about 17 ohms at 15°K. The resistance thermometer was calibrated during the measurements by means of copper–constantan thermocouple No. 16 which had been compared with a hydrogen gas thermometer.[5] However one of the five parallel constantan wires in the thermocouple had accidentally been broken since the original calibration. This wire was discarded and after the completion of the measurements the thermocouple was compared with the oxygen and hydrogen vapor pressure thermometers.[5b] The thermocouple was also checked against the melting point, 54.39°K. and higher transition point, 43.76°K., of oxygen.[1c] On the basis of these comparisons a small correction to the original calibration was readily made.

Helium gas was introduced into the space between the two walls by means of a German silver tube, A. A similar German silver tube was soldered by means of Wood's metal into the cap, B. The sample, C, was transferred through this tube into the calorimeter, and helium gas at one atmosphere pressure admitted. The German silver tube was then heated and removed from the cap, leaving the hole sealed with Wood's metal. After the measurements on the full calorimeter had been completed, the calorimeter was heated to the melting point of the Wood's metal (72°C.) and the water completely pumped out without dismantling the apparatus. The heat capacity of the empty calorimeter was then measured.

The remainder of the heat capacity apparatus, the method of making the measurements and calculations, and accuracy considerations were similar to those previously described.[1a,c]

Purification of Water.—Distilled water from the laboratory still was transferred into the vacuum-tight purification apparatus constructed from Pyrex glass. The apparatus was evacuated to remove dissolved gases, and flushed out several times with helium gas. The water was distilled into a receiving bulb, the first fraction being discarded. The calorimeter had previously been attached to the purification system and evacuated. When sufficient water had collected in the receiving bulb, it was transferred into the calorimeter. Helium gas at one atmosphere pressure was admitted to the calorimeter which was then sealed off as described above.

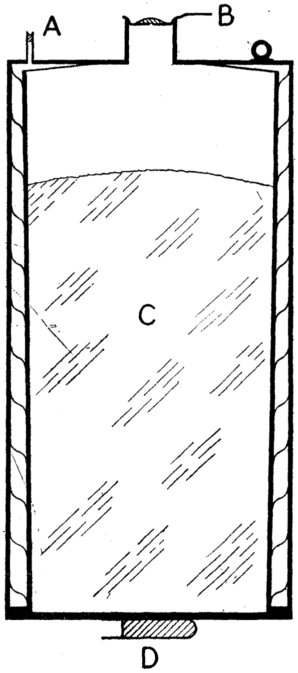

Fig. 1.—Calorimeter.

A series of short heat capacity measurements were made in the temperature region immediately below the melting point in order to determine the pre-melting effect due to liquid-soluble solid-insoluble impurity. From these measurements it was calculated that the mole fraction of impurity was three parts in a million.

The Heat Capacity of Ice.—The results of the heat capacity measurements are given in Table I. The data are shown in Fig. 2.

In the calculations one 15° calorie was taken as equal to 4.1832 international joules. The calorimeter contained 72.348 g. of ice.

In order to allow time for the establishment of an equilibrium state in the solid, the ice was cooled

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[2] (a) (H_2O), *Bur. Standards J. Research*, **6**, 1 (1931); (b) (HCl), *ibid.*, **9**, 583 (1932).

[3] See summary by Eastman, Circular 6125, U. S. Dept. of Comm., Bur. of Mines (1929).

[4] Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

[5] (a) Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927); (b) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

very slowly. The following are temperatures reached at various times after the ice was frozen: 0 hours, 273.1°; 12 hours, 246°; 37 hours, 203°; 60 hours, 180°; 84 hours, 168°; 92 hours, 156°; 108 hours, 105°; 120 hours, 91°; 156 hours, 90°. The sample was then cooled from 90 to 68° in about three hours and the heat capacity measurements of series I taken. Next the calorimeter was cooled to the temperatures of liquid hydrogen at the following rate: 0 hours, 85°; 1.5 hours, 72°; 2 hours, 60°; 2.5 hours, 56°; 7 hours, 39°; (liquid hydrogen evaporated) 17.5 hours, 49°; 22 hours, 50° (more liquid hydrogen added); 23 hours, 41°; 27 hours, 13°. The measurements of series II were then made.

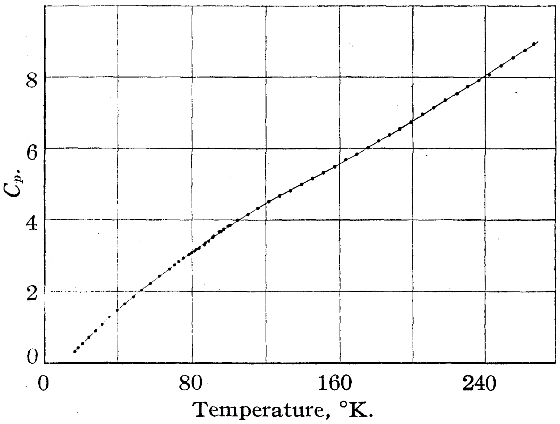

Fig. 2.—Heat capacity in calories per degree per mole of ice.

During this series of measurements which extended from 15°K. to the melting point, and covered a period of eighty hours, the calorimeter was under constant observation. To make certain that no unusual thermal situation was present in the solid near the melting point, the heat of fusion was determined at the end of the above series of measurements. The value obtained, 1436 cal./mole, agrees well with that which has been chosen for the entropy calculation.

Table I

Heat Capacity of Ice

(Molecular weight, 18.0156) 0°C. = 273.10°K.

T, °K.	ΔT	C_p cal./deg./mole	Series
16.43	1.403	0.303	II
18.37	1.729	.410	II
20.78	2.964	.528	II
24.20	3.815	.700	II
28.05	3.596	.883	II
31.64	3.578	1.065	II
35.46	4.073	1.251	II
39.62	4.242	1.449	II
43.96	4.469	1.641	II
48.52	4.571	1.837	II
52.98	4.361	2.014	II
57.66	5.041	2.203	II
62.63	5.228	2.418	II
67.83	4.910	2.612	II
70.61	5.403	2.723	I
73.01	5.737	2.821	II
75.60	4.638	2.922	I
78.51	4.991	3.016	II
79.98	4.133	3.070	I
81.44	5.538	3.115	III
82.42	4.860	3.163	IV
83.72	5.438	3.191	II
83.94	3.765	3.199	I
86.66	4.893	3.286	III
87.25	4.756	3.336	IV
89.20	5.557	3.389	II
91.32	4.394	3.488	III
91.93	4.651	3.532	IV
94.93	5.233	3.649	II
95.85	4.649	3.660	III
97.37	6.234	3.724	IV
99.57	4.778	3.814	II
100.69	4.980	3.832	III
104.69	5.497	3.985	II
110.13	5.373	4.136	II
115.84	6.031	4.315	II
121.74	5.908	4.489	II
127.54	5.813	4.655	II
133.50	6.005	4.808	II
139.48	5.952	4.978	II
145.43	5.928	5.135	II
151.43	6.240	5.306	II
157.48	5.837	5.466	II
163.52	5.851	5.663	II
169.42	5.908	5.842	II
175.36	5.996	6.007	II
181.25	5.678	6.185	II
187.20	5.983	6.359	II
192.96	5.658	6.530	II
199.11	6.133	6.710	II
205.32	6.309	6.935	II
211.56	6.554	7.119	II
217.97	6.200	7.326	II
224.36	5.935	7.519	II
230.08	6.068	7.711	II
236.19	6.101	7.887	II
242.40	6.795	8.048	II
249.31	6.903	8.295	II
256.17	6.591	8.526	II
262.81	6.303	8.732	II
267.77	4.465	8.909	II

In the heat capacity measurements between 85 and 100°K., the attainment of temperature equilibrium in the solid was much less rapid than at other temperatures. This observation is of considerable interest and some of its implications will be discussed below.

To study possible effects due to rapid cooling the sample was cooled from 273.1 to 90° in four hours. The heat capacities in series III were then measured. Slow equilibrium was again encountered, and the heat capacities were not significantly different from those previously obtained.

To determine whether the ice was being transformed from an unstable to an equilibrium condition at an appreciable rate, measurements extending over several hours each were made of the rate of temperature drift at 60, 72, 78 and 85°K. After correcting for the known heat interchange with the surroundings, the rate of evolution of heat due to internal changes was zero within the limits of experimental error. An amount of 0.0008 calorie per mole per minute could have been detected.

The calorimeter was allowed to stand for four days at temperatures between 60 and 80° before taking the measurements in series IV. Again the measurements were not significantly different from those previously obtained.

In Table II are listed the values of the heat capacity at even temperatures as read off a smooth curve through the observations. These values are compared with those of previous investigators. A review of the measurements prior to 1913 has been given by Dickinson and Osborne.[6] Of these the measurements of Nernst and co-workers are most important. The values used for comparison in Table II are calculated from an equation proposed by Nernst, Koref and Lindemann[7] as representing these data. Pollitzer[8] made measurements between 20 and 90°K. His measurements were plotted and a smooth curve drawn through them to give the values compared in Table II. The very accurate work of Dickinson and Osborne[6] between 0 and −40°C. has been calculated from an equation proposed by these authors. Maass and Waldbauer[9] and Barnes and Maass[10] have measured the total change in heat content from various low temperatures to 25°C., and from the results have proposed equations for the specific heat of ice. Simon[11] lists values for the heat capacity of ice from 10°K. to the melting point.

Professor Simon[12] informs us that, of the values listed in the "Handbuch der Physik," only the one at 10°K. is based on the results of his own measurements. The heat capacities at higher temperatures were calculated from the work of earlier observers. The experimental results of Simon[12] are in excellent agreement with the continuation of the curve drawn through our measurements. We have included in Table II a value for the heat capacity of ice at 10°K. picked from a smooth curve through Simon's data.

TABLE II

HEAT CAPACITY OF ICE

(Molecular Weight, 18.0156) 0°C. = 273.10°K.

Values taken from smooth curve through observations

	C_p, cal./deg./mole	Deviations previous results—This research, %				
T,°K.		Nernst 1910	Pollitzer 1913	D. and O. 1915	M. and W. 1925	B. and M. 1930
10[13]	0.066					
20	.490		−13.3			
30	.984		− 0.8			
40	1.466		+13.1			
50	1.896		+ 4.1			
60	2.304		+ 2.8			
70	2.701	+ 8.5				
80	3.075	+ 4.4	+ 6.6			
90	3.448	+ 1.3	− 0.4		−29.6	
100	3.796	− 0.6			−22.4	
110	4.130	− 1.9			−16.8	
120	4.434	− 2.3			−11.8	
130	4.728	− 2.4			− 7.6	
140	4.993	− 1.8			− 3.8	
150	5.265	− 1.5			− 0.8	
160	5.550	− 1.4			+ 1.3	
170	5.845	− 1.5			+ 2.5	
180	6.142	− 1.5			+ 3.4	
190	6.438	− 1.5			+ 3.9	
200	6.744	− 1.5			+ 3.9	−2.1
210	7.073	− 1.7			+ 3.3	−0.9
220	7.391	− 1.7			+ 2.6	− .1
230	7.701	− 1.3		−0.5	+ 1.9	+ .3
240	8.013	− 0.4		− .2	+ 0.9	+ .2
250	8.326	+ 1.3		+ .1	− 0.3	− .4
260	8.642	+ 6.1		+ .3	− 1.6	−1.3
270	8.960	+43.8		+ .5	− 3.2	−2.6

The Entropy of Water.—Values of the heat of fusion, heat capacity of the liquid and heat of

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(6) Dickinson and Osborne, *Bull. U. S. Bur. Standards*, **12**, 49 (1915).

(7) Nernst, Koref and Lindemann, *Sitzber. Berlin Akad. Wiss.*, 247 (1910).

(8) Pollitzer, *Z. Elektrochem.*, **19**, 513 (1913).

(9) Maass and Waldbauer, THIS JOURNAL, **47**, 1 (1925).

(10) Barnes and Maass, *Can. J. Research*, **3**, 205 (1930).

(11) Simon, "Handbuch der Physik," Vol. X, 1926, p. 363.

(12) Simon, personal communication. Measurements of the heat capacity of ice between 9 and 13°K. were made in 1923 by Simon, but the results have not as yet been published. Since these values are of considerable interest in connection with the present investigation, we are, with Professor Simon's kind permission, presenting them here.

HEAT CAPACITY OF ICE BETWEEN 9 AND 13°K. MEASUREMENTS OF F. SIMON

T, °K.	9.47	9.88[a]	10.46	11.35	11.55[a]	12.10	12.85
C_p cal./deg./mole	0.056	0.063	0.075	0.096	0.102	0.118	0.141

[a] Obtained in an independent second experiment.

(13) Calculated from data of Simon, see Ref. 12.

vaporization of water are so accurately known that further investigation was unnecessary.

The heat of fusion of ice has been accurately determined by a number of workers. The measurements prior to 1913 have been critically summarized by Dickinson, Harper and Osborne,[14] who also made a number of measurements of the heat of fusion both by an electrical method and by the method of mixtures. Dickinson and Osborne[6] measured the heat of fusion in an aneroid calorimeter, using electrical heating. The measurements in which energy was introduced electrically were recalculated by us on the basis of 1 int. joule = 4.1832 calories (15°). A weighted average of all the reported values yields 1435.7 cal./mole with an estimated accuracy of ±0.9 cal./mole, for the heat of fusion.

Fiock[15] has reviewed the measurements of the heat of vaporization of water and compared them with the results of determinations at the Bureau of Standards[16] extending down to 50°. All measurements were converted into international joules. Of the data considered by Fiock, those of Griffiths, of Smith and of Henning contained measurements in the neighborhood of 25°C. Giving equal weight to the result of each of the above three observers and to the value extrapolated from the Bureau of Standards measurements, and taking 1 calorie (15°) = 4.1832 int. joules, we obtained an average value of 10,499 ± 3 (av. dev.) calories/mole for the heat of vaporization of water at 25°.

The "I.C.T." values for the heat capacity of liquid water[17] were plotted against the logarithm of the absolute temperature and integrated graphically to obtain the entropy between 0 and 25°. The value for the vapor pressure at 25° was also obtained from the "I.C.T."[18] Using Berthelot's equation of state and thermodynamics it can be shown that the entropy correction[1a] to the ideal gas state is almost negligible in this case The critical constants[19] used were $T_c = 647.1$°K. and $P_c = 217.7$ atm.

The entropy between 10 and 273.10°K. was obtained by graphical integration of the measured heat capacities. The entropy between 0 and 10°K. was calculated by means of the Debye equation, using $h\nu/k = 192$. A summary of the entropy calculation is given in Table III.

TABLE III

CALCULATION OF ENTROPY OF WATER

0–10°K., Debye function $h\nu/k = 192$	0.022
10–273.10°K., graphical	9.081
Fusion 1435.7/273.10	5.257
273.10–298.10°K., graphical	1.580
Vaporization 10499/298.10	35.220
Correction for gas imperfection	0.002
Compression $R \ln 2.3756/760$	−6.886
Cal./deg./mole	44.28±0.05

The value of the entropy given in Table III may be compared with that calculated from spectroscopic data. Giauque and Ashley[4] utilized the preliminary molecular constants of water as given by Mecke and Baumann[20] to determine the entropy of water. Later Gordon[21] recalculated the thermodynamic quantities for water using the revised moments of inertia of Freudenberg and Mecke.[22] He obtained $S°_{298\cdot1} = 45.10$ cal./deg./mole. The difference between the spectroscopic and calorimetric values is 0.82 cal./deg./mole.

The Problem of the False Equilibrium in Ice.—To account for the discrepancy between the calorimetric and spectroscopic values for the entropy of water Giauque and Ashley[4] offered an explanation based on the assumption that the ortho and para molecular states, which are known to exist in gaseous water, had persisted in the crystalline state at low temperatures. The situation was assumed to be similar to that which accounts for the entropy discrepancy in the case of solid hydrogen.[1b,d] The ortho water was assumed to have non-polar clockwise and counter clockwise rotations in ice, since the dielectric constant of ice at low temperatures corresponds to that of non-polar substances. This leads to a calculated discrepancy of $^3/_4 R \ln 2 = 1.03$ cal./deg./mole.

We have had many interesting private discussions with Professor Linus Pauling who has consistently objected to the ortho-para explanation. During the course of the present investigation Pauling[23] offered an alternative explanation based

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(14) Dickinson, Harper and Osborne, *Bull. U. S. Bur. Standards*, **10**, 235 (1914).

(15) Fiock, *Bur. Standards J. Research*, **5**, 481 (1930).

(16) (a) Osborne, Stimson and Fiock, *ibid.*, **5**, 411 (1930); (b) Fiock and Ginnings, *ibid.*, **8**, 321 (1932).

(17) "International Critical Tables," McGraw-Hill Book Co., New York, Vol. V, 1926, p. 113.

(18) "I. C. T.," Vol. III, p. 211.

(19) "I. C. T.," Vol. III, p. 248.

(20) Mecke and Baumann, (a) *Naturwiss.*, **20**, 657 (1932); (b) *Phys. Z.*, **33**, 833 (1932).

(21) Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

(22) Freudenberg and Mecke, *Z. Physik*, **81**, 465 (1933).

(23) Pauling, (a) personal communication; (b) THIS JOURNAL, **57**, 2680 (1935).

on the random orientation of hydrogen bonds in ice. Crystal structure investigations have shown that each oxygen atom is surrounded by four equivalent oxygen atoms. Although the positions of the hydrogen atoms have not been determined experimentally it seems reasonable to assume that they are located on lines joining adjacent oxygens. Since the oxygen–oxygen distance is considerably greater than twice the separation which is characteristic of an oxygen–hydrogen linkage, it has been assumed by Bernal and Fowler[24] that each oxygen is joined to two close and two distant hydrogen atoms. At higher temperatures the bond directions of the close or distant hydrogen atoms of a given oxygen are a matter of chance. We quote from the paper of Bernal and Fowler. "Therefore it is quite conceivable and even likely that at temperatures just below the melting point the molecular arrangement is still partially or even largely irregular, though preserving at every point tetrahedral coördination and balanced dipoles. In that case ice would be crystalline only in the position of its molecules but glass-like in their orientation. Such a hypothesis may be still necessary to explain the dielectric constant and the absence of pyroelectricity."

Pauling assumes further that when ice is cooled to low temperatures, it fails to attain the ordered arrangement which would correspond to zero entropy. He shows that the discrepancy corresponding to the above lack of order would be $R \ln 6/4 = 0.806$ cal./deg./mole. This is in very close agreement with the experimentally determined discrepancy of 0.82 ± 0.05 cal./deg./mole.

However, it should be pointed out that in two previous cases, carbon monoxide[25] and NNO[26] where random molecular orientations led to entropy discrepancies, the experimental discrepancy was a few tenths of a unit lower than the calculated value due to partial attainment of an ordered state. If this were the case in ice, the ortho-para explanation might be correct. However, we consider that the explanation advanced by Pauling is the more plausible as well as being in better agreement with the experimental results.

It is of interest to note that MacDougall and Giauque[27] investigated ice from 0.2 to 4°K. and found no appreciable heat capacity in this region.

One of the purposes of the present work was to investigate the possibility of more complete attainment of equilibrium. We have mentioned above that various experiments, in which ice was cooled slowly or rapidly to low temperatures, or was allowed to stand for long periods of time at low temperatures, resulted in heat capacities which were not appreciably different in the various series of measurements. At temperatures between 85 and 100°K. the attainment of thermal equilibrium in the solid was very much less rapid than at other temperatures. For this reason the heat capacity measurements in this region are somewhat less accurate than the others. This slow equilibrium presumably is due to the initial stages of excitation of some new degrees of freedom. From the value of the heat capacity this evidently is connected with motion of the hydrogen atoms. At temperatures below the region of slow equilibrium the dielectric constant[28] is of the order of magnitude characteristic of a nonpolar substance. At higher temperatures the dielectric constant rises rapidly and the orientation time of the dipole decreases. From this it would appear that the new degrees of freedom referred to above are associated with the dipole orientation mechanism.

From the temperature drift experiments at 60, 72, 78 and 85°K. it appears that no great change in the heat content would be expected if ice were kept at these temperatures for a considerable period of time.

We may mention in passing that low temperature heat capacity measurements on some of the high pressure forms of ice would undoubtedly lead to correct values for the entropy of water.

It is perhaps worth noting that while the theory of random bond orientation would lead to the same discrepancy, $R \ln 3/2 = 0.806$ cal./deg./mole in both hydrogen and deuterium oxides, the theory of molecular rotation in ortho states of water would lead to different values for the calculated discrepancy. For hydrogen oxide the value is $3/4\, R \ln 2 = 1.033$, for deuterium oxide, $1/3\, R \ln 2 = 0.459$ cal./deg./mole. Although we believe the latter theory to be less plausible it will be of interest to make the comparison when measurements on deuterium oxide become available.

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(24) Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

(25) Clayton and Giauque, THIS JOURNAL, **54**, 2610 (1932).

(26) (a) Clusius, *Z. Elektrochem.*, **40**, 99 (1934); (b) Blue and Giauque, THIS JOURNAL, **57**, 991 (1935).

(27) MacDougall and Giauque, *ibid.*, **58**, 1032 (1936).

(28) "I. C. T.," Vol. VI, page 78.

We wish to thank Mr. C. C. Stephenson for assisting with the experimental work.

Summary

The heat capacity of ice has been measured between 15 and 273°K.

It has previously been shown by Giauque and Ashley that a discrepancy exists between the spectroscopic value of the entropy and the $\int_0^T C_p\, d \ln T$ for water.

The purpose of the present investigation was to make an accurate determination of the discrepancy.

With the assistance of the well-known values for the heats of fusion and vaporization of water we find that the $\int_0^T C_p\, d \ln T = 44.28 \pm 0.05$ cal./deg./mole for H_2O (g.) at one atmosphere and 298.1°K. The spectroscopic value is 45.10 leading to a discrepancy of 0.82 cal./deg./mole. This is in excellent agreement with the theoretical discrepancy 0.806 calculated by Pauling on the assumption of random orientation of hydrogen bond directions in ice.

Experiments have been described in which ice was cooled slowly or rapidly to low temperatures or was allowed to stand for long periods of time at low temperatures. No difference in the thermal properties of ice was observed in these experiments.

BERKELEY, CALIF. RECEIVED MARCH 30, 1936

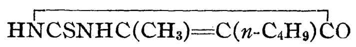
[CONTRIBUTION FROM THE NATIONAL RESEARCH INSTITUTE OF CHEMISTRY, ACADEMIA SINICA]

Pyrimidine Research. Synthesis of 4-Methyl-5-*n*-butylcytosine

BY YUOH-FONG CHI

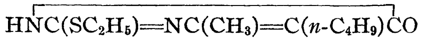
In this paper is described a method of synthesizing 4-methyl-5-*n*-butylcytosine (VII), which is prepared as its hydrobromide from 2-ethylmercapto-4-methyl-5-*n*-butylcytosine (VI) by hydrolysis with concentrated hydrobromic acid. The free base (VII) is liberated from its hydrobromide by neutralizing with ammonia. For the preparation of 2-ethylmercapto-4-methyl-5-*n*-butylcytosine (VI), the starting point is the corresponding 6-oxypyrimidine, 2-ethylmercapto-4-methyl-5-*n*-butyl-6-oxypyrimidine (II). This is treated with phosphorus oxychloride to form the corresponding 6-chloropyrimidine (V), and the latter then heated with alcoholic ammonia at 170–180° to give the desired 2-mercapto-6-amino derivative (VI).

2 - Ethylmercapto - 4 - methyl - 5 - *n* - butyl-6-oxypyrimidine was prepared according to the general method of Wheeler and Liddle.[1] Ethyl *n*-butylacetoacetate is first condensed with thiourea in the presence of sodium ethylate to give 2-thio-4-methyl-5-*n*-butyl-6-oxypyrimidine (I), which is then treated in the presence of sodium ethylate with ethyl bromide to give 2-ethylmercaptopyrimidine (II). Alkylation of the latter with methyl iodide gives the corresponding 2-methylmercapto compound (III), and with ethyl chloroacetate to give ethyl 4-methyl-5-*n*-butyl-6-oxypyrimidine-2-thioglycolate (IV).



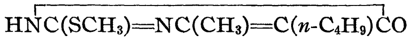
$HNCSNHC(CH_3){=}C(n\text{-}C_4H_9)CO$

I



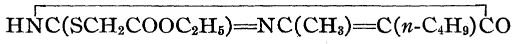
$HNC(SC_2H_5){=}NC(CH_3){=}C(n\text{-}C_4H_9)CO$

II



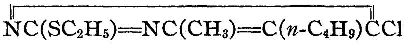
$HNC(SCH_3){=}NC(CH_3){=}C(n\text{-}C_4H_9)CO$

III



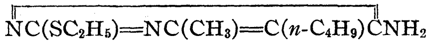
$HNC(SCH_2COOC_2H_5){=}NC(CH_3){=}C(n\text{-}C_4H_9)CO$

IV



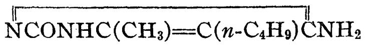
$NC(SC_2H_5){=}NC(CH_3){=}C(n\text{-}C_4H_9)CCl$

V



$NC(SC_2H_5){=}NC(CH_3){=}C(n\text{-}C_4H_9)CNH_2$

VI



$NCONHC(CH_3){=}C(n\text{-}C_4H_9)CNH_2$

VII

Experimental Part

2 - Thio - 4 - methyl - 5 - *n* - butyl - 6 - oxypyrimidine I.—Twenty-six grams of sodium was dissolved in 500 cc. of absolute alcohol and 210 g. of ethyl *n*-butylacetoacetate and 94 g. of thiourea added to the solution. This was then heated on a water-bath for ten hours and the excess of alcohol removed by heating under diminished pressure. The crude sodium salt of the desired pyrimidine was dissolved in water and the solution acidified with acetic acid, when the thiopyrimidine separated. It crystallized from hot water in needles, melting at 197–198°. The yield was 144 g.

Anal. Calcd. for $C_9H_{14}ON_2S$: N, 14.14. Found: N, 14.03, 13.98, 14.00.

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[1] Wheeler and Liddle, *Am. Chem. J.*, **40**, 547 (1908).

2 - Ethylmercapto - 4 - methyl - 5 - *n* - butyl - 6 - oxypyrimidine II.—Eight and one-tenth grams of sodium was dissolved in 200 cc. of absolute alcohol and 70 g. of the above thiopyrimidine and 42.5 g. of ethyl bromide were added to the solution. This was then heated on a water-bath until the solution became neutral. The excess alcohol was then distilled off under diminished pressure, and the mercaptopyrimidine washed with water and recrystallized from dilute alcohol. It separated in long needles, melting at 92–93° to a clear oil.

Anal. Calcd. for $C_{11}H_{18}ON_2S$: N, 12.39. Found: N, 12.8, 12.6, 12.5.

4-Methyl-5-*n*-butyluracil. A.—This is easily prepared by digestion of the above 2-thiopyrimidine with chloroacetic acid in aqueous solution. This pyrimidine separated in the form of needles and was purified by recrystallization from hot water. It melted at 245°.

Anal. Calcd. for $C_9H_{14}O_2N_2$: N, 15.38. Found: N, 15.22, 15.10.

B.—This same pyrimidine is also formed from 2-ethylmercapto-4-methyl-5-*n*-butyl-6-oxypyrimidine by digestion with concentrated hydrobromic acid for several hours. It melted at 245°.

2 - Methylmercapto - 4 - methyl - 5 - *n* - butyl - 6 - oxypyrimidine III.—This is formed by alkylation of the 2-thiopyrimidine with methyl iodide. It was purified by crystallization from alcohol and it separated as needles, melting at 158–159° to a clear oil.

Anal. Calcd. for $C_{10}H_{16}ON_2S$: C, 56.55; H, 7.60; N, 13.20. Found: C, 56.33; H, 7.94; N, 13.0, 13.1.

Ethyl - 4 - methyl - 5 - *n* - butyl - 6 - oxypyrimidine - 2 - thioglycolate IV.—This was prepared by the action of ethyl chloroacetate on the sodium salt of the 2-thiopyrimidine. The ester was purified by crystallization from dilute alcohol, whereupon it separated in needles, melting at 110–111°.

Anal. Calcd. for $C_{13}H_{20}O_3N_2S$: N, 9.86. Found: N, 9.94, 10.00.

4 - Methyl - 5 - *n* - butyluracil - 2 - thioglycolic Acid.—Two grams of the thioglycolate was warmed with aqueous potassium hydroxide on a water-bath for half an hour. After cooling, the solution was acidified with dilute hydrochloric acid, when the thioglycolic acid separated in a crystalline condition. The yield was nearly quantitative. It was purified by recrystallizing from dilute alcohol, and melted at 117–118°.

Anal. Calcd. for $C_{11}H_{16}O_3N_2S$: C, 51.52; H, 6.29; N, 10.94. Found: C, 51.55; H, 6.63; N, 11.3, 11.5.

2 - Ethylmercapto - 4 - methyl - 5 - *n* - butyl - 6 - chloropyrimidine V.—Twenty-two and six-tenths grams of the oxypyrimidine was dissolved in 80 cc. of cold phosphorus oxychloride and the solution heated on an oil-bath at 110–120° for seven hours. The excess of phosphorus oxychloride was then removed under diminished pressure. A sirup was obtained which was treated with cold water to decompose phosphorus compounds and then extracted with ether. The ethereal solution was separated and dried, and the solvent removed, leaving behind the desired pyrimidine as an oil. It was distilled under diminished pressure and boiled at 160° at 2 mm. The yield was 19 g.

Anal. Calcd. for $C_{11}H_{17}N_2ClS$: C, 53.95; H, 7.00. Found: C, 54.11; H, 7.33.

2 - Ethylmercapto - 4 - methyl - 5 - *n* - butyl - 6 - aminopyrimidine. VI.—The corresponding 6-chloropyrimidine was heated with alcoholic ammonia under pressure for three hours at 170–180°. The solution was filtered from the insoluble ammonium chloride, and then evaporated to dryness on a water-bath, yielding the desired compound. The aminopyridine crystallized from a benzene–petroleum ether mixture and melted at 104–105°. The yield was 1.7 g. from 5 g. of the chloropyrimidine.

Anal. Calcd. for $C_{11}H_{19}N_3S$: C, 58.60; H, 8.50. Found: C, 59.06, 59.15; H, 8.87, 8.90.

4-Methyl-5-*n*-butylcytosine Hydrobromide.—The above 2 - ethylmercapto - 4 - methyl - 5 - *n* - butyl - 6 - aminopyrimidine was boiled with concentrated hydrobromic acid (48%) for sixteen hours. On evaporating this solution to dryness, cytosine hydrobromide was obtained and crystallized in prisms from hot water, melting at 222° with decomposition.

Anal. Calcd. for $C_9H_{15}ON_3{\cdot}HBr$: C, 41.21; H, 6.15. Found: C, 41.15; H, 6.06.

4-Methyl-5-*n*-butylcytosine VII.—An aqueous solution of the above cytosine hydrobromide was treated with ammonia. The free base separated and after purification by recrystallizing from very dilute alcohol (about 10%) it separated in prisms, melting at 299–300° with decomposition.

Anal. Calcd. for $C_9H_{15}ON_3{\cdot}{}^3/_4(H_2O)$: C, 55.48; H, 8.55; N, 21.59. Found: C, 55.97, 55.88; H, 8.03, 8.37; N, 21.20, 21.42.

Hydrochloride.—The cytosine was treated with a small quantity of hydrochloric acid, when the cytosine hydrochloride separated in prisms, melting at 235° to a clear oil. It was purified by recrystallizing from hot water.

Anal. Calcd. for $C_9H_{15}ON_3{\cdot}HCl$: C, 49.63; H, 7.41. Found: C, 49.41; H, 7.36.

Summary

1. Ethyl *n*-butylacetoacetate condenses with thiourea in the presence of sodium ethylate to form 2-thio-4-methyl-5-*n*-butyl-6-oxypyrimidine.

2. This 2-thiopyrimidine reacts in presence of sodium ethylate with ethyl bromide and methyl iodide to give 2-ethylmercapto-4-methyl-5-*n*-butyl-6-oxypyrimidine and 2-methylmercapto-4-methyl-5-*n*-butyl-6-oxypyrimidine, respectively.

3. Ethylmercapto - 4 - methyl - 5 - *n* - butyl - 6-oxypyrimidine when treated with phosphorus oxychloride gives the corresponding chloropyrimidine which reacts with ammonia to form 2-ethylmercapto - 4 - methyl - 5 - *n* - butyl - 6 - aminopyrimidine. This pyrimidine is converted by boiling with concentrated hydrobromic acid into 4 - methyl - 5 - *n*-butylcytosine.

SHANGHAI, CHINA RECEIVED FEBRUARY 26, 1936

[CONTRIBUTION FROM THE NATIONAL RESEARCH INSTITUTE OF CHEMISTRY, ACADEMIA SINICA]

Synthesis of 1-Phenyl-2-methyl-4-ethylpyrazol-5-one

BY YUOH-FONG CHI[1] AND MARGARET CHUN-HWA YANG

This short paper describes a method for synthesizing 1-phenyl-2-methyl-4-ethylpyrazol-5-one, a compound similar in constitution to the well-known antipyretic, antipyrine, and which may prove to have similar physiological action. Starting with ethyl formylbutyrate, the sodium salt of which was prepared by Johnson and Menge[2] and Chi and Tien,[3] the writers were able to synthesize this pyrazolone in a good yield by reaction of the aldo-ester with phenylhydrazine to form 1-phenyl-4-ethylpyrazol-5-one, followed by treatment of the latter with methyl iodide in methyl alcoholic solution.

Experimental Part

Ethyl Formylbutyrate.—Twenty-three grams of sodium (1 mole) in wire form was suspended in anhydrous ether, and a mixture of 127.6 g. of ethyl butyrate (1.1 mole) and 81.4 g. of ethyl formate (1.1 mole) dissolved in anhydrous ether were added slowly. For the completion of the reaction, it required about forty hours at ordinary temperature. The mixture was then shaken with ice water, to dissolve the sodium salt of ethyl formylbutyrate. The ethereal solution containing the unreacted esters assumed a red color, and was separated from the aqueous solution containing the sodium salt of the required aldo-ester. This aqueous solution, cooled in ice mixture, was acidified with the calculated amount of acetic acid, whereupon the free aldo-ester separated as a brownish-yellow oil. It was then extracted with ether, washed with sodium carbonate solution, and with water and lastly dried over sodium sulfate. After the solvent had been removed, it was fractionated under vacuum several times. The ester boiled at 37–38° at 2 mm. pressure, and the yield was 16 g.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.29; H, 8.39. Found: C, 57.90, 58.01; H, 8.35, 8.55.

Semicarbazone.—The aldo-ester and semicarbazide interacted normally in alcohol solution at ordinary temperature to give the semicarbazone. This was recrystallized from boiling water and melted at 108–108.5°.

Anal. Calcd. for $C_8H_{15}O_3N_3$: C, 47.73; H, 7.52; N 20.89. Found: C, 47.75; H, 7.63; N, 21.22, 21.08.

4-Ethylisoxazol-5-one.—Five grams of ethyl formylbutyrate was added to an aqueous solution of hydroxylamine prepared by treating 7.4 g. of hydroxylamine hydrochloride dissolved in water with 3.25 g. of aniline. After heating on a water-bath for two hours water was added and the isoxazol extracted with ether and the solution dried with sodium sulfate. The isoxazol boiled at 113–114° at 2 mm. pressure. The yield was 2.1 g.

Anal. Calcd. for $C_5H_7O_2N$: N, 12.39. Found: N, 12.1, 12.11.

1-Phenyl-4-ethylpyrazol-5-one. Method A.—One gram of the aldo-ester was treated with 0.75 g. of phenylhydrazine, and the mixture heated on a water-bath for about two hours. After cooling, the reaction mixture solidified to a crystalline mass of the required pyrazol. This crystallized from 95% alcohol or from benzene–petroleum ether in colorless prisms, melting at 99–99.5°. The yield was 70%.

Anal. Calcd. for $C_{11}H_{12}ON_2$: C, 70.17; H, 6.43; N, 14.90. Found: C, 69.76; H, 6.52; N, 15.3, 15.07.

Method B.—Ethyl formylbutyrate was treated with an aqueous solution of the required amount of phenylhydrazine hydrochloride, and then acidified with a few drops of concentrated hydrochloric acid. The mixture was shaken occasionally, and allowed to stand for about eight to nine days. The ester gradually dissolved and finally a yellowish oil appeared suspended in the solution. This was separated and the filtrate was exactly neutralized with 25% ammonia, when the pyrazolone separated. On account of its amphoteric character an excess of ammonia was avoided. It was recrystallized from benzene–petroleum ether in prisms and melted at 99.5°. The yield was poor.

Anal. Calcd. for $C_{11}H_{12}ON_2$: N, 14.90. Found: N, 14.94, 15.13.

1-*p*-Nitrophenyl-4-ethylpyrazol-5-one.—One gram of the aldo-ester interacted at water-bath temperature with *p*-nitrophenylhydrazine to form this pyrazole compound. It was purified by recrystallization from 95% alcohol, and melted at 212–214° with slight decomposition.

Anal. Calcd. for $C_{11}H_{11}O_3N_3$: N, 18.03. Found: N, 18.15, 18.33.

1-*p*-Bromophenyl-4-ethylpyrazol-5-one.—By action of the aldo-ester on *p*-bromophenylhydrazine for one and one-half hours. After purification by recrystallization from benzene–petroleum ether, it melted at 170–171°.

Anal. Calcd. for $C_{11}H_{11}ON_2Br$: Br, 29.93. Found: Br, 29.81.

1-Phenyl-2-methyl-4-ethylpyrazol-5-one.—Five-tenths gram of 1-phenyl-4-ethylpyrazol-5-one and 0.38 g. of methyl iodide were dissolved in a small quantity of methyl alcohol and heated at 100–110° in a bomb tube for about eight hours. After the completion of the reaction the solvent was removed and the residue, after decolorizing with sulfurous acid, was treated with dilute sodium hydroxide solution to dissolve unchanged pyrazolone. The fraction insoluble in alkali solution was extracted with benzene. From the benzene solution the above pyrazole separated in crystalline form. The yield was 0.2 g. It was purified by recrystallization from benzene–petroleum ether, and melted at 121–121.5°.

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(1) The writers wish to thank Mr. Yao-Tseng Huang for his assistance in making the micro-analyses. They also desire to express appreciation of the help given by Professor Treat B. Johnson of Yale University in organizing this paper for publication.

(2) Johnson and Menge, *J. Biol. Chem.*, **2**, 105 (1906).

(3) Chi and Tien, THIS JOURNAL, **57**, 215 (1935).

Anal. Calcd. for $C_{12}H_{14}ON_2$: C, 71.25; H, 6.98; N, 13.86. Found: C, 70.96; H, 6.99; N, 13.84.

Summary

1. The preparation of pure ethyl formylbutyrate is described.
2. This aldo-ester reacted with phenylhydrazine, nitrophenylhydrazine and bromophenylhydrazine to give the corresponding pyrazolone compounds.
3. The aldo-ester reacted with hydroxylamine to give 4-ethylisoxazol-5-one.
4. The methylation of 1-phenyl-4-ethylpyrazol-5-one gave 1-phenyl-2-methyl-4-ethylpyrazol-5-one.

Shanghai, China Received February 26, 1936

[Contribution from the Chemical Laboratory of the University of California at Los Angeles]

Kinetics of the Trivalent Vanadium–Iodine Reaction

By J. B. Ramsey and M. J. Heldman

In oxidations by iodine in aqueous solutions, usually containing iodide, several possible oxidizing molecular species exist: namely, iodine molecules, triiodide ions, hypoiodite ions and hypoiodous acid molecules. That iodine atoms may be involved under ordinary conditions in the dark seems improbable, although such an interpretation is warranted in the photochemical oxidation of oxalate.[1] Iodine molecules have been shown to be a reacting species in several oxidations, among them, that of phosphorous acid,[2] of trivalent titanium[3] and of ferrous iron.[4] The oxidation of arsenious acid by iodine[5] is an outstanding historical example of those reactions in which hypoiodous acid molecules are involved in the rate determining step. Triiodide ion is at least one of the reacting molecular species in the oxidations of phosphorous acid,[2] of ferrous iron,[4] and of hypophosphorous acid.[6] It seems probable that some relation may be found between the molecular species of iodine involved and the nature of the reducing species or of its transformation, after a larger number of kinetic studies has been made.

The more immediate interest in this reaction is due to its possible importance in the interpretation of the induced catalysis of the autoxidation of hydriodic acid by vanadic acid.[7] In a general qualitative survey of the reactions of vanadium in its different valence states Rutter[8] observed that the trivalent vanadium–iodine reaction proceeded at a moderate rate. The stoichiometry of the reaction may be represented by the following equation.

$$2V^{+++} + I_3^- + 2H_2O = 2VO^{++} + 3I^- + 4H^+$$

Preparation and Standardization of Stock Solutions.—All chemicals were of c. p. grade. The sodium perchlorate and sodium iodide were shown free from possible impurities by methods recommended by Murray.[9] Sodium oxalate from the Bureau of Standards was the primary standard. Known solutions of each of the following substances were obtained as indicated: potassium permanganate, with sodium oxalate; sodium thiosulfate, by the Volhard method, under conditions recommended by Bray and Miller;[10] sodium triiodide and potassium iodate, with the sodium thiosulfate; perchloric acid, with potassium iodate by the method of Kolthoff;[11] sodium iodide and sodium perchlorate, from accurately weighed quantities which had been dried carefully (the former checked by the method of Andrews[12]); ammonium vanadate, iodometrically.[13]

The stock solutions of vanadic perchlorate, $V(ClO_4)_3$, were prepared by electrolytic reduction of vanadyl perchlorate, VO_2ClO_4. The latter was formed by mixing vanadium pentoxide, from thermal decomposition of pure ammonium vanadate, with perchloric acid. The oxide dissolved as the reduction progressed. A platinized platinum cathode and a platinum anode were used. The reduction was followed analytically (by a method

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[1] Griffith and McKeown, *Trans. Faraday Soc.*, **28**, 752 (1932).

[2] Mitchell, *J. Chem. Soc.*, **123**, 2241 (1923).

[3] Yost and Zabaro, This Journal, **48**, 1181 (1926).

[4] Unpublished work of Bray and Hershey, presented at the San Francisco meeting of the American Chemical Society, Aug. 20, 1935.

[5] (a) Roebuck, *J. Phys. Chem.*, **6**, 365 (1902); **9**, 727 (1905); (b) Liebhafsky, *ibid.*, **35**, 1648 (1931).

[6] Mitchell, *J. Chem. Soc.*, **117**, 1322 (1920).

[7] Bray and Ramsey, This Journal, **55**, 2279 (1933).

[8] Rutter, *Z. anorg. Chem.*, **52**, 368 (1907).

[9] Murray, "Standards and Tests for Reagents and c. p. Chemicals," D. Van Nostrand Co., N. Y., 1927.

[10] Bray and Miller, This Journal, **46**, 2204 (1924).

[11] Kolthoff, *ibid.*, **48**, 1447 (1926).

[12] Andrews, *ibid.*, **25**, 756 (1903).

[13] Ramsey, *ibid.*, **49**, 1138 (1927).

to be described later) and stopped with a small quantity of vanadium still remaining in the tetravalent state. Washed carbon dioxide from a cylinder passed through the solution during the electrolysis and was kept over it during use. The resulting solutions were usually about 0.5 normal in perchloric acid.

The combined equivalent concentration of the tri- and tetravalent vanadium in this solution was obtained by adding a pipetted aliquot to an ammonium vanadate solution containing slightly more than enough vanadate to oxidize the trivalent vanadium, heating almost to boiling, and titrating with permanganate, thus oxidizing the tetravalent vanadium to the pentavalent state. That no oxygen error was involved during the oxidation of trivalent vanadium by the vanadate (which occurred instantaneously in these solutions) was shown by previously freeing the vanadate solution from air before adding the aliquot.

The concentration of the trivalent vanadium alone was found by adding a known volume of the solution to a measured quantity of known vanadate in excess, then determining the vanadate remaining by the iodometric method.[13]

Finally the concentration of the perchloric acid was found by adding a standard base in slight excess to a measured volume of the solution, filtering off the two hydroxides formed, and titrating with standard acid. The perchloric acid concentration may be calculated knowing that the trivalent and tetravalent vanadium are present as V^{+++} and VO^{++}, respectively.

These stock solutions of vanadic perchlorate were quite stable. Over a period of some three weeks the trivalent vanadium was converted to the tetravalent state to a slight extent, both by oxygen and by perchlorate. The extreme slowness of the latter oxidation was shown by tests for chloride during the period of use.

Rate Measurements.—The reaction was followed by determining the iodine present in measured aliquots (10 to 25 ml.), removed from the reacting mixture at suitable intervals. The following possible sources of error were considered: (1) loss of iodine by volatilization; (2) oxidation of trivalent vanadium by oxygen and perchlorate; and (3) oxidation of iodide by oxygen. Also the possibility of induction of one of these reactions by another or by the reaction being considered was not overlooked.

Experiments were carried out in the same manner and under the same conditions as those finally adopted in the rate measurements but with vanadium absent. With the concentrations of iodine and iodide such as to give the maximum volatility existing in any experiment, the loss of iodine was found negligible. That none of the reactions listed under (2) and (3) above occurred to a measurable extent under the conditions adopted was proven by the fact that during several of the experiments the equivalents of trivalent vanadium oxidized were determined at intervals and found at all times to be precisely equivalent to the iodine reduced.

Prior to the addition of the triiodide solution, the last reagent added, the solution of the other reagents was freed from oxygen with carbon dioxide. In those runs requiring more than two or three hours, it was found necessary to maintain an atmosphere of carbon dioxide in the reaction flask. This was accomplished by providing that carbon dioxide passed through the flask above the solution only during the removal of aliquots, since a continuous stream of carbon dioxide caused an appreciable loss of iodine. In experiments requiring less time the maintenance of an atmosphere of carbon dioxide was found unnecessary. The initial time was taken as that at which one-half of the triiodide solution had been added.

Preliminary experiments had shown that the reaction rate decreased with increasing concentration of acid. It was found that adequate quenching was provided if the 10- to 25-ml. aliquots were added to approximately 100 ml. of ice-cooled 0.5 *N* sulfuric acid. The 0.01 *N* sodium thiosulfate was freshly prepared from the stock 0.1 *N* solution. A 10-ml. buret was used for the titrations; the end-point was determinable within 0.02 ml.

Order of the Reaction.—The ionic strength of the reaction mixture was maintained substantially constant at 1.00 by means of sodium perchlorate. At the same initial total iodide and iodine concentrations, variation in the quantity of the stock vanadic perchlorate–perchloric acid solution in a given volume of the reacting mixture caused no variation in the initial rate as determined by slopes. This shows the net order with respect to trivalent vanadium and acid to be zero. Other experiments in which the initial concentration of the acid alone was varied showed definitely that the rate was inversely proportional to the acid concentration. From these preliminary results it followed that the reaction is first order with respect to trivalent vanadium. These conclusions were confirmed throughout the range of concentrations of vanadium and acid used. It is apparent from these results that the hydrolysis of both tri- and tetravalent vanadium must be negligible.

Results obtained by varying the triiodide and iodide concentrations indicated that iodine molecules might be the only oxidizing species; if this were the case, the rate equation would be

$$\frac{-\mathrm{d}[\Sigma(\mathrm{I}_2)]}{\mathrm{d}t} = k\,\frac{(\mathrm{V}^{+++})}{(\mathrm{H}^+)}\,(\mathrm{I}_2) \qquad (1)$$

in which $\Sigma(I_2)$ represents the total iodine concentration. On account of the known equilibrium between triiodide, iodine and iodide this equation may be written

$$\frac{-\mathrm{d}[\Sigma(\mathrm{I}_2)]}{\mathrm{d}t} = k'\,\frac{(\mathrm{V}^{+++})(\mathrm{I}_3^-)}{(\mathrm{H}^+)(\mathrm{I}^-)} \qquad (2)$$

The results obtained by use of equation (2) are given in Table I. In experiments 1–9 and 16–17, inclusive, the iodine and vanadic ion were the only substances involved whose concentrations changed appreciably during the experiment. Also the (I_2) was negligible relative to the (I_3^-), which in turn was negligible relative to the (I^-). In these experiments it was therefore convenient to determine k' from an integrated expression. In these cases equation (2) can be written

$$\frac{-\mathrm{d}[\Sigma(\mathrm{I}_2)]}{\mathrm{d}t} = k'\,\frac{(\mathrm{I}_3^-)}{(\mathrm{H}^+)(\mathrm{I}^-)}\,[(\mathrm{V}^{+++})_0 - 2\{(\mathrm{I}_3^-)_0 - (\mathrm{I}_3^-)\}] \qquad (3)$$

TABLE I

KINETIC RESULTS AT $\mu = 1.00$ AND $T = 24.95 \pm 0.02°$

Initial concentrations in moles/liter

Expt.[a]	(V^{+++})	(H^+)	$\Sigma(I^-)$	$\Sigma(I_2) \times 10^3$	$(VO^{+++}) \times 10^3$	$k' \times 10^3$
1	0.0241	0.107	0.256	2.52	2.50	1.14
2	.0476	.214	.132	2.52	5.60	1.32
3	.0241	.107	.132	2.52	2.50	1.28
4	.0180	.0869	.501	2.50	3.40	1.04
5	.0658	.333	.105	2.00	19.4	1.30
6	.0217	.0590	.508	2.50	1.75	1.12
7	.0217	.0590	.258	2.50	1.75	1.14
8	.0217	.559	.158	2.56	1.75	1.20
9	.0217	.0590	.108	2.58	1.75	1.34
10	.00433	.0118	.158	2.52	0.350	1.25
11	.0362	.125	.00827	2.47	10.9	0.91
12	.0362	.125	.0283	2.48	10.9	1.07
13	.0347	.127	.0133	2.57	12.8	0.98
14	.0347	.127	.0337	2.57	12.8	.97
15	.0347	.127	.0483	2.47	12.8	1.15
16	.0347	.127	.208	2.63	12.8	1.14
17	.0317	.132	.0583	2.54	15.8	1.34

[a] Numbered chronologically.

in which the subscript 0 indicates initial concentration. Letting $c = (I_3^-) \doteqdot (I_3^-) + (I_2)$, and $b = (V^{+++})_0 - 2(I_3^-)_0$, equation (3) becomes

$$\frac{-\mathrm{d}c}{\mathrm{d}t} = \frac{k'}{(\mathrm{H}^+)(\mathrm{I}^-)} \times c(2c + b) \qquad (4)$$

which on integration gives

$$k' = \frac{2.303(\mathrm{H}^+)(\mathrm{I}^-)}{b(t - t_0)}\,\log_{10}\frac{(2c + b)(c_0)}{(2c_0 + b)(c)} \qquad (5)$$

The values of k' given for each of these experiments are averages of those determined from at least five well distributed points on the best concentration–time curve.

Since in experiments 10–15 inclusive the concentrations of the acid and/or iodide, as well as those of the vanadium and iodine, were so low that their concentrations changed appreciably during a run, the graphical slope method was employed to evaluate k' from equation (2). In each experiment slopes were obtained at not less than five well distributed points by use of both the Latshaw tangentimeter[14] and the Richards–Roope Tangent Meter.[15] Application of this method to a few of the experiments in which the "integration" method had been used, gave in each case satisfactory agreement in the values of k'. The value 0.00140 for the triiodide equilibrium constant at 25° was considered sufficiently accurate for the purpose of calculating the ratios of $(I_3^-)/(I^-)$.[16]

In none of the experiments was the average deviation of the values of k' from that given greater than 5%, and in most, less than 3%. Also there was no trend in the values of k' in any particular experiment. Several of the experiments were run in duplicate, and such pairs gave values of k' agreeing within these limits. The small variation in the values of k' over the wide range of concentrations used establishes equation (2) as the rate law.

Among the factors which may be effective in producing the small variation in the values of k' obtained are (1) the possibility of formation of vanadic–iodide complexes, and (2) the inadequacy of "ionic strength" alone as a criterion of constant ionic environment in solutions of such high concentrations of mixed electrolytes.

That the presence of tetravalent vanadium had no effect on the rate is shown by the results of experiment 5, in which the vanadyl perchlorate

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[14] Latshaw, THIS JOURNAL, **47**, 793 (1925).

[15] Richards and Roope, *Science*, **71**, 290 (1930).

[16] (a) Jones and Kaplan, THIS JOURNAL, **50**, 1845 (1928); (b) La Mer and Lewinsohn, *J. Phys. Chem.*, **38**, 171 (1934).

was purposely made initially greater than that finally produced in any other experiment.

The Salt Effect.—Several experiments were carried out at various ionic strengths between 0.31 and 1.76, and at a constant iodide concentration of 0.108 molal. The large negative non-linear salt effect is shown in Fig. 1.

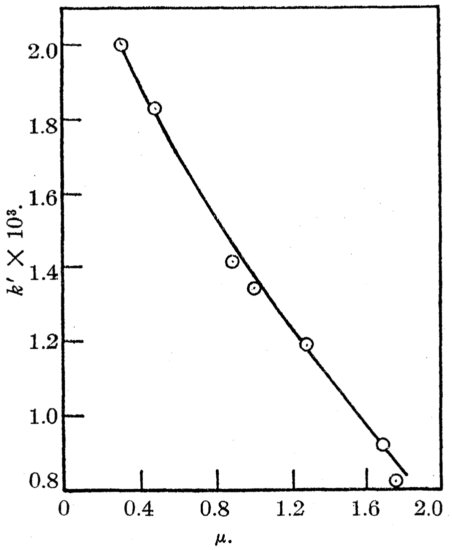

Fig. 1.—The salt effect.

Discussion.—The rate law established at constant ionic strength may be interpreted as meaning that the sole rate-determining step is a bimolecular one between iodine molecules and hydrolyzed vanadium ions, VOH^{++}. $(VOH^{++}) = K_2(V^{+++})/(H^+) = K_2$(total trivalent vanadium)$/(H^+)$, since the (VOH^{++}) is negligible compared to the (V^{+++}).

If a slow reaction between HIO and V^{+++} occurs to any measurable extent, a second term, $k''(V^{+++})(I_3^-)/(H^+)(I^-)^2$ (considering the mass-action expression for the small hydrolysis of iodine, $I_2 + H_2O = H^+ + I^- + HIO$), would have appeared in the rate equation. The constancy of k' over the eighty-fold range of iodide concentration is conclusive evidence that this reaction is not measurably involved.

Several rapid follow-up reaction mechanisms are possible. (1) The $VOH{\cdot}I_2^{++}$ critical complex[17] may break down directly to vanadyl vanadium and I_2^-, the latter immediately oxidizing trivalent vanadium or reacting with another of its own kind to form iodine and iodide ions. Diiodide ion has been previously assumed as an intermediate by Wagner.[18] (2) The complex may decompose into iodide and pentavalent vanadium, the latter immediately reacting with trivalent vanadium. (3) VOH^{++} may react rapidly with the complex to form vanadyl vanadium and iodide. This last mechanism is similar to that proposed by Yost and Zabaro[3] in their kinetic study of the entirely analogous trivalent titanium–iodine reaction.

Application of Brönsted's theory[17] to this reaction results in the expression

$$\text{rate} = k_B K_1 \frac{(I_3^-)}{(I^-)} K_2 \frac{(V^{+++})}{(H^+)} \frac{\gamma_{VOH^{++}} \cdot \gamma_{I_2}}{\gamma_{VOH \cdot I_2^{++}}} \qquad (6)$$

in which k_B is the Brönsted specific reaction rate, K_1 and K_2 are the mass action "constants" for the triiodide equilibrium and the vanadium hydrolysis, respectively, and the γ's are activity coefficients. It is evident that at constant ionic strength the above equation reduces to the experimentally found rate law.

It is possible to draw certain rather qualitative conclusions regarding K_2 if the assumption is made that the large negative salt effect found is principally due to changes in the activity coefficients of the chemical species as the ionic strength is varied, rather than to a solvent effect brought about by this variation. The ratio $\gamma_{VOH^{++}}/\gamma_{VOH \cdot I_2^{++}}$ may be assumed not to change to any great extent over the range of salt concentrations considered; both K_1 and γ_{I_2} are known to be substantially constant over the range of ionic strength of 0.0 to 2.0.[16b] According to this theory, the assumptions made, and the facts stated, it follows that this large negative salt effect is due to a rapid decrease of K_2 as the salt concentration is increased. This is equivalent to stating that the quotient, $\gamma_{V^{+++}}/\gamma_{H^+}\gamma_{VOH^{++}}$, decreases rapidly as the ionic strength increases. That this be so does not require that these ion activity coefficients individually decrease over the range of ionic strength used. In fact, from the well known variation in the activity coefficients of the uni-univalent strong acids over this range of ionic strength, it seems probable that the activity coefficient of the hydrogen ion does pass through a minimum at some ionic strength between 0.3 and 1.8.

Summary

The rate of the reaction at 24.95° between iodine and trivalent vanadium in perchloric acid solutions has been measured, and found to be, at constant ionic strength, directly proportional to

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(17) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

(18) Wagner, *ibid.*, **113**, 261 (1924).

the concentrations of triiodide and vanadic ions, and inversely proportional to the concentrations of the hydrogen and iodide ions. This result is in agreement with the postulation that the single rate determining step is one between hydrolyzed vanadic ions, VOH^{++}, and iodine molecules. Several possible rapid follow-up mechanisms have been suggested. The salt effect has been measured over the range of ionic strengths from 0.31 to 1.76, and a possible explanation for its large negative magnitude has been advanced.

LOS ANGELES, CALIF. RECEIVED APRIL 23, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Mechanism of Substitution Reactions. Substitution of Bromine and Chlorine in Phenylbromo and Phenylchloroacetic Acids by Chloride and Bromide Ions in Aqueous Solution

BY M. J. YOUNG AND A. R. OLSON

When an optically active bromo compound is treated with chloride ion, a whole system of reactions is initiated. By making a kinetic study of the system of reactions which occurs when *l*-bromosuccinic acid is treated with chloride ion in aqueous solution, Olson and Long[1] were able to prove the correctness of the theory of the mechanism of substitution reactions advanced by Olson,[2] and by Bergmann, Polanyi and Szabo,[3] according to which configurational inversion accompanies every single-step substitution.

The present study deals with the kinetics of the corresponding system of reactions produced by treating *l*-phenylbromoacetic acid with chloride ion in aqueous solution. The results provide additional confirmation of the above-mentioned theory.

The relations between the heats of activation of the various reactions in the succinic system, studied by Olson and Long,[4] are again apparent in this system. The same is true of the temperature independent factors.

Preparation of Materials

Phenylbromoacetic acid and phenylchloroacetic acid were prepared from mandelic acid (phenylhydroxyacetic acid) by treatment with the corresponding phosphorus pentahalides, following the procedure given by Walden and Bischoff.[5] The acids were resolved by fractional crystallization of their morphine salts from methyl alcohol, following the procedure of McKenzie and Clough.[6] The products were shown to be chemically pure by the usual analyses. Complete resolution was not obtained in all cases but as is shown by the rate laws, optical purity is in no way essential. It is essential that the assumption that *l*-phenylchloroacetic acid and *l*-phenylbromoacetic acid have the same configuration be correct. This assumption is in accord with the opinion of those who have worked with such compounds.

Apparatus

For all measurements of optical activity a laboratory constructed polarimeter of the Lippich type was used, with monochromatic light (λ 5461) obtained from a mercury arc and suitable filters. The angle of rotation was determined from the deflection of the image of an illuminated scale, four meters distant, produced in a small plane mirror mounted nearly on the axis of the analyser, and reflected into a telescope parallel to the optic axis by means of a periscope arrangement. This device enabled rotations to be read directly to 0.007° (1 mm. of scale) and estimated to 0.001°. A given setting can be duplicated to 0.005°. A thermostat provided with glass windows was mounted directly on the polarimeter so that tubes did not have to be removed for observation.

Experimental Procedure

Due to the slowness with which the phenylhalogenoacetic acids dissolve in water, the following procedure was adopted. A weighed amount of the active acid was dissolved in 0.4 cc. of methyl alcohol. To this solution was added the required amount of 2.00 N perchloric acid (about 10 cc.) followed, after re-solution had occurred, by the required amount of 2.00 N halogen acid (about 10 cc.). The addition of so small an amount of methyl alcohol has no observable effect on the reaction rates. All solutions were prepared at the temperature of the experiment. After the solution process, the material was transferred rapidly to a 30-cm. polarimeter tube and placed in the thermostat. Zero time was taken as the moment of addition of halide ion. The time interval between this addition and the first reading was never more than four minutes. In all experiments the concentrations are: active acid 0.015 M, halide ion 1.00 M, hydrogen ion 2.00 M, unless otherwise specified.

The Formation of Mandelic Acid from Phenylhalogenoacetic Acids.—The detailed mechanism

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[1] A. R. Olson and F. A. Long, THIS JOURNAL, **56**, 1294 (1934).

[2] A. R. Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[3] Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, **B20**, 161 (1933).

[4] A. R. Olson and F. A. Long, THIS JOURNAL, **58**, 393 (1936).

[5] Walden and Bischoff, *Ann.*, **279**, 122 (1894).

[6] McKenzie and Clough, *J. Chem. Soc.*, **93**, 818 (1908).

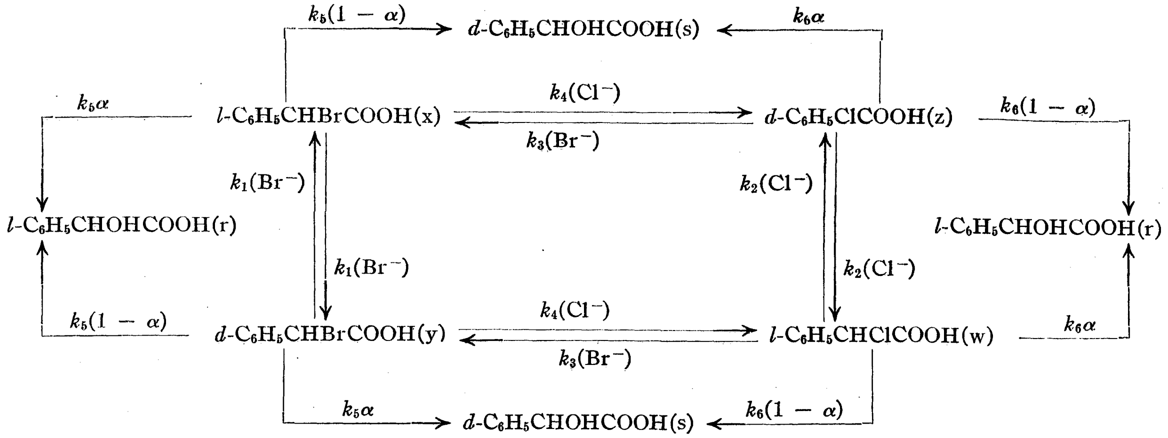
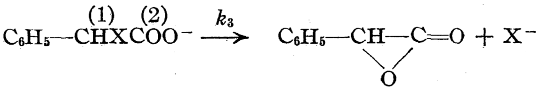


Fig. 1.—System of reactions occurring when *l*-phenylbromoacetic acid is treated with chloride ion in aqueous solution, assuming complete inversion accompanies each single-step substitution.

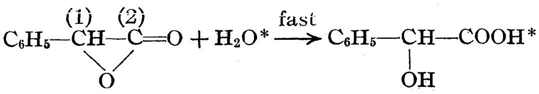
of the reactions between phenylbromoacetic acid or phenylchloroacetic acid and water, by which mandelic acid, hydrogen ion and halide ion are produced, is not completely understood in spite of the amount of investigation to which it has been subjected.[7,8,9] The specific rate, measured by the rate of formation of hydrogen ion, is in accord with the assumption that the undissociated acid reacts more slowly than its ion. Measurement of the decrease of optical activity with time makes it necessary to suppose that the ion can react with water in either of two different ways, one reaction producing a *d*-mandelic acid, and the other an *l*-mandelic acid. The following mechanism can account for this effect and is at the same time in accord with the theory that inversion in configuration accompanies each single-step substitution.

$$\text{(1)}\quad C_6H_5\text{—}\overset{(1)}{CHX}\text{—}\overset{(2)}{COOH} + H_2O \xrightarrow{k_1} C_6H_5CHOHCOOH + H^+ + X^- \ \text{(inversion at C(1))}$$

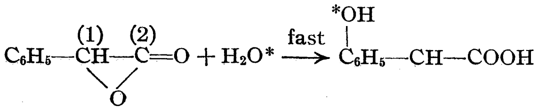
$$\text{(2)}\quad C_6H_5\text{—}\overset{(1)}{CHX}\text{—}\overset{(2)}{COO^-} + H_2O \xrightarrow{k_2} C_6H_5CHOHCOOH + X^- \ \text{(inversion at C(1))}$$

(3)


(inversion at C(1))

(4)


(inversion at C(2))

(5)


(inversion at C(1))

Reactions (1), (2) and the sequence (3), (4) lead to a mandelic acid of configuration opposite to that of the $C_6H_5CHXCOOH$. The sequence (3), (5), involving a double inversion at C(1), leads to a mandelic acid of the same configuration as that of the $C_6H_5CHXCOOH$. The relative amounts of levo and dextro mandelic acids depend on the relation between the specific rates of the various reactions under the conditions of the experiment.

Although we failed to isolate the postulated lactone, a similar compound is known to be formed in the hydrolysis of bromosuccinic acid.

When the hydrogen-ion concentration is large, this mechanism predicts that *l*-$C_6H_5CHXCOOH$ will disappear at a specific rate $k_1 + \{(k_2 + k_3) k_a/(H^+)\}$, where k_a is the dissociation constant of $C_6H_5CHXCOOH$, and that *d* and *l* mandelic acids will appear at specific rates $k_1 + \{(k_2 + k_3\beta)k_a/(H^+)\}$ and $k_3(1 - \beta)k_a/(H^+)$, respectively, where β is the fraction of the lactone hydrolyzing by reaction (4) and $(1 - \beta)$ the fraction hydrolyzing by reaction (5). If the specific rate of disappearance of *l*-$C_6H_5CHXCOOH$ is represented by K, the specific rates of production of *l* and *d* mandelic acid can be represented by $K(\alpha)$, and $K(1-\alpha)$, respectively, where $\alpha = 1-\{k_3\beta k_a/[k_1(H^+) + k_2k_a + k_3k_a]\}$.

Rate Laws

Following the system of reactions and the notation shown in Fig. 1, we can write the differen-

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[7] (a) Senter and Tucker, *J. Chem. Soc.*, **109**, 690 (1916); (b) Senter, *ibid.*, **107**, 908 (1915); (c) Senter and Drew, *ibid.*, **107**, 638 (1915).

[8] A. McKenzie and N. Walker, *ibid.*, **107**, 1685 (1915).

[9] A. M. Ward, *ibid.*, 1184 (1926).

tial equations for the rate of change of the concentration of each substance.

(1) $dx/dt = -k_1(\mathrm{Br}^-)x + k_1(\mathrm{Br}^-)y + k_3(\mathrm{Br}^-)z - k_4(\mathrm{Cl}^-)x - k_5x$

(2) $dy/dt = -k_1(\mathrm{Br}^-)y + k_1(\mathrm{Br}^-)x + k_3(\mathrm{Br}^-)w - k_4(\mathrm{Cl}^-)y - k_5y$

(3) $dw/dt = -k_2(\mathrm{Cl}^-)w + k_2(\mathrm{Cl}^-)z - k_3(\mathrm{Br}^-)w + k_4(\mathrm{Cl}^-)y - k_6w$

(4) $dz/dt = -k_2(\mathrm{Cl}^-)z + k_2(\mathrm{Cl}^-)w - k_3(\mathrm{Br}^-)z + k_4(\mathrm{Cl}^-)x - k_6z$

(5) $dr/dt = k_5\alpha x + k_5(1-\alpha)y + k_6\alpha w + k_6(1-\alpha)z$

(6) $ds/dt = k_5\alpha y + k_5(1-\alpha)x + k_6\alpha z + k_6(1-\alpha)w$

(7) $d(\mathrm{Br}^-)/dt = k_4(\mathrm{Cl}^-)(x+y) - k_3(\mathrm{Br}^-)(w+z) + k_5(x+y)$

(8) $d(\mathrm{Cl}^-)/dt = -k_4(\mathrm{Cl}^-)(x+y) + k_3(\mathrm{Br}^-)(w+z) + k_6(w+z)$

For the determination of the angle of rotation only the quantities $(x - y)$, $(w - z)$ and $(r - s)$ need be calculated, for $\theta = C_1(x - y) + C_2(w - z) + C_3(r - s)$. For the evaluation of the six specific rates, a series of experiments was devised each involving only one unknown specific rate. This series, and the corresponding integrated rate laws, are shown in Table I.

TABLE I

(1) Initial conditions: $(x - y) = (x - y)_0$, $(w - z) = 0$, $(r - s) = 0$, $(\mathrm{Cl}^-) = 0$, $(\mathrm{Br}^-) = 1\ M$, $(\mathrm{H}^+) = 2\ M$

Additional assumption: $k_1 >> k_5$ so that k_5 can be neglected. (Br^-) = constant

Rate law: $\Theta/\Theta_0 = e^{-2k_1(\mathrm{Br}^-)t}$

(2) Initial conditions: $(x - y) = 0$, $(w - z) = (w - z)_0$, $(r - s) = 0$, $(\mathrm{Cl}^-) = 0$, $(\mathrm{Br}^-) = 0$, $(\mathrm{H}^+) = 2\ M$

Additional assumption: Since (Cl^-) remains small, $k_2(\mathrm{Cl}^-)$ can be neglected compared to k_6

Rate law: $(\Theta - \Theta_\infty)/(\Theta_0 - \Theta_\infty) = e^{-k_6t}$, $\Theta_\infty = C_3(w - z)_0(2\alpha - 1)$

(3) Initial conditions: $(x - y) = 0$, $(w - z) = (w - z)_0$, $(r - s) = 0$, $(\mathrm{Cl}^-) = 1\ M$, $(\mathrm{Br}^-) = 0$, $(\mathrm{H}^+) = 2\ M$

Additional assumption: (Cl^-) = constant

Rate law: $(\Theta - \Theta_\infty)/(\Theta_0 - \Theta_\infty) = e^{-[2k_2(\mathrm{Cl}^-)+k_6]t}$, $\Theta_\infty = C_3(w - z)_0k_6(2\alpha - 1)/\{2k_2(\mathrm{Cl}^-) + k_6\}$

(4) Initial conditions: $A = (x - y) = (x - y)_0$, $(w - z) = 0$, $(r - s) = 0$, $(\mathrm{Cl}^-) = 0$, $(\mathrm{Br}^-) = 0$, $(\mathrm{H}^+) = 2\ M$

Additional assumptions: none

Rate law: $(\Theta - \Theta_\infty)/(\Theta_0 - \Theta_\infty) = e^{-(2k_1A+k_5)t+\{2k_1A(1-e^{-k_5t})/k_5\}}$ $\Theta_\infty = C_3(x - y)_0(2\alpha - 1)k_5/(2k_1A + k_5)$

(5) Initial conditions: $(x - y) = 0$, $(w - z) = (w - z)_0$, $(r - s) = 0$, $(\mathrm{Cl}^-) = 0$, $(\mathrm{Br}^-) = 1\ M$, $(\mathrm{H}^+) = 2\ M$

Additional assumptions: (1) $k_1 >> k_3$ so that ϕCHBr-COOH is racemized as fast as it is formed; *i. e.*, $(x - y) = 0$; k_5 makes no contribution to $(r - s)$.
(2) (Cl^-) is so small that $k_2(\mathrm{Cl}^-)$ and $k_4(\mathrm{Cl}^-)$ are negligible.
(3) (Br^-) = constant

Rate law: $(\Theta - \Theta_\infty)/(\Theta_0 - \Theta_\infty) = e^{-[k_3(\mathrm{Br}^-)+k_6]t}$, $\Theta_\infty = k_6(w - z)_0C_3(2\alpha - 1)/(k_3(\mathrm{Br}^-) + k_6)$

(6) Initial conditions: $(x - y) = (x - y)_0 = A$, $(w - z) = 0$, $(r - s) = 0$, $(\mathrm{Cl}^-) = 1\ M$, $(\mathrm{Br}^-) = 0$, $(\mathrm{H}^+) = 2\ M$

Additional assumptions: (1) $k_3(\mathrm{Br}^-)$ can be neglected,
(2) $k_6 << k_5$,
(3) (Cl^-) = constant,
(4) $\Theta_\infty = 0$ (experimentally true)

Rate law: $\theta/\theta_0 = (1 + R)e^{-Q(t)} - Re^{-[2k_2(\mathrm{Cl}^-)+k_6]t}$
$R = [C_2/C_1]k_4(\mathrm{Cl}^-)/[2k_1A + k_4(\mathrm{Cl}^-) + k_5 - 2k_2(\mathrm{Cl}^-) - k_6]$
$Q(t) = [2k_1A + k_4(\mathrm{Cl}^-) + k_5]t - 2k_1A[(1 - e^{-[k_4(\mathrm{Cl}^-)+k_5]t})/(k_4(\mathrm{Cl}^-) + k_5)]$.

The rate laws for experiment series (1), (2), (3) and (5) follow in a perfectly straightforward manner from the differential equations; those for experiment series (4) and (6) involve an integral of the form

$$I = \int_0^t e^{-(a+b)t+[a(1-e^{-bt})/b]}dt$$

We have been unable to evaluate this integral exactly in terms of elementary functions. Olson and Long handled it by means of a series expansion and term by term integration. We have found the following procedure more convenient in this case. Integration by parts gives

$$I = \left\{ (1 - e^{-(a+b)t+[a(1-e^{-bt})/b]} \right\} \Big/ (a+b) + \left\{ a\int_0^t e^{-(a+2b)t+[a(1-e^{-bt})/b]}\,dt \right\} \Big/ (a+b)$$

The second integral can be neglected for two reasons. The integrand is smaller by a factor e^{bt}, and the coefficient a is small compared to 1, in the time units employed. The error introduced by this neglect is never more than 0.3%.

The constants appearing in expressions (1), (2), (3) and (5) can be evaluated by calculating one value from each observation and averaging the results in the usual manner, or by obtaining a value of the slope of the line

$$\ln (\Theta - \Theta_\infty)/(\Theta_0 - \Theta_\infty) = -kt$$

using the method of least squares. The expressions (4) and (6) cannot be solved explicitly for the unknown specific rates k_5 and k_4, respectively. In these cases a value of the specific rate was determined by a trial and error process to fit one observation; the remaining observations were plotted on a curve calculated using this constant, and agreement was found satisfactory in all cases. The results obtained are given in Tables II–VIII. The values of k(calcd.) are those obtained from the activation energies and temperature independent factors shown in Table VIII. All times are in minutes unless otherwise specified.

Results

TABLE II

$$l\text{-}C_6H_5CHBrCOOH + Br^- \overset{k_1}{=} d\text{-}C_6H_5CHBrCOOH + Br^-$$

T, °K.	No. of runs	(Br⁻) moles/ liter	k_1	Mean deviation, %	k_1 calcd.
288.1	2	0.984	0.004358	0.5	0.004363
298.1	2	.208	.01198	.1	....
298.1	3	.965	.01268	.3	.01251
303.23	2	.965	.01984	.3	.0209
307.02	2	.964	.02974	1	.03020
310.70	1	.960	.04294	..	.04294

TABLE III

$$l\text{-}C_6H_5CHClCOOH + H_2O \xrightarrow{k_6} C_6H_5CHOHCOOH + H^+ + Cl^-$$

T, °K.	No. of runs	k_6	Mean deviation, %
323.1	2	2.20×10^{-4}	2
308.1	2	3.65×10^{-5}	2
298.1	2	1.03×10^{-5}	2

TABLE IV

$$l\text{-}C_6H_5CHClCOOH + Cl^- \overset{k_2}{=} d\text{-}C_6H_5CHClCOOH + Cl^-$$

T, °K.	No. of runs	$k_{\text{obsd.}} = 2k_2(\text{Cl}^-)+k_6$	(Cl⁻)	k_2	Mean deviation, %
308.1	2	5.067×10^{-4}	2.00	1.178×10^{-4}	1.6
323.1	2	2.660×10^{-3}	2.00	6.100×10^{-4}	1.5

TABLE V

$$l\text{-}C_6H_5CHClCOOH + Br^- \xrightarrow{k_3} d\text{-}C_6H_5CHBrCOOH + Cl^-$$

T, °K.	No. of runs	$k_{\text{obsd.}} = k_3(\text{Br}^-)+k_6$	(Br⁻)
322.54	6	3.260×10^{-3}	0.980
308.05	5	7.326×10^{-4}	.980
298.1	2	2.457×10^{-4}	.980

k_3	Mean deviation, %	k_3, calcd.
3.114×10^{-3}	1.5	3.104×10^{-3}
7.104×10^{-4}	1.9	7.141×10^{-4}
2.402×10^{-4}	2.0	2.397×10^{-4}

TABLE VI

$$l\text{-}C_6H_5CHBrCOOH + H_2O \xrightarrow{k_5} d\text{-}C_6H_5CHOHCOOH + H^+ + Br^-$$

T,°K.	No. of runs	k_5
324.0	2	0.00174
307.92	2	0.000318

TABLE VII

$$l\text{-}C_6H_5CHBrCOOH + Cl^- \xrightarrow{k_4} d\text{-}C_6H_5CHClCOOH + Br^-$$

T, °K.	No. of runs	k_4	k_4, calcd.
322.54	3	0.01582	0.01576
307.92	2	.003610	.003632
298.1	2	.001253	.001250

TABLE VIII

Reaction	$E_{\text{cal.}}$/mole	$A \times 10^{-9}$ (sec.⁻ moles⁻¹ liters)
l-$C_6H_5CHBrCOOH + Br^-$	17,971 ± 150	3.13
l-$C_6H_5CHClCOOH + Cl^-$	21,683	4.74
l-$C_6H_5CHClCOOH + Br^-$	20,016 ± 87	1.90
l-$C_6H_5CHBrCOOH + Cl^-$	19,805 ± 100	6.93

No values of E and A for the hydrolysis reactions (Tables III and VI) were calculated for they would be of doubtful significance since the specific rates are complex averages over several reactions. The listed probable errors are mean deviations from the average of the values of E calculated for each temperature interval.

It can be shown that the introduction of the assumption of incomplete inversion in configuration, giving rise to the system of reactions appearing in Fig. 2, where the Greek letters represent in each case the fraction of the reaction occurring without inversion, results in an alteration of the rate laws which is not detectable except in the case of expression 6. In this case the new rate law is

$$\Theta/\Theta_0 = (1 + R)e^{-Q(t)} - Re^{-[2k_2(\text{Cl}^-)+k_6]t}$$

$$\text{where } R = C_2k_4(\text{Cl}^-)(1 - 2\epsilon)/C_1[2k_1A + k_4(\text{Cl}^-)(1 - 2\epsilon) + k_5 - 2k_2(\text{Cl}^-) - k_6]$$

$$Q(t) = [2k_1A + k_4(\text{Cl}^-)(1 - 2\epsilon) + k_5]t - \{2k_1A(1 - e^{-[k_4(\text{Cl}^-)+k_5]t})/[k_4(\text{Cl}^-) + k_5]\}$$

The effect which this modification has on the calculated value of θ for various times and for various values of ϵ is shown in Table IX for the

TABLE IX

Time min.	Θ cm. $\epsilon = 0$	ΔΘ $\epsilon = 0.03$	ΔΘ $\epsilon = 0.05$	ΔΘ $\epsilon = 0.07$
0	−15.76	0	0	0
10	11.18	0	+0.01	+0.01
20	7.27	+0.01	+ .02	+ .03
30	3.98	− .02	− .03	.00
40	1.21	− .03	− .04	− .05
50	+1.09	− .03	− .06	− .07
60	2.45	− .03	− .06	− .08
70	4.52	− .03	− .05	− .09
80	5.75	− .03	− .05	− .08
90	6.75	− .03	− .04	− .08
100	7.54	− .02	− .03	− .07
150	9.48	− .01	− .02	− .03
200	9.72	− .01	− .01	− .01

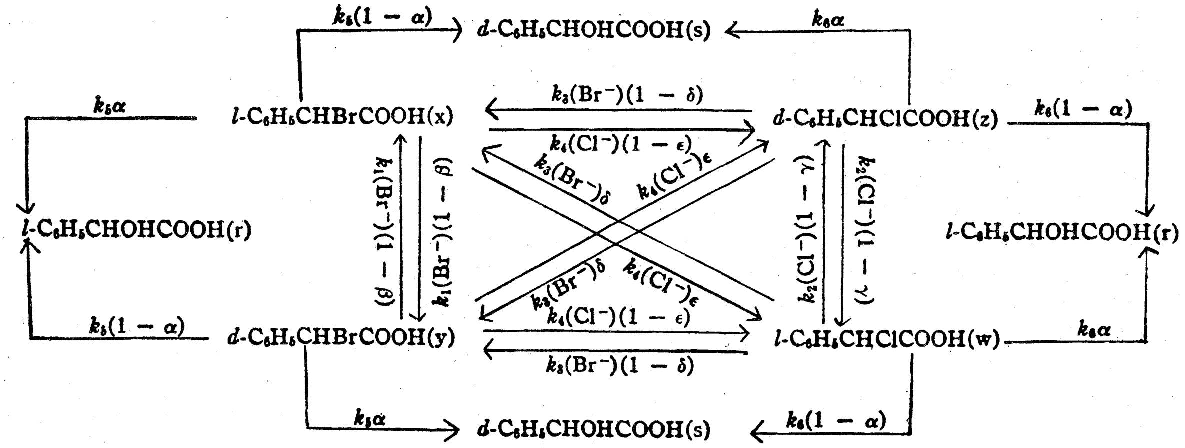

Fig. 2.—System of reactions occurring when *l*-phenylbromoacetic acid is treated with chloride ion in aqueous solution, assuming some substitution without inversion can occur.

experiments at 322.54°K. The curve calculated for $\epsilon = 0$ on which the experimental points have been superimposed is shown in Fig. 3. ($\Delta\theta$ is taken positive when the value for $\epsilon = 0$ is larger in absolute magnitude than that for $\epsilon \neq 0$.)

Since the average deviation of the experimental points from the calculated curve is 0.06 cm. with no trend, one can conclude that inversion is complete within the limits of detectability (5%). The rather large limits on ϵ are a result of the small value of A, the initial concentration of bromo acid, made necessary by its slow solubility. $\Delta\theta$ is directly proportional to A.

Discussion of Results

The results obtained are compared with those of Olson and Long[4] in Table X.

TABLE X

Reaction	Activation energy cal./mole Phenyl-acetic system	Succinic system	Δ	Collision number × 10^{-9} sec.$^{-1}$ moles^{-1} liters Phenyl-acetic system	Succinic system	Ratio
1 BrA + Br⁻	17,971	21,800	3829	3.13	14.9	4.76
2 ClA + Cl⁻	21,683	24,770	3087	4.74	8.42	1.78
3 ClA + Br⁻	20,016	23,540	3524	1.90	6.24	3.28
4 BrA + Cl⁻	19,805	23,650	3845	6.93	39.5	5.71

(1) The difference between the activation energies of the two series is nearly the same for all reactions, although it is somewhat larger for the bromo acids than for the chloro acids. This 3600 calories is a composite of the alterations in bond strength and resistance to inversion brought about by substituting $-CH_2COOH$ for C_6H_5 in the reacting molecule. Nothing quantitative can be said about the relative contributions of the two factors.

(2) The fact that the activation energy of the exchange reactions (the same for both within experimental error) is closer to that of ClA + Cl⁻ than to that of BrA + Br⁻ may mean that the unstable intermediate $(BrACl)^-$, where A is the rest of the molecule resembles $(ClACl)^-$ more closely than $(BrABr)^-$.

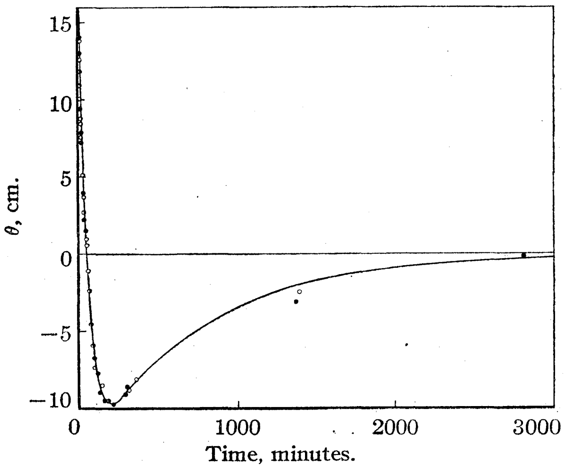

Fig. 3.—Angle of rotation plotted against time for the reaction between *l*-phenylbromoacetic acid and chloride ion in aqueous solution at 322.54°K.

(3) The collision numbers of reactions involving Cl⁻ are larger than those involving Br⁻, while those involving bromo acids are larger than those involving chloro acids, and the collision number of the exchange reaction BrA + Cl⁻ is larger than that of ClA + Br⁻ in the ratio one would expect from the two tendencies in combination.

A calculation of the total number of collisions for comparison with the observed collision number is somewhat arbitrary because of the uncertainty in collision diameter. The arbitrary selection of a value 1.75 times the length of the bond to be formed, leads to a steric factor of from $^1/_{40}$ to $^1/_{10}$. The face centered addition of X^- at C_6H_5CHY-COOH leads to an orientation factor of less than $^1/_2$ for $C_6H_5CHYCOOH$; solvation of X^- may introduce an additional orientation factor. Furthermore, one must take into account the efficiency of transfer between translational and vibrational energy which Rice[10] has found to vary widely from case to case. The most that one can say is, that there is nothing in the collision numbers to invalidate the given picture of the reaction.

The correlation between the kinetic and thermodynamic interpretations of a chemical equilibrium leads to a relation between the ratio of the collision numbers of the forward and reverse reaction and the standard entropy change. For reactions (3) and (4) this relation is

$$R \ln (A_4/A_3) = S^0(\mathrm{Br}^-) + S^0(\mathrm{Cl}A) - S^0(\mathrm{Cl}^-) - S^0(\mathrm{Br}A)$$

where S^0 is the molal entropy of the given substance when its concentration is 1 M in an ideal aqueous solution, based on $S^0(\mathrm{H}^+) = 0$ for comparison. Latimer, Schutz and Hicks[11] give 5.9 e. u. as the difference between $S^0(\mathrm{Br}^-)$ and $S^0(\mathrm{Cl}^-)$. Using this value, and the experimental values of A_4 and A_3 we calculate that the difference in entropy between solutions of l-BrA and l-ClA is 2.7 ± 1 e. u., a not unreasonable result.

Rice and Gershinowitz[12] have made use of the relation between entropy and collision number to develop a method for calculating the collision numbers of bimolecular associations. The reactions studied can be looked upon as being of this type followed by the almost instantaneous decomposition of the associated pentavalent carbon "complex." We have applied this method in calculating the collision numbers of the four reactions, omitting consideration of vibrational entropy, and calculating moments of inertia from rough geometrical models of the reactants. The results are shown in Table XI.

TABLE XI

	Reaction	$A \times 10^{-9}$ calcd.	$A \times 10^{-9}$ obsd.
(1)	l-$C_6H_5CHBrCOOH + Br^-$	3.22	3.13
(2)	l-$C_6H_5CHClCOOH + Cl^-$	6.43	4.74
(3)	l-$C_6H_5CHClCOOH + Br^-$	3.54	1.90
(4)	l-$C_6H_5CHBrCOOH + Cl^-$	6.33	6.93

Considering the nature of the calculation the agreement is striking. All of the features of the general reaction picture (inversion, face centered addition) have been included in the calculation and no additional ones.

Summary

The specific rates in aqueous solution of the following four reactions, at several temperatures in the interval 15–50°, have been determined.

(1) l-$C_6H_5CHBrCOOH + Br^- = d$-$C_6H_5CHBrCOOH + Br^-$

(2) l-$C_6H_5CHClCOOH + Cl^- = d$-$C_6H_5CHClCOOH + Cl^-$

(3) l-$C_6H_5CHClCOOH + Br^- \longrightarrow d$-$C_6H_5CHBrCOOH + Cl^-$

(4) l-$C_6H_5CHBrCOOH + Cl^- \longrightarrow d$-$C_6H_5CHClCOOH + Br^-$

It was shown that reaction 4, which alone provides information on this point, is accompanied by complete inversion in configuration, in accord with the theory.

The activation energies of the four reactions bear relations to each other similar to those in the corresponding reactions of the halogenosuccinic acids.

The collision numbers of the four reactions, considered from a kinetic viewpoint, are not in disagreement with what might have been predicted from the theory. They are in close agreement with values calculated by a statistical mechanical method embodying the essential features of the theory.

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[10] O. K. Rice, THIS JOURNAL, 54, 4558 (1932).

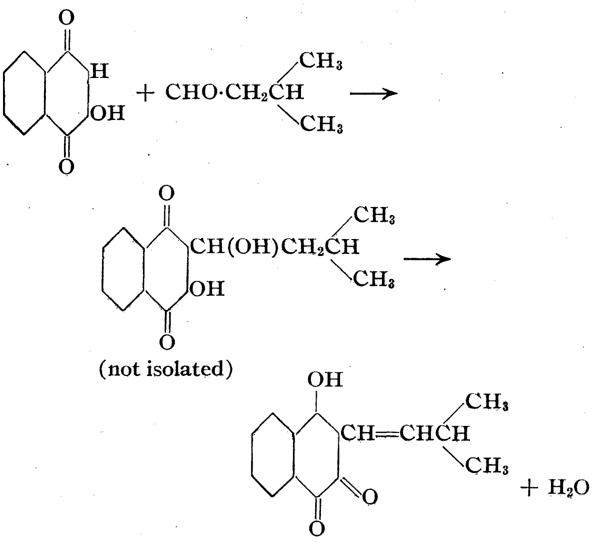
[11] W. M. Latimer, P. W. Schutz and J. F. G. Hicks, *J. Chem. Phys.*, 2, 82 (1934).

[12] O. K. Rice and H. Gershinowitz, *ibid.*, 2, 853 (1934).

Condensation of Aldehydes with β-Hydroxy-α-naphthoquinone. Synthesis of Hydrolapachol[1,2]

BY SAMUEL C. HOOKER

In the course of my researches on the constitution of lapachol and in hope of synthesizing this substance I studied in 1896 the interaction of isovaleraldehyde and 2-hydroxy-1,4-naphthoquinone,[3] and was thus led to a compound isomeric with lapachol which I was able to convert into several substances which I had previously obtained from lapachol itself, and which contained the full complement of carbon atoms. With these facts in mind the condensation was interpreted as follows:



(not isolated)

Iso-β-lapachol

It was originally thought that this condensation compound owing to its *red* color must be considered a derivative of β-naphthoquinone and it was referred to as iso-β-lapachol in consequence. Fieser,[4] who has examined many of the compounds obtained in my laboratory, has shown however that the reduction potential of iso-β-lapachol agrees very closely with that of derivatives of 2-hydroxy-1,4-naphthoquinone having

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(1) This is the first of a group of eleven papers reporting the results of investigations carried out by the late Dr. Samuel Cox Hooker (1864–1935) in continuation of his studies of lapachol, lomatiol, and related compounds as described for the most part in papers published in 1889–1896 in the *Journal of the Chemical Society*. The early investigations were resumed shortly after Dr. Hooker's retirement from the board of directors of the American Sugar Refining Company in 1915 and the work was continued to the time of his death on October 12, 1935 (see obituary sketch by Dr. C. A. Browne, *J. Chem. Soc.*, 550 (1936)). The papers have been assembled and prepared for purification by Dr. L. F. Fieser, of Harvard University, in whose care Dr. Hooker left the samples from all of his investigations. Dr. Fieser states that the collection includes a large supply of lapachol and a moderate amount of lomatiol, and that it was Dr. Hooker's intention that these be made available to other interested investigators.—THE EDITOR.

(2) Dr. Hooker had no intention of withholding the results accumulating in the course of twenty years of research, but he was reluctant to publish work on any one of the closely related problems until quite satisfied that all phases of the different investigations had been adequately explored. With one or two minor exceptions, this point had been reached at the time of his death and he had already prepared the manuscript for the theoretical part of several of the papers. Frequent periods of ill health and eventually death prevented him from completing the writing, but fortunately his observations had been recorded with such fluent expression and his records kept with such meticulous care that the experiments can be reported with complete accuracy, if not always in Dr. Hooker's own clear style.

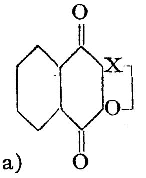
The theoretical part of the present paper, with the exception of the last paragraph, is taken from an original draft written by Dr. Hooker in 1934 and the second section of the experimental part, excepting the last paragraph, is likewise compiled almost entirely from original summaries. Dr. Hooker was assisted in the experiments by Dr. G. H. Connitt (1926–1927), Dr. C. A. Lear (1932–1933), and Dr. A. Steyermark (1934–1935). Four of the analyses were carried out by Dr. Connitt and the remainder were done by Dr. D. Price of Columbia University. Dr. Steyermark has been very helpful in collecting the notes.

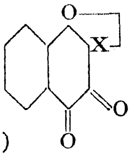
Certain statements in these papers cannot be properly appreciated without some explanation of the special and perhaps unique methods of identification and characterization which Dr. Hooker developed and on which he placed great reliance. Most of these involved the microscopic examination of crystals obtained in different ways, using merely a simple, low-powered instrument. In his "fusion test" a few granules of material are spread on a cover glass and barely fused over a small flame, giving characteristic crystalline patterns. An acidic substance is dissolved in 1% sodium hydroxide or other alkali and a drop of the solution allowed to evaporate on a slide and deposit crystals of the salt, or acidified under microscopic observation. A drop of a solution of the substance in concentrated sulfuric acid on being exposed on a slide absorbs moisture and deposits characteristic crystals, at first at the edges and then in the body of the solution. In Dr. Hooker's skilled hands these tests provided a means of making a positive identification which he felt was at least as reliable as a mixed melting point determination. Such microscopic examination proved to be of invaluable service in working with substances which when heated decompose rather than melt. The tests were also employed to advantage in following the progress of a reaction and in working out methods of purification and separation. In purifying small amounts of material, Dr. Hooker made much use of the "dry crystallization method." A dilute solution of the substance is allowed to go to dryness in an Erlenmeyer flask set in an inclined position with the liquid covering less than half of the bottom. Often the impurities are deposited in an outer ring while uncontaminated crystals of the substance appear at the lowest part of the vessel and can be detached and caught on the clean part of the flask after this has been rotated to the proper position. Very sensitive substances frequently can be crystallized satisfactorily by this method, the solution being prepared at room temperature. The homogeneity of a colored, acidic substance was tested to advantage by dusting a small amount of the powdered material onto the surface of 1% sodium hydroxide, when the presence of more than one compound often could be detected by a differential coloration of the solution. Dr. Hooker took full advantage of the beautiful color phenomena peculiar to the group of compounds under investigation, but many of his methods of experimentation can be applied quite generally. Of considerable importance in paving the way to discoveries was his habit of looking for any changes which might occur in solutions of his compounds or even in the solid state, often over long periods of time, and his practice of conducting reactions under the mildest conditions sufficient to effect a change.—L. F. FIESER.

(3) Hooker, *J. Chem. Soc.*, **69**, 1356 (1896).

(4) Fieser, THIS JOURNAL, **50**, 439 (1928).

similarly located side chains, and further that it agrees almost exactly with the values of lapachol and hydrolapachol, both of which are *yellow*. The reduction potential of iso-β-lapachol also agrees far better with the values determined for compounds of the general formula (a) derived from lapachol than it does with those obtained for substances of the general formula (b), having the ortho quinone group.

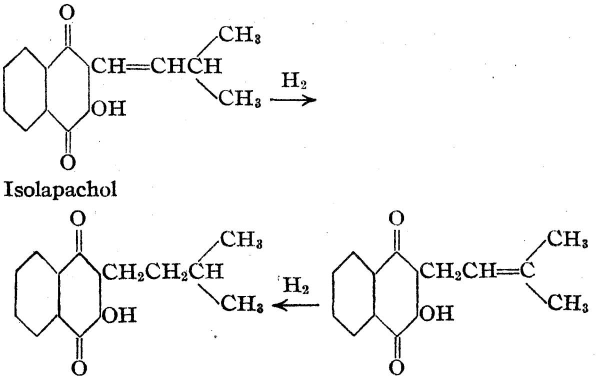

(a) Yellow


(b) Red

It would seem necessary therefore to accept for iso-β-lapachol the paraquinone structure as suggested by Fieser and the compound will in future be referred to as isolapachol. The *red* color of isolapachol, however, is not without significance and I shall return to its consideration later in another paper.

The study of the above condensation has been extended to a number of other aldehydes as the resulting compounds were required for an investigation on the oxidation of derivatives of 2-hydroxy-1,4-naphthoquinone. In most cases fairly uniform results have been obtained and the reaction has thus proved to be a general one.

Hydrocinnamaldehyde, phenylacetaldehyde, oenanthol, *n*-valeraldehyde, *n*-butyraldehyde, and propionaldehyde have all yielded compounds corresponding to isolapachol, which like it are much deeper in color than the previously known derivatives of 2-hydroxy-1,4-naphthoquinone. They vary from a deep orange or orange-red to a deep red in color, and all give intensely violet solutions with 1% alkali from which the sodium salts can be readily obtained in crystalline form. Hydrogen addition is easily effected by Roger Adams' method with platinum oxide–platinum black, the resulting substances affording ample proof of the structure assigned to the condensation products, as the latter are thus converted into compounds identical with the hydrogenation products of similar substances of known structure differing only from the condensation products in having the double bond in the chain located other than in the α,β-position. Thus isolapachol and lapachol yield the same compound, namely, hydrolapachol. Incidentally it may be noted that this step completes the synthesis of hydrolapachol.

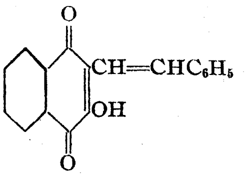


The other 2-hydroxy-1,4-naphthoquinone derivatives examined which have yielded identical compounds on hydrogenation are shown side by side in the following columns, the chains only being given.

$—CH{=}CHCH_2CH_3$	$—CH_2CH{=}CHCH_3$
$—CH{=}CHCH_3$	$—CH_2CH{=}CH_2$
$—CH{=}CHCH_2C_6H_5$	$—CH_2CH{=}CHC_6H_5$

The first column contains the chains of the aldehyde condensation compounds; the second those of compounds obtained by Fieser[5] in part by the Claisen rearrangement and in part by direct carbon alkylation. The identity of the hydrogenation products of the two sets of compounds leaves no doubt, therefore, as to the correctness of the interpretation of the aldehyde condensation. I am greatly indebted to Dr. Fieser for the substances represented in the second column which were hydrogenated in my laboratory.

In the earlier work[3] attention was called to the striking difference in color between the orange-red isolapachol and its yellow acetyl derivative. It was suggested at the time that acetylation may be attended with a change from a β- to an α-quinone group, but it is now recognized that both compounds very probably are α-quinones and that the difference in color is attributable to the effect of masking the free hydroxyl group. In order to extend the observations two additional acetyl derivatives were prepared. The first of these, 2-α-butenyl-3-acetoxy-1,4-naphthoquinone,



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[5] Fieser, THIS JOURNAL, **48**, 3201 (1926); **49**, 857 (1927).

is similarly yellow, in comparison with the red hydroxy compound from which it is derived. 2-β-Phenylvinyl-3-hydroxy-1,4-naphthoquinone is deeper in color (deep red) than the condensation products having completely aliphatic side chains (orange-red) or the chain $-CH{=}CHCH_2C_6H_5$ (orange), an effect doubtless attributable to the conjugation of the phenyl group with the chromophoric system. Acetylation in this case also was found to lighten the color, and the interesting observation was made that the acetyl derivative is capable of existing in two distinct modifications. The two forms are orange-yellow and bright red and they separate from the same solvents under similar conditions. The latter substance changes to the former on heating, and only one melting point is observed.

Experimental Part

1. Condensation of Aldehydes with 2-Hydroxy-1,4-naphthoquinone

Following a number of trials, 2-α-butenyl-3-hydroxy-1,4-naphthoquinone was most satisfactorily obtained by the following procedure, which served with minor changes for the other condensations investigated. Two grams of 2-hydroxy-1,4-naphthoquinone was dissolved in 35 cc. of hot glacial acetic acid, the temperature was brought to 80° and concentrated hydrochloric acid (2 cc.) was added, followed at once by *n*-butyraldehyde (5 cc.). The mixture was digested at 75–80° for one and one-half hours and poured into 200–300 cc. of water. After allowing several hours for the dark, resinous, partly crystalline material to collect, the aqueous solution was decanted through a filter, the oily residue was dissolved in 100 cc. of ether (or in benzene or ether–benzene) and the solution was extracted with 200 cc. of aqueous 1% sodium hydroxide solution. On acidifying the intensely violet alkaline extract a deep orange oil precipitated and gradually became crystalline. After washing and drying, the crude material (1.5 g.) was extracted with petroleum ether (b. p. 35–55°) in the Soxhlet apparatus. This left a brown, earthy residue and gave 1.1 g. of purified material as orange-red plates. The sample for analysis was recrystallized from alcohol.

In the condensation of hydroxynaphthoquinone with other aldehydes some variations in the proportions of the reagents and in the time of heating were found advisable, as indicated in Table I. The reaction can be followed readily by removing from the mixture during digestion a fraction of a drop, evaporating this to dryness, dissolving the residue in a drop of alcohol, and adding a drop of 1% alkali. As the condensation progresses the test solution becomes increasingly violet, and when the color ceases to increase in intensity the reaction may be assumed to be reasonably complete. The digestion is then stopped. The time varies with the different aldehydes from about fifteen minutes to one and one-half hours, and can be shortened and the yield slightly increased by using larger quantities of the aldehyde. As a general rule about five molecules of the aldehyde to one of the hydroxynaphthoquinone give satisfactory results.

Attempts to prepare condensation products under similar conditions from acetaldehyde and from isobutyraldehyde were unsuccessful. In the case of the latter aldehyde the reaction mixture was heated for a total of five hours, but

TABLE I

PREPARATION AND PROPERTIES OF THE CONDENSATION PRODUCTS

	For 2 g. hydroxynaphthoquine		Time of heating, min.			2-α-Alkenyl-3-hydroxy-1,4-naphthoquinones						
Aldehyde	Aldehyde, cc.	Concd. HCl, cc.		Yield in g., Crude	Pure	Alkenyl group	M. p., °C.	Crystalline form	Calcd., % C	H	Found, % C	H
Propionaldehyde	5	2	75	1.22[a]	0.56	α-Propenyl	135.2–135.7	Orange-red plates[b]	72.87	4.71	72.79	4.85
n-Butyraldehyde	5	2	90	1.5	1.1	α-Butenyl	107.5	Orange-red plates[b]	73.68	5.26	73.66 73.61	5.36 5.43
n-Valeraldehyde	6.4	6	37	1.2		α-Pentenyl	98–98.5	Orange-red needles	74.35	5.83	74.53	6.03
Heptaldehyde	12	10	25	1.6	1.1	α-Heptenyl	86.5	Orange-red needles, voluminously grouped; also as plates	75.30	6.69	75.28 75.55	6.68 6.66
Phenylacetaldehyde (50% alcoholic solution)	13.6	6	20	1.94	1.3	β-Phenylvinyl	166.5–167.5	Red scales, or small, heavy needles, or voluminous branches	78.23	4.38	77.99	4.56
Hydrocinnamaldehyde	7	10	90	1.6		γ-Phenyl-α-propenyl	140.5–141.5, dec.	Orange-red needles[c]	78.59	4.86	78.62	4.86

[a] By concentrating the benzene solution after extraction with alkali, brown, sword-shaped crystals of a by-product (0.2 g.) were obtained. Recrystallized from alcohol, the substance formed light yellow, arrowhead-shaped crystals, m. p. 160–160.5°. (Found: C, 84.87; H, 5.24; mol. wt., 241.4.)

[b] Best crystallized from petroleum ether; the material decomposes badly when crystallized in large lots from alcohol.

[c] The substance undergoes far-reaching changes when the crude material is crystallized from alcohol or benzene. Acetic acid gave better results but the recovery was less than 50%.

color tests made throughout this period failed to give any indication of the formation of a compound of the desired type. With acetaldehyde it appeared that a condensation product if formed is rapidly destroyed in the acid mixture.

The condensation products having aliphatic side chains are very soluble in benzene or acetone and somewhat less soluble in alcohol. A phenyl group decreases the solubility. Characteristic of all of the compounds is the intense violet color of their sodium salts, and distinctive patterns often can be observed by allowing a drop of the alkaline solution to evaporate under the microscope. Some decomposition usually occurs at the melting point.

The crystallization of the crude condensation products presents some difficulties for the quinones are subject to decomposition in solution, particularly in the presence of impurities. The crude materials may suffer extensive destruction when crystallized directly from alcohol or benzene, and it is best first to extract the products with petroleum ether. The purified substances then can be crystallized successfully from alcohol or benzene if care is taken to avoid undue heating or prolonged exposure of the solutions to the air. Even the most highly purified samples in time undergo far-reaching changes in contact with these solvents, and in a preliminary study of these changes carried out in conjunction with Dr. Steyermark it was found possible in some cases to isolate crystalline transformation products. Thus a solution of 1 g. of 2-γ-phenyl-α-propenyl-3-hydroxy-1,4-naphthoquinone in 45 cc. of benzene after standing with free access to the air for about four days deposited 0.04 g. of yellow needles which after recrystallization from benzene (sparingly soluble) melted at 227–228°, dec. The analyses are suggestive of a formula having one atom of oxygen more than the starting material (calcd. for $C_{19}H_{14}O_4$: C, 74.51; H, 4.57. Found: C, 73.95, 74.10; H, 4.61, 4.51) and it is perhaps safe to conclude that in this case an oxidation is involved. The substance is neutral, but it dissolves in boiling alkali and the yellow material is precipitated unchanged on acidifying the red, alkaline solution.

Yellow, neutral decomposition products were obtained from some of the unsaturated quinones in alcoholic solution but the substances have not been characterized. The propenyl compound, refluxed in alcoholic solution for about ten hours in the course of three days, gave in 10% yield a substance forming yellow prisms from benzene, m. p. 197–198°, dec., insoluble in cold alkali (found: C, 73.16, 73.20; H, 4.69, 4.81; mol. wt., 364). A solution of the butenyl compound in alcohol on standing for four months at room temperature deposited in 11% yield a yellow substance which formed yellow plates from dilute acetic acid, m. p. 207–208°, dec. (found: C, 70.63; H, 5.05). Like the other substances it is insoluble in cold alkali and dissolves on boiling to give a crimson solution.

2-α-Butenyl-3-acetoxy-1,4-naphthoquinone.—A mixture of 1 g. of 2-α-butenyl-3-hydroxy-1,4-naphthoquinone, 2 g. of fused sodium acetate and 20 cc. of acetic anhydride was boiled for three minutes, when the initially red solution had become brownish-yellow in color. The mixture was poured into water and the green oil which separated crystallized on standing overnight. The yield was quantitative. On crystallization from alcohol the substance formed bright yellow needles, m. p. 83.5–84.0°. The compound is insoluble in dilute alkali in the cold but it dissolves readily on boiling and the original hydroxyquinone is obtained on acidifying the solution.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.08; H, 5.22. Found: C, 71.28; H, 5.55.

2-β-Phenylvinyl-3-acetoxy-1,4-naphthoquinone.—This compound was prepared in good yield by the above procedure and crystallized from alcohol or from acetic acid. The substance crystallizes from these solvents either as orange-yellow needles or as bright red needles, the orange-yellow form being the more common. Both forms melt sharply at 138.7–139.2°, and it appears that the red form changes into the other modification before this temperature is reached, for on gentle heating the red needles become coated with small yellowish needles, making them appear opaque. Neither form contains solvent of crystallization, for a mixture of the two lost no weight on being heated at 130° for one-half hour. Both forms yield the original hydroxy quinone on alkaline hydrolysis and they impart a purple coloration to concentrated sulfuric acid. Both varieties become resinous on rubbing.

Anal. Calcd. for $C_{20}H_{14}O_4$: C, 75.45; H, 4.44. Found: C, 75.60; H, 4.56.

2. Hydrogenations

The condensation products are of the type $C_{10}H_4\left\{\begin{matrix}O_2\\ CH{=}\\ OH\end{matrix}\right.$ $CHCH_2X$ are deep orange in color and they dissolve in dilute alkalies to intensely violet solutions varying but little in tone. In these respects they differ materially from the compounds of the general type $C_{10}H_4\left\{\begin{matrix}O_2\\ CH_2CH_2CH_2X\\ OH\end{matrix}\right.$ into which they are readily converted by hydrogenation. These are yellow (occasionally golden brown when in fair sized crystals) and give solutions with alkalies of a claret red shade. These differences between the two classes of compounds enable the hydrogenation of very small quantities to be satisfactorily followed. The catalyst was prepared in accordance with the directions of Roger Adams and the hydrogenations were carried out in the cold, mostly in alcoholic solution at a pressure of 38–40 lb. (2.53–2.66 atm.). The time necessary varies from a few minutes to several hours, depending on the quantity and condition of the catalyst. To ascertain when the hydrogenation is complete, it is simply necessary to remove a trace of the solution from the pressure flask, allow it to evaporate to dryness, and redissolve the residue in a drop of 1% sodium hydroxide solution. If the oxidation of the hydroquinone group resulting from the action of the hydrogen has not already taken place by atmospheric oxygen during evaporation, it will be almost instantly effected in contact with the alkali. The hydrogenation may be considered complete as soon as the alkaline solution obtained is red without any trace of violet. A drop of dilute hydrochloric acid added to the alkaline solution also should yield a yellow precipitate instead of the orange one given by the substance before hydrogenation.

Hydrolapachol was first prepared by Monti[6] by the action of hydrogen in the presence of palladium black on the acetyl derivative of lapachol, followed by hydrolysis

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[6] Monti, *Gazz. chim. ital.*, **45**, II, 52 (1915).

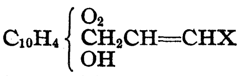
TABLE II

HYDROGENATION PRODUCTS

Substances hydrogenated, side chains	2-Alkyl-3-hydroxy-1,4-naphthoquinones						
	Alkyl group	M. p., °C.	Crystalline form	Calcd., %		Found, %	
				C	H	C	H
—$CH{=}CHCH_3$ —$CH_2CH{=}CH_2$	*n*-Propyl	100.5–101.5	Bright yellow, prismatic needles	72.19	5.60	72.11	5.80
—$CH{=}CHCH_2CH_3$ —$CH_2CH{=}CHCH_3$	*n*-Butyl	101–101.5	Radiating clusters of yellow needles	73.04	6.08	72.85	6.16
—$CH{=}CH(CH_2)_2CH_3$	*n*-Amyl	104–104.3	Long, yellow needles	73.73	6.61	73.69	6.72
—$CH{=}CHCH(CH_3)_2$ —$CH_2CH{=}C(CH_3)_2$	*i*-Amyl	93.5–94.5	Fine, silky needles	73.73	6.61	73.90	6.72
—$CH{=}CH(CH_2)_4CH_3$	*n*-Heptyl	82.7–83.3	Bright yellow plates	74.96	7.41	74.96	7.56
—$CH{=}CHC_6H_5$	β-Phenylethyl	171.5–172.5	Orange-yellow prismatic plates	77.67	5.07	77.56	5.26
—$CH{=}CHCH_2C_6H_5$ —$CH_2CH{=}CHC_6H_5$	Hydrocinnamyl	131.7–132.2	Golden-yellow plates	78.05	5.52	78.17	5.48

and exposure of the solution to the oxidizing action of the air. Fieser and Brodie[7] obtained hydrolapachol from lapachol itself by employing the method of hydrogenation of Roger Adams. A more detailed study of hydrolapachol has been undertaken here in order that the identity of the substance obtained by the hydrogenation of isolapachol might be established without doubt. Several lots of hydrolapachol have been prepared in my laboratory from lapachol with very satisfactory results by Adams' method, a yield of fully 97% being obtained. The reaction was carried out at room temperature, using 6 g. of lapachol in 100 cc. of alcohol and 0.2 g. of catalyst. The progress of the absorption may be followed and its end determined by removing a drop of the solution from time to time and allowing it to evaporate completely on a watch glass. As evaporation proceeds the hydroquinone is again oxidized and the residue on solution in concentrated sulfuric acid and subsequent dilution gives a *yellow* suspension when the hydrogenation is complete, in place of the *orange* β-lapachone which would be obtained from lapachol under like circumstances.

In preparing moderately large lots of hydrolapachol the oxidation of the hydroquinone may be advantageously hastened by drawing air through the alcoholic solution. After oxidation the solution was evaporated to about 50 cc. and cautiously diluted with water, the dilution being increased from time to time as crystallization proceeded. The fine, silky needles obtained were washed with 50% alcohol. Recrystallized, the substance melted constantly at 93.5–94.5°, a temperature considerably higher than that reported by Monti (87–89°) and by Fieser and Brodie (88–89°). Isolapachol, hydrogenated in the same manner, gave a substance identified by melting point, mixed melting point and all other properties, as hydrolapachol. In hydrogenating the synthetic compounds of the type


$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2CH{=}CHX\\ OH\end{array}\right.$

the progress of the reaction was followed by the color test with sulfuric acid, as in the case of lapachol.

The yields in the hydrogenation experiments were uniformly good and the quinones with reduced side chains were easily obtained in a pure condition, usually by crystallization from alcohol. 2-*n*-Propyl-3-hydroxy-1,4-naphthoquinone crystallized well from petroleum ether. The properties and analyses of the compounds are recorded in Table II. In those cases in which it is indicated that the same hydrogenation product was obtained from two different quinones, the identity was established by melting point and mixed melting point determinations and by a careful comparison of the crystalline forms and color reactions of the two substances.

Summary

1. The condensation of aldehydes with 2-hydroxy-1,4-naphthoquinone, which in the case of isovaleraldehyde resulted in the formation of isolapachol, is shown to be generally applicable to the preparation of corresponding alkenyl derivatives of hydroxynaphthoquinone, the alkenyl group being situated in the quinone ring adjoining the hydroxyl, and the double bond occupying the α,β-position in the chain.

2. It is shown that by the addition of hydrogen to the synthetic isolapachol the same product, namely, hydrolapachol, is formed as is obtained from the natural product, lapachol, under similar circumstances.

82 REMSEN STREET
BROOKLYN, NEW YORK

RECEIVED MARCH 11, 1936

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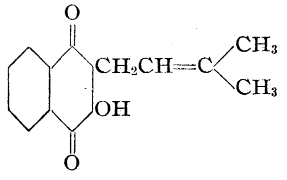
[7] Fieser and Brodie, THIS JOURNAL, 50, 449 (1928).

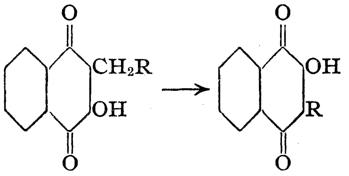
The Constitution of Lapachol and its Derivatives. Part IV.[1] Oxidation with Potassium Permanganate[2,3]

BY SAMUEL C. HOOKER

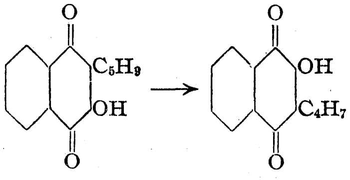
In the course of my researches on the constitution of lapachol, oxidation with alkaline permanganate was studied in anticipation of additional confirmation regarding the structure of the amylene chain in this compound. The results obtained were, however, entirely unexpected. Instead of helping substantiate in a simple way the conclusions I had reached, they themselves gave rise to a major problem, the solution of which has led to the discovery of a most interesting general reaction by means of which substances of the general formula (a) can be readily converted in good yield into others of the formula (b) with the elimination of CH_2 from the body of the chain, a conclusion which would be difficult to accept but for the very conclusive evidence I shall give in this and succeeding papers. In this way as a result of the action of alkaline permanganate on lapachol one carbon and two hydrogen atoms are removed, as indicated in the formulas:



Lapachol

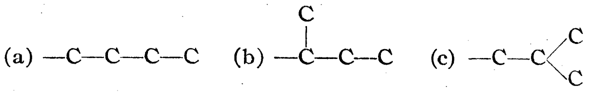


(a) (b)



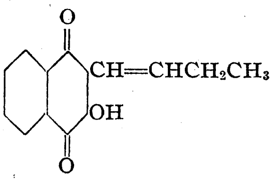
I II

That the oxidation product is still a derivative of hydroxynaphthoquinone can be demonstrated by the formation of hydroxynaphthoquinone itself therefrom by further oxidation. Moreover, in many of its reactions it parallels lapachol itself, including its ability to add on hydrogen. This unmistakably demonstrates the presence of a double bond in the side chain, as the resulting hydrogenated compound still shows the essential characteristics of a hydroxynaphthoquinone derivative. Now a chain C_4H_7 must have one of the following skeleton structures:

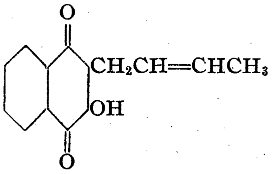


and I shall show that the last of these (c) is that present in the oxidation product.

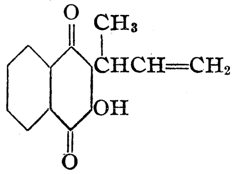
Of eight possible derivatives of hydroxynaphthoquinone having the unsaturated chain C_4H_7 in the β-position of the ring, three are known in addition to the lapachol oxidation product, namely, III, IV and V. Of these III has been prepared by the condensation of *n*-butyraldehyde with hydroxynaphthoquinone,[4] and IV and V were obtained by Dr. Louis F. Fieser in the course of his researches on the alkylation of hydroxynaphthoquinone,[5] to whom I am greatly indebted for samples of these substances which have considerably facilitated my work. By the hydrogenation of the above hydroxynaphthoquinone derivatives it is possible to determine the structure of the lapachol oxidation product. Thus, as I have



III



IV



V

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[1] Previous papers: Hooker, (a) *J. Chem. Soc.*, **61**, 611 (1892); (b) **63**, 1376 (1893); (c) **69**, 1356 (1896).

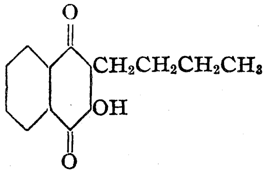
[2] See Editor's note (1) to the preceding paper.

[3] The theoretical part of this paper was written by Dr. Hooker in 1934 and only one or two minor changes have been made. The experimental part has been constructed from notes assembled by Dr. A. Steyermark. In the experimental work Dr. Hooker was in part assisted by Mr. J. G. Walsh, Jun., in the period 1893–1894, and by Dr. G. H. Connitt in 1927–1928. Isolated experiments were made by Mr. L. D. Gibson and Dr. A. Steyermark and certain of the analyses are by Dr. D. Price.—L. F. FIESER.

[4] Hooker, THIS JOURNAL, **58**, 1163 (1936).

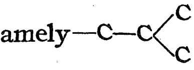
[5] Fieser, *ibid.*, **49**, 458 (1927).

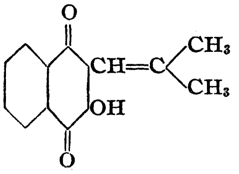
previously shown,[4] III and IV give the same compound, namely, VI, and as this differs from that



VI

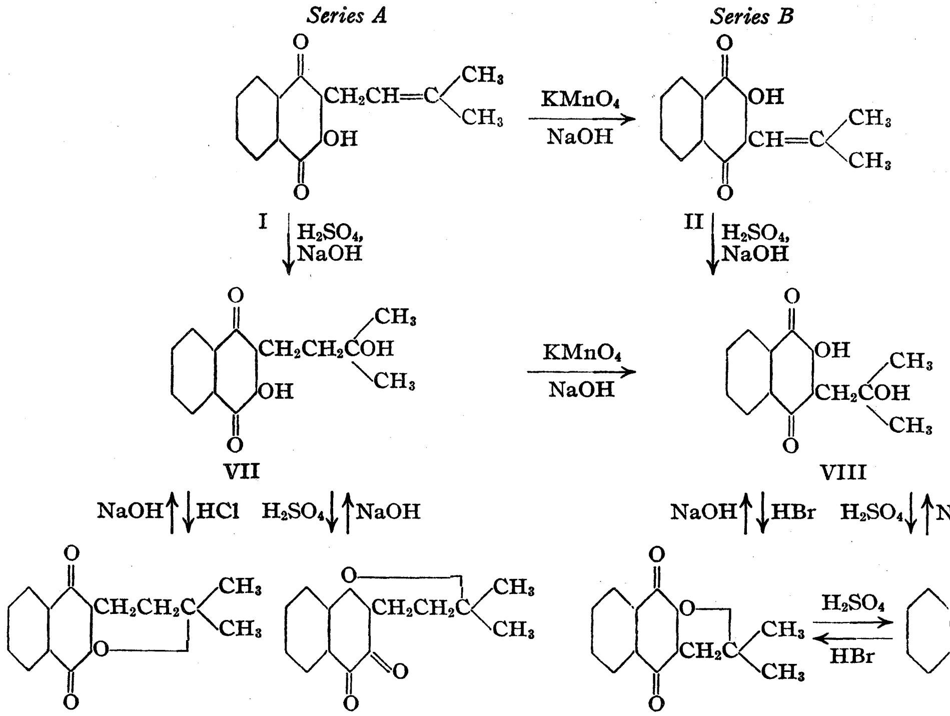
obtained by the addition of hydrogen to the lapachol oxidation product the latter cannot have the chain —$CH_2CH_2CH{=}CH_2$.

To V, I have likewise added hydrogen and the product also differs from that arising from the lapachol compound. There remains therefore for the chain of the latter only one possible skeleton, namely $\text{—C—C}\!\left\langle\begin{smallmatrix}C\\C\end{smallmatrix}\right.$, and as the double bond has taken no part in the oxidation it may be most reasonably assumed that no change has occurred in its position relative to the methyl groups. The oxidation product must therefore have the formula:



The position of the double bond is confirmed by the red color of the substance, as I have recently shown[4] that all 2-alkenyl derivatives of hydroxynaphthoquinone having the double bond in the α,β-position are deep orange to red, and that if the double bond is otherwise situated they are yellow. The formula thus assigned to the oxidation product necessitates the conclusion that CH_2 has disappeared from the body of the chain and has not been removed by oxidation from its extremity.

The following series of changes show the relations existing between lapachol (I) and its oxidation product (II). Substances can be produced from II having their exact counterpart in substances obtained under similar circumstances from I. The preparation, constitution and relationship to each other of the compounds in Series A were discussed by me many years ago;[1a,c] the compounds of Series B are now described for the first time.[6] (Among other transformations re-



IX X XI XII

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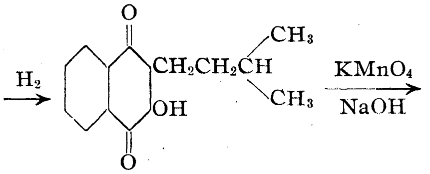
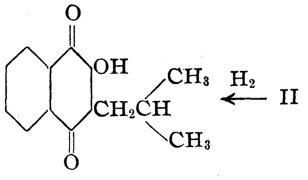
[6] Dr. Hooker did not assign names to compounds XI and XII or to a host of other ring compounds to be described in subsequent papers. On considering all of the various types of side rings, including variously substituted 5- and 6-membered saturated and unsaturated structures, and taking account of the desirability of correlating both α- and β-quinones with open-chain compounds such as VIII, I have decided to adopt the following nomenclature, which I believe would conform with Dr. Hooker's taste for simplicity and clarity (see next page).

ported in the experimental part is the formation from the substance II of a condensation product with *o*-phenylenediamine. The yield is not as good as in the case of lapachol,[1b] but it is of interest that some reaction occurs for under the same conditions the similarly constituted aldehyde condensation products[4] do not form azines.—L. F. F.)

Inasmuch as the attack of alkaline permanganate might be expected to occur at the double bond of the side chain of lapachol, it should again be emphasized that this bond takes no part whatever in the change. By reference to the above diagrammatic table it will be seen that VIII, which is formed by the action of alkali on XI and XII, also results from VII by oxidation with alkaline permanganate. Another example of this remarkable change is thus afforded and, as there is no double bond in the chain of VII, this is further evidence that the oxidation of I also occurs without reference to the double bond. Still another example is shown below.



XIII



XIV

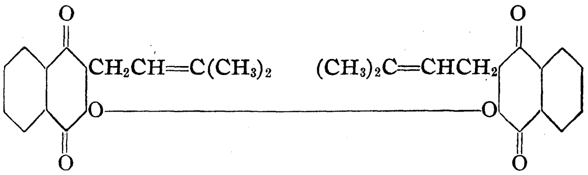
The above considerations and a study of the tables seem to leave no doubt as to the correctness of the formulas attributed to the alkaline permanganate oxidation products of lapachol and its derivatives. It remains therefore to attempt to explain how these compounds have been formed and to show how the carbon and hydrogen have been removed. I believe the following theory satisfactorily explains these changes.

Briefly, it may be assumed that in the course of the oxidation the first step is the splitting of the quinone ring, following which the ring is again formed. In the process of the new ring formation the carbon atom of the original ring attached to hydroxyl is eliminated as carbon dioxide, a carbon atom of the side chain takes its place and a new hydroxynaphthoquinone derivative is generated with the relative positions of hydroxyl and side chain reversed.

In a paper I hope to publish shortly I shall fully discuss the theory of this change and show that the reaction is applicable generally to derivatives of hydroxynaphthoquinone.

Addendum[7]

Lapachol Peroxide.—In connection with the above observations some study was made of the action of other oxidizing agents on lapachol. It was found that in acetic acid solution the hydroxyquinone is converted by lead peroxide into a neutral, sparingly soluble, yellow compound having the composition and molecular weight of a peroxide, XV. The peroxide is slowly attacked by boiling alkali and is in large part reconverted by the reagent into lapachol. 2-*n*-Amyl-3-hydroxy-1,4-naphthoquinone forms a peroxide on similar treatment with lead peroxide, while hydroxynaphthoquinone is converted only into a lead salt.



XV

Experimental Part

The lapachol required for this and other investigations was obtained largely from logs of Surinam Greenheart apparently very rich in the pigment and known in the trade as Bethabarra wood. The wood was reduced by various mills in turn to planks, to chips, and to a powder, but, as the fine sawdust did not allow the free passage of extracting solution, a mixture of 1140 lb. (518 kg.) of the ground wood with 614 lb. (279 kg.) of coarser planings of similar wood was used. This was charged in portions into a stoneware percolator and extracted with warm 1% sodium carbonate solution. The crude material which precipitated on acidification was collected and washed in a filter

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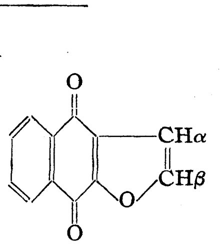

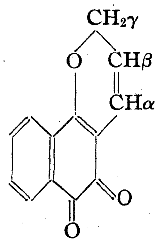

Furano-1,4-naphthoquinone Pyrano-1,2-naphthoquinone

Compound XI is thus β,β-dimethyldihydrofurano-1,4-naphthoquinone; β-lapachone (X) is γ,γ-dimethyldihydropyrano-1,2-naphthoquinone.—L. F. F.

(7) Dr. Hooker left no instructions regarding the publication of this material. The work was carried out with the experimental assistance of Dr. A. Steyermark.—L. F. F.

press. The dried solid contained 60–70% of lapachol, which was easily extracted with benzene from an insoluble resin.

Permanganate Oxidations[8]

(a) **Lapachol.**—Ten grams of lapachol was dissolved in 1 liter of 1% sodium hydroxide solution and the red solution was cooled to about 0°. A solution of 10 g. of potassium permanganate in 1 liter of water was cooled to about 0° and added quickly in one portion to the lapachol solution. The mixture immediately became green and then changed to olive-green and to brown, and finally manganese dioxide separated leaving the solution almost colorless. The faintly pink supernatant solution became more strongly red on standing. After three to four hours the solution was filtered from the manganese dioxide and the now red solution was acidified. Orange-red needles separated slowly and after several hours the collected material amounted to 4–4.5 g. This material was found to consist largely of 2-β,β-dimethylvinyl-3-hydroxy-1,4-naphthoquinone, contaminated with some unchanged lapachol and with small amounts of other oxidation products. A separation was accomplished by fractional precipitation from 0.25–1% alkali. The lapachol was precipitated first, followed by the main reaction product. The mother liquor, after further acidification, yielded a small amount of an orange substance, and on concentrating the solution a colorless compound and some phthalic acid were obtained. The by-products were not further investigated.

2 - β,β - Dimethylvinyl - 3 - hydroxy - 1,4 - naphthoquinone (II) was obtained in yield of about 3.3 g. Crystallized from alcohol, in which it is readily soluble, the substance forms red needles melting at 119–120°. The quinone also dissolves readily in benzene or glacial acetic acid. It dissolves in cold dilute alkali to form a reddish-purple solution from which the material may be recovered unchanged on acidification.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.26. Found (Hooker): C, 73.60; H, 5.28.

The acetyl derivative was prepared by boiling for one to two minutes a mixture of the hydroxyquinone (10 g.), fused sodium acetate (10 g.), and acetic anhydride (25 cc.) and pouring it into 700 cc. of cold water. The crude product was digested for a few minutes with cold 0.25% alkali in order to extract some unacetylated material (0.92 g.) and the residue was dried and crystallized from benzene–petroleum ether and finally from alcohol. The substance forms yellow prisms, m. p. 85.5–86°. It can be hydrolyzed with boiling alkali and yields the original quinone. The solution in concentrated sulfuric acid is at first crimson, but changes almost instantly to purple, violet and finally a rich blue.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.11; H, 5.18. Found (Walsh, Hooker): C, 70.67, 71.15; H, 5.35, 5.23.

The eurhodol (eurhodone?) derivative of II was prepared as follows. A mixture of 1 g. of the oxidation product, 0.86 g. of *o*-phenylenediamine hydrochloride, 3 g. of crystalline sodium acetate, and 20 cc. of glacial acetic acid was heated on the steam-bath for one and one-quarter hours, during which time the color of the solution changed from red to brown and orange-brown prisms were deposited. After cooling, the solid was collected and washed with 50% acetic acid, with water, with cold 0.25% alkali to remove unchanged material, and with water; yield, 0.6 g. Dilution of the mother liquor gave chiefly the starting material, mixed with some condensation product. The reaction product crystallized from alcohol (200 cc. per g.) in the form of amber prisms melting at 226–227° with decomposition.

Anal. Calcd. for $C_{20}H_{16}ON_2$: C, 79.96; H, 5.37. Found (Price): C, 80.39; H, 5.16.

The experiment was repeated several times using up to 25% excess of the diamine, but without material increase in the yield. In the case of lapachol the condensation product is formed in practically quantitative yield. On the other hand 2-α-butenyl- and 2-β-phenylvinyl-3-hydroxy-1,4-naphthoquinone[4] did not condense with *o*-phenylenediamine after several hours of heating. It would seem that a double bond in the α,β-position of the side chain inhibits or even prevents this type of reaction. Another difference is that the azine derivative of lapachol is dark red, and perhaps is to be regarded as a eurhodone;[1b] the condensation product from the oxidation product II is amber-yellow, a possible indication that it has the alternate structure of a eurhodol.

(b) **Hydroxyhydrolapachol (VII).**—A solution of 1 g. of hydroxyhydrolapachol[1a,c] in 100 cc. of 15% sodium hydroxide solution was cooled under the tap and treated as quickly as possible in one operation with a solution of 1 g. of potassium permanganate in 100 cc. of water. The color changes were as described above, and after three hours the filtered, red solution was acidified. The material first formed an emulsion and then became crystalline. The yield of nearly pure material was 0.71–0.73 g. **2-β-Hydroxyisobutyl-3-hydroxy-1,4-naphthoquinone (VIII)** dissolves readily in alcohol or benzene and crystallizes from these solvents in the form of silky, yellow needles, m. p. 121–122°.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.29; H, 5.69; mol. wt., 246.1. Found (Hooker, Connitt): C, 68.24; H, 5.70; mol. wt., 257.6 (av. of 6 determinations).

(c) **Hydrolapachol (XIII).**—One-half gram of hydrolapachol[4] was immersed in 50 cc. of 10% alkali, stirred, broken up and shaken until the whole appeared to be converted into the sodium salt which however did not all dissolve. The solution containing suspended matter was cooled in ice and 0.5 g. of potassium permanganate dissolved in 50 cc. of water, also ice cold, was quickly added. After standing about half an hour the manganese dioxide was filtered off and the deep claret red solution was rendered slightly acidic. This caused the separation of a bright yellow emulsion which soon gave way to microscopic needles; yield 0.34 g.

By one crystallization from alcohol the **2-isobutyl-3-hydroxy-1,4-naphthoquinone (XIV)** was obtained in bright yellow needles melting at 132–133°.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.04; H, 6.08. Found (Connitt): C, 72.73; H, 5.98.

In another experiment hydrolapachol was dissolved in 1% alkali and oxidized under conditions otherwise similar

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[8] Quinones having saturated side chains are best oxidized in a strongly alkaline solution, while dilute alkali gives better results with the unsaturated compounds. Further observations regarding the optimum conditions are given in later papers.—L. F. F.

to those above. Only a very small yield of isobutylhydroxynaphthoquinone was obtained and an odor strongly suggestive of butyric acid was noticed.

It was afterward found that in oxidations of this type necessitating the use of strongly alkaline solutions it is best to dissolve the substance to be oxidized in dilute alkali, adding the remaining alkali required to the permanganate solution. In this way substances usually are readily dissolved.

Structure of the Lapachol Oxidation Product (II)

Hydrogenation.—The oxidation product, 2-β,β-dimethylvinyl-3-hydroxy-1,4-naphthoquinone (5 g.) was hydrogenated in alcoholic solution (100 cc.) in the presence of Adams catalyst (0.2 g.). The filtered solution was allowed to stand overnight with access of air and on concentration it yielded yellow needles of 2-isobutyl-3-hydroxy-1,4-naphthoquinone (XIV); total yield, 4.25 g. Recrystallized from alcohol it formed yellow needles, m. p. 132.5–133.5°.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.04; H, 6.08; mol. wt., 230.1. Found (Connitt): C, 72.72; H, 6.07; mol. wt., 226.2, 227.4, 226.1.

The substance gave no depression in melting point when mixed with the oxidation product obtained from hydrolapachol, but a considerable depression of the melting points of 2-*n*-butyl-3-hydroxy-1,4-naphthoquinone[4] and of 2-*s*-butyl-3-hydroxy-1,4-naphthoquinone (see below) was noted.

2-*s*-Butyl-3-hydroxy-1,4-naphthoquinone.— 2-α-Methylallyl-3-hydroxy-1,4-naphthoquinone[5] on hydrogenation as above gave in good yield a substance which crystallized from dilute alcohol in the form of yellow needles melting at 92.5–93°.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.04; H, 6.08. Found (Connitt): C, 72.93; H, 6.06.

Oxidation.—A solution of 2 g. of 2-β,β-dimethylvinyl-3-hydroxy-1,4-naphthoquinone in 200 cc. of 1% sodium hydroxide solution was cooled to 3° and treated quickly with 2 g. of potassium permanganate in 200 cc. of cold water (1°). After one and one-half hours the filtered, red-brown solution was acidified to faint turbidity, when 0.1 g. of unchanged starting material separated. On adding an excess of hydrochloric acid the filtrate soon became cloudy and after standing deposited a dark brown precipitate which was discarded. The filtrate was made faintly alkaline with sodium carbonate and evaporated to a volume of 212 cc. A brown scum, which increased in amount on standing, was removed after two days and the solution on being acidified then yielded 0.42 g. of 2-hydroxy-1,4-naphthoquinone. On further evaporation as before an additional amount (0.16 g.) was obtained. Recrystallized from alcohol the product was obtained in the form of light brownish-yellow plates melting at 189.5–190.5°, dec. The substance showed no depression when mixed with an authentic sample of the quinone, m. p. 190–191°, dec.

Ring Compounds from 2-β,β-Dimethylvinyl-3-hydroxy-1,4-naphthoquinone (II)

The following is an account of the transformations summarized in part by the formulas in Series B in the above chart. The correctness of the 5-membered ring formulas, as in XII, is established by observations which will be presented in a later paper. A substance of the same carbon skeleton as XII but having a 6-membered oxide ring has been prepared in my laboratory and it is not identical with XII but is an isomer of this substance.

β,β - Dimethyldihydrofurano - 1,2 - naphthoquinone (XII).—Five grams of the unsaturated oxidation product (II) was dissolved in 25 cc. of cold, concentrated sulfuric acid, and after standing for a few minutes the brownish-red solution was poured into 600 cc. of cold water. The cyclic compound separated as a red, crystalline precipitate in quantitative yield. Crystallized from alcohol the compound formed deep red needles melting at 186.5–187°. An identical product was obtained from 2-β-hydroxyisobutyl-3-hydroxy-1,4-naphthoquinone (VIII) by allowing a solution of 10 g. of the quinone in 25 cc. of concentrated sulfuric acid to stand at room temperature for one-half hour and pouring the solution into water; yield, 9.3 g. (deep red needles from benzene, m. p. 187–188°).

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.26. Found (Walsh, Hooker): C, 73.12, 73.55; H, 5.39, 5.28.

The oxide ring of the ortho quinone is easily cleaved by alkali. On boiling a mixture of 0.24 g. of the substance XII with 18 cc. of 1% sodium hydroxide solution the material nearly all dissolved. The red solution was cooled, filtered, and acidified with acetic acid, giving a yellow oil which soon gave rise to yellow crystals. After reprecipitation from dilute alkali the material melted at 118.5–120° and proved to be identical with the dihydroxyisobutylnaphthoquinone (VIII) obtained by other methods.

The azine of XII was prepared (a) by heating the components in glacial acetic acid for one and one-quarter hours on the steam-bath (0.1 g. yielded the same weight of product), and (b) by dissolving 0.3 g. of the eurhodol of II in concentrated sulfuric acid and pouring the yellow-green solution into water. In the latter case the azine precipitated in the form of an orange-red sulfate, from which the free base was recovered by rendering the suspension alkaline and warming it on the steam-bath (yield, 0.3 g.). The azine dissolves in alcohol to give an orange solution with a green fluorescence, and the compound crystallizes as golden yellow needles, m. p. 154–155°.

Anal. Calcd. for $C_{20}H_{16}ON_2$: C, 79.96; H, 5.37. Found (Price): C, 79.88; H, 5.42.

2-β-Chloroisobutyl-3-hydroxy-1,4-naphthoquinone.—The oxide ring of the red ortho quinone XII can be opened by the action of hydrochloric acid in such a way as to give the chloro compound. Thus 1.4 g. of the compound was dissolved in 42 cc. of a mixture of equal volumes of concentrated hydrochloric acid and water and the deep red solution was heated at 50–55° for one hour and then at 60–65° for an additional half-hour. Yellow crystals were deposited during the heating, and after cooling the mixture these were collected on glass wool and washed with dilute hydrochloric acid followed by water. The chloro compound was crystallized from alcohol, forming bright yellow scales melting at 147–148° with decomposition. Prolonged heating of the alcoholic solution decomposes the substance. The compound dissolves readily in cold dilute alkali, giving a red solution. With concentrated sulfuric acid it slowly evolves hydrogen chloride.

Anal. Calcd. for $C_{14}H_{13}O_3Cl$: C, 63.51; H, 4.91; Cl, 13.42. Found (Walsh): C, 63.00; H, 4.79; Cl, 12.83.

β,β - Dimethyldihydrofurano - 1,4 - naphthoquinone (XI).—By the action of hydrogen bromide the red ortho quinone XII can be isomerized to the yellow para quinone XI. Probably the oxide ring first opens to give the hydroxy compound VIII, with subsequent ring closure in a different direction. To bring about the transformation 1.87 g. of β,β-dimethyldihydrofurano-1,2-naphthoquinone (XII) was dissolved in 18.7 cc. of hydrobromic acid (sp. gr. 1.49) and the red solution was heated at 65–69° for thirty-five minutes. On cooling, the reaction product was deposited in the form of greenish-yellow crystals which, when washed with concentrated hydrochloric acid and with water and dried, weighed 1.38 g. An additional 0.21 g. was obtained on diluting the mother liquor with water after it had stood for two weeks. The compound formed light yellow scales from alcohol, m. p. 183–184°.

The yellow quinone was also obtained as follows from 2 - β - hydroxyisobutyl - 3 - hydroxy - 1,4 - naphthoquinone (VIII). One gram of the material was made into a paste with a mixture of 15 cc. of concentrated sulfuric acid and 85 cc. of water and this was refluxed for one-half hour. The substance was first converted into red crystals of the ortho quinone (XII), which were slowly converted into yellow masses of the para quinone (XI). The yield was 0.88–0.89 g. and on crystallization from benzene the substance formed heavy yellow crystalline masses, m. p. 183–184°.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.26. Found (Walsh, Hooker): C, 73.17, 73.69; H, 5.42, 5.31.

The substance was also prepared by refluxing the dihydroxy compound VIII with equal volumes of concentrated hydrochloric acid and water.

β,β-Dimethyldihydrofurano-1,4-naphthoquinone (XI) can be converted into the dihydroxy compound VIII by short boiling with 1% alkali, followed by acidification with acetic acid. The yield of reprecipitated material, m. p. 118.5–120° was 0.72 g. from 0.75 g. A conversion of the para quinone into the ortho quinone XII was accomplished by allowing a solution of the material in concentrated sulfuric acid to stand for one hour at room temperature and pouring the solution into water. The product, obtained in quantitative yield, melted at 186–187°.

Lapachol Peroxide

A solution of 10 g. of lapachol in 100 cc. of glacial acetic acid was heated to boiling, the source of heat was removed, and 10 g. of lead peroxide was added. The hot mixture was shaken for a minute or two and filtered to remove oxides of lead, and the filtrate on cooling very slowly deposited large yellow crystals of the peroxide. Collected after six days this amounted to 2.7 g., and an additional 0.6 g. of crystalline material separated after diluting the mother liquor with 40 cc. of water. Lapachol peroxide crystallizes from glacial acetic acid as heavy, orange-yellow prisms melting at 154–155°. Some decomposition occurs on crystallization from alcohol or benzene.

Anal. Calcd. for $C_{30}H_{26}O_6$: C, 74.68; H, 5.39; mol. wt., 482.0. Found (Price): C, 74.33; H, 5.38; mol. wt., 467.0, 470.6.

When a suspension of 0.5 g. of the finely powdered peroxide was boiled with 50–60 cc. of 1% sodium hydroxide solution the material dissolved completely in about five minutes. On acidifying the red solution a crystalline yellow precipitate consisting of nearly pure lapachol (0.4 g.) was obtained. Extraction of the mother liquor with ether gave only resinous material.

Treated with lead peroxide in the same manner, 2-*n*-amyl-3-hydroxy-1,4-naphthoquinone (1 g.) gave a crystalline yellow product (0.6 g.) closely resembling lapachol peroxide. The crude material melted at 113–114° and one crystallization from dilute acetic acid gave crystals melting at 117–118°. The substance partially decomposed on further crystallization and it was not analyzed.

Summary

Lapachol has been found to undergo a remarkable change when submitted to reaction with cold alkaline permanganate. The double bond in the side chain —$CH_2CH{=}C(CH_3)_2$ remains undisturbed and a hydroxyquinone is formed which differs from the starting material only in that CH_2 has been removed from the body of the side chain, which has become —$CH{=}C(CH_3)_2$. The structure of the oxidation product is fully established by comparison of its hydro derivative with known compounds and by a number of transformations parallel to those of lapachol. The observation that hydrolapachol and hydroxyhydrolapachol similarly lose CH_2 from the side chain on oxidation shows that the double bond plays no part in the transformation and indicates that the reaction is a general one. It is suggested that the quinone ring opens in the course of the reaction and closes in a different position.

82 REMSEN STREET
BROOKLYN, NEW YORK

RECEIVED MARCH 11, 1936

On the Oxidation of 2-Hydroxy-1,4-naphthoquinone Derivatives with Alkaline Potassium Permanganate[1,2]

BY SAMUEL C. HOOKER

I have shown in a recent paper[3] on the constitution of lapachol that the following extraordinary changes are brought about by oxidation with alkaline potassium permanganate:

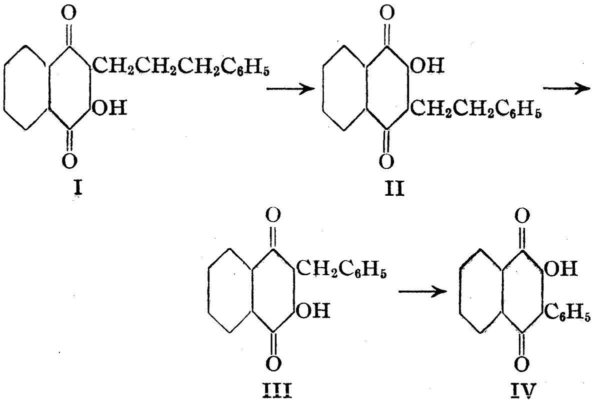
$$(1)\quad C_{10}H_4O_2\left\{\begin{array}{l}CH_2CH_2CH(CH_3)_2\\ OH\end{array}\right.\ \text{becomes}\ C_{10}H_4O_2\left\{\begin{array}{l}OH\\ CH_2CH(CH_3)_2\end{array}\right.$$

$$(2)\quad C_{10}H_4O_2\left\{\begin{array}{l}CH_2CH{=}C(CH_3)_2\\ OH\end{array}\right.\ \text{becomes}\ C_{10}H_4O_2\left\{\begin{array}{l}OH\\ CH{=}C(CH_3)_2\end{array}\right.$$

$$(3)\quad C_{10}H_4O_2\left\{\begin{array}{l}CH_2CH_2COH(CH_3)_2\\ OH\end{array}\right.\ \text{becomes}\ C_{10}H_4O_2\left\{\begin{array}{l}OH\\ CH_2COH(CH_3)_2\end{array}\right.$$

The full discussion of the mechanism involved I have reserved for the present paper.

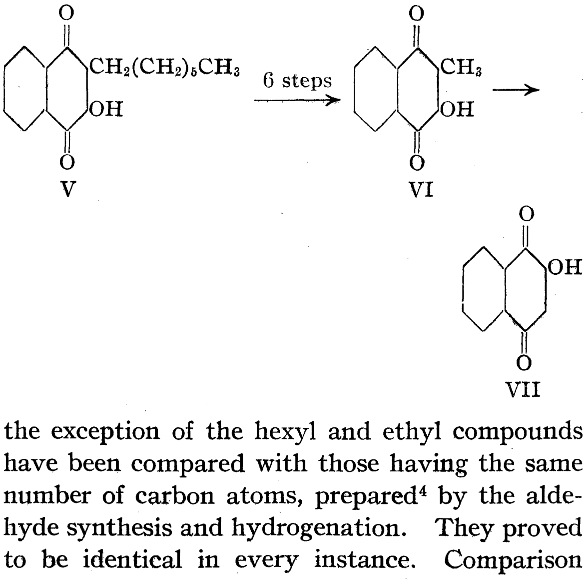
In view of the varied chains from which CH_2 was eliminated as shown in the above examples, the conclusion seemed inevitable that the reaction would prove to be a general one, and further study has fully confirmed this anticipation. Thus through successive oxidations the following compounds have been prepared from 2-γ-phenylpropyl-3-hydroxy-1,4-naphthoquinone:



I II III IV

The starting material (I) was prepared by the hydrogenation of the condensation product of hydrocinnamaldehyde with hydroxynaphthoquinone, and the first oxidation product (II) proved to be identical with the quinone similarly obtained[4] from the condensation product from phenylacetaldehyde. The product of the second oxidation (III) was compared directly and found to be identical with 2-benzyl-3-hydroxy-1,4-naphthoquinone,[5] kindly sent to me by Dr. L. F. Fieser. The final product (IV) is undoubtedly identical with "β-phenylhydroxynaphthoquinone" of Zincke.[6]

In another series of experiments starting with *n*-heptylhydroxynaphthoquinone (V) CH_2 has been removed step by step passing through hexyl-, pentyl-, butyl-, propyl-, ethyl-, and methyl-hydroxynaphthoquinone until finally hydroxynaphthoquinone itself has been reached. This series of oxidations has yielded substances which with the exception of the hexyl and ethyl compounds have been compared with those having the same number of carbon atoms, prepared[4] by the aldehyde synthesis and hydrogenation. They proved to be identical in every instance. Comparison was not made in the case of the hexyl compound because hexyl aldehyde was not commercially available, and, as it was not possible to obtain a condensation product of the required type with acetaldehyde, comparison was made with the ethyl product prepared by the hydrogenation of



V VI VII

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[1] See Editor's note (1), THIS JOURNAL, **58**, 1163 (1936).

[2] The theoretical part of this paper, the summary, and the last section of the experimental part are reproduced essentially as they were written by Dr. Hooker in 1934, although it has seemed expedient to rearrange some of the material. The experiments were carried out largely by Dr. A. Steyermark, who has been of great assistance in collecting the data. Dr. C. A. Lear also contributed to the experimental work, and the analyses were all done by Dr. D. Price of Columbia University.—L. F. FIESER.

[3] Hooker, THIS JOURNAL, **58**, 1168 (1936).

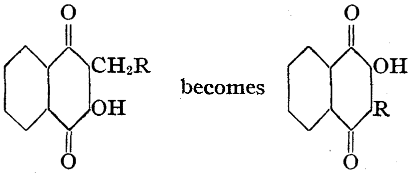
[4] Hooker, *ibid.*, **58**, 1163 (1936).

[5] Fieser, *ibid.*, **48**, 3201 (1926).

[6] Zincke and Breuer, *Ann.*, **226**, 32 (1884); Zincke, *ibid.*, **240**, 140 (1887).

the vinyl compound[7] resulting from the oxidation of 2-allyl-3-hydroxy-1,4-naphthoquinone. The next to last oxidation product, 2-methyl-3-hydroxy-1,4-naphthoquinone (VI), was compared directly and found to be identical with synthetic phthiocol,[8] kindly sent to me by Professor R. J. Anderson. The final product of the reaction was fully identified as 2-hydroxy-1,4-naphthoquinone, a result which shows clearly that the new reaction can be extended for the purpose of eliminating completely a saturated radical attached to the quinone group.

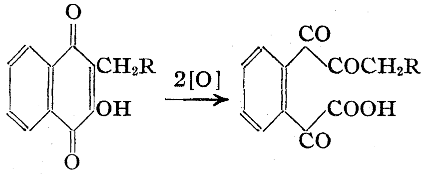
Stated generally, by suitable oxidation with alkaline potassium permanganate



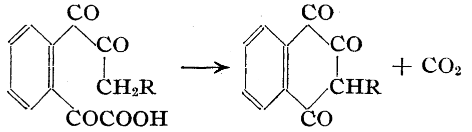
The conditions most suitable for bringing about the transformation are more clearly defined in the experimental part of the present paper. For the oxidation of quinones having saturated side chains a rather strongly alkaline solution is required and the reaction is conducted at 0–5°. The quantity of permanganate used is sufficient to supply two atoms of oxygen to the molecule of the hydroxyquinone plus 5%. In carrying out the reaction, solutions of the hydroxyquinone in 1% alkali and of the permanganate in 10% alkali are cooled in ice and quickly mixed. In the course of the reaction the crimson solution of the sodium salt of the hydroxynaphthoquinone derivative becomes *almost colorless* as manganese dioxide is being deposited. In a short time, varying somewhat with the substance oxidized, sometimes very rapidly, *the solution again becomes more or less intensely crimson.* On acidification of the filtered solution the oxidation product is obtained in a crystalline, usually yellow condition. The purity of the oxidation product is excellent and the yield generally ranges from 70 to over 80% of the weight of the material taken. It has been found in some cases that still better yields may be obtained by increasing the concentration of alkali, and conversely a decrease in the alkalinity may result in diminished yields.

The above remarks and method of procedure apply to derivatives with saturated chains. In oxidizing those with a double bond in the chain it has proved desirable to use a much less strongly alkaline medium. In this case the permanganate is dissolved in water containing no alkali and in other respects the procedure is the same. The yields are considerably less, ranging from 35–40% of the material oxidized as a maximum in the substances examined, and may be much smaller. If the double bond now occupies the α,β-position the substance obtained varies in color from deep orange to red instead of being yellow.

The oxidation appears to take place in at least three stages, as follows: (1) The hydroxyquinone ring probably is split thus:

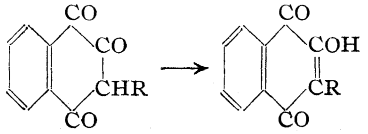


(2) A six-membered ring is again formed, the carbon originally attached to hydroxyl, however, being eliminated as carbon dioxide and the carbon in the α-position in the chain entering into the ring:



The ring as first formed probably has no double bonds, as the compound appears to be colorless, or nearly so. Whether the carbon dioxide is eliminated at the time of the formation of the ring or before or subsequent to its formation can only be surmised, as it has not yet been possible to isolate the intermediate compound or compounds.

(3) By tautomeric change the colorless compound becomes a hydroxynaphthoquinone derivative:



As the oxygen supplied by the permanganate up to the formation of manganese dioxide is sufficient only for the opening of the ring, it was originally thought that the oxidation is effected first by the oxygen derived from the permanganate and then, corresponding to the reddening of the

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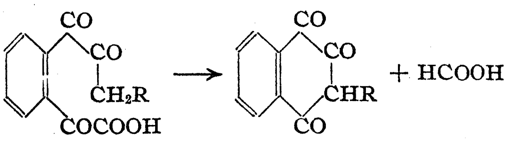
[7] Details of experiments conducted in conjunction with Dr. Al Steyermark will be recorded in another paper describing the formation of this compound by permanganate oxidation of the allyl derivative.

[8] Anderson and Newman, *J. Biol. Chem.*, **103**, 197, 405 (1933); Anderson, Crowder and Newman, *ibid.*, **105**, 279 (1934).

colorless solution, by oxygen of the air. This view was found to be incorrect, as the same changes occurred in an atmosphere of nitrogen. It was also shown that the reddening of the solution takes place equally readily after removal of the manganese dioxide by filtration, and oxidation by the dioxide at this stage was thus eliminated as a possibility.

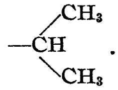
Ring closure without oxidation was also considered for the second stage, but a careful search for formic acid failed to yield any evidence of its presence, both when reddening of the solution occurred in contact with the precipitated manganese dioxide and also after filtration from it.



In view of all the above considerations it became evident that the final change probably is a tautomeric one only, since it involves no oxidation, as the ring formation does. Further, as the oxygen derived from the permanganate up to the formation of the manganese dioxide is sufficient for only about two-thirds of that required for the complete change, the remaining oxygen most probably is supplied by the manganese dioxide itself previous to the reddening of the solution.

In the attempts to isolate the intermediate compound previous to the reddening of the solution, it was found that the final change could be arrested by the addition of acid. The substance in acid solution gave evidence of only partial change after a number of days, for the reddening was resumed on the addition of alkali, but not to the same extent as if the change had been allowed to proceed uninterruptedly. It was also found that by using weaker alkali for the oxidation the reddening was retarded, and thus it was possible to filter off the manganese dioxide and acidify the solution before the final change had proceeded too far; but this did not facilitate obtaining the intermediate compound, as a much smaller yield of the desired substance and an increased quantity of other products probably made its isolation more difficult.

It is seen that while the hydroxynaphthoquinone ring is broken and then regenerated in the course of such oxidations, an essential change has occurred which however may be masked by the symmetry of the compounds involved. The hydroxyl and the side chain no longer occupy the same positions as formerly. They are reversed as the result of the oxidation. The experiments recorded in this paper offer sufficient evidence of this fact, but still more positive proof could be furnished by oxidizing derivatives in which one hydrogen atom has been replaced by some other group or element in the ring adjoining the quinone ring and in this way breaking the symmetry. As owing to advancing age and uncertain health the work I am able to do is unfortunately quite limited, I am glad that Dr. Louis F. Fieser, who has been much interested in ring formation and to whom I have from time to time communicated my results, has undertaken at his own suggestion some experiments in this direction. The results obtained, Dr. Fieser has kindly informed me, support the theoretical conclusions I have reached.

As the oxidation generally is easily effected and the resulting product is obtained in excellent yield and high purity, it will undoubtedly prove valuable not only in the preparation of substances which might be otherwise difficult to make, but also as an aid in determining the structure of the side chain in the quinone ring of 2-hydroxy-1,4-naphthoquinone derivatives. For instance, let us suppose it is necessary to determine the structure of a chain $-C_3H_7$, which could be either (1) $-CH_2CH_2CH_3$ or (2)  $-CH(CH_3)_2$. If on oxidation CH_2 were removed and the resulting compound remained a hydroxynaphthoquinone derivative the chain would have the structure (1); if no hydroxynaphthoquinone resulted with loss of CH_2 the structure (2) would be probable. Similarly the reaction undoubtedly could at times be used for the determination of the position of a double bond in the chain. I have shown that in 2-hydroxy-1,4-naphthoquinone derivatives a double bond between the α and β carbon atoms of the chain invariably results in a much more highly colored compound than if located elsewhere. This may be brick red, deep red or deep orange, but it is always very different from the yellow or orange-yellow of the compounds with the double bond elsewhere in the chain.

Lapachol may be taken as an example. As the result of many experiments I showed in 1896 that lapachol had probably the structure VIII[9] instead of IX, that assigned to it by Paternò. This

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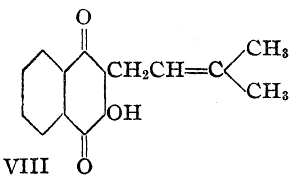
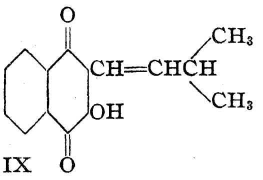
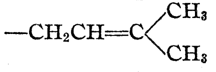
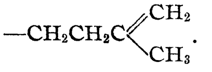
[9] Hooker, *J. Chem. Soc.*, **69**, 1355 (1896).

formula (VIII) was confirmed by Fieser by synthesis many years later.[10] Now in view of my


VIII


IX

more recent experiments, as lapachol is *yellow* it could not have the formula IX for the position of the double bond in this case would require the substance to be *red* or *orange-red*. Synthesis of IX has substantiated this; it is red.[9] On oxidation lapachol loses CH_2 and the resulting hydroxynaphthoquinone derivative is *red*. The bond therefore has moved one step to the left as the result of the removal of CH_2 and lapachol therefore has the side chain  $-CH_2CH{=}C(CH_3)_2$ and not  $-CH_2CH_2C({=}CH_2)CH_3$. I have proved independently[3] that the substance resulting from the oxidation actually has the chain $-CH{=}C(CH_3)_2$ which the above considerations would require.

As Fieser has shown[11] that the chemistry of polycyclic β-hydroxy-α-quinones closely follows in a number of respects that of 2-hydroxy-1,4-naphthoquinone, it is not unreasonable to expect that they too would be subject to the aldehyde synthesis and their derivatives to the permanganate oxidation described in this and preceding papers.

Experimental Part

Potassium Permanganate Oxidations

The amounts of materials oxidized in the different experiments and the quantities of potassium permanganate and of alkali employed are indicated in Table I, which records also the yields, properties and analyses of the oxidation products. It is evident from the results that the yield is improved by using a rather strongly alkaline solution. The alkali is added to the permanganate solution rather than to the solution containing the hydroxynaphthoquinone because the troublesome separation of the sodium salt is in this way avoided. Generally very satisfactory results are obtained by operating in the following manner.

General Procedure.—For the oxidation of an alkylhydroxynaphthoquinone, for example of the molecular weight 230, 1 g. of the material is dissolved in 100 cc. of 0.5% sodium hydroxide solution and the crimson solution is cooled in ice water. The second solution is prepared by dissolving 0.96 g. of potassium permanganate, an amount sufficient to furnish two atoms of oxygen plus 5% in excess, in 100 cc. of 10% sodium hydroxide, and this is likewise cooled in ice water. The two solutions are mixed rapidly in one operation and kept in ice water until manganese dioxide separates, the crimson solution of the hydroxynaphthoquinone derivative on the addition of the permanganate usually becoming successively bright green, olive green, brown, and as the manganese dioxide separates almost colorless. In order that the manganese dioxide may be completely deposited it is well to allow the solution to stand for several hours at room temperature, during which time a crimson color develops at a rate varying with the substance oxidized.[12] The manganese dioxide is filtered off and thoroughly washed so as to redissolve any sodium salt of the new product which may have crystallized from the alkaline solution. The addition of dilute hydrochloric acid precipitates the new substance, which may separate as an emulsion but is soon obtained well crystallized, usually in small, bright yellow needles. The products usually crystallize well from either alcohol or petroleum ether.

Of the entire list of products, only two are described for the first time, namely, 2-*n*-hexyl- and 2-ethyl-3-hydroxy-1,4-naphthoquinone. Samples of all of the other compounds, with the exception of 2-phenyl-3-hydroxy-1,4-naphthoquinone, were available for comparison and mixed melting point determinations with the substances prepared by other methods showed no depressions. Microscopic examinations further established the identity of the oxidation products.

The Effect of Oxygen.—In special experiments the oxidation of 2-*n*-butyl-, 2-*n*-heptyl- and 2-*n*-hexyl-3-hydroxy-1,4-naphthoquinone was conducted in the absence of oxygen. The solutions of the quinone and of the permanganate were boiled to expel air and placed in vessels connected in a train whereby the system could be evacuated thoroughly and filled with nitrogen. The cooled solutions were mixed by forcing the permanganate solution into the quinone solution under nitrogen pressure. The oxidations proceeded exactly as when carried out with free access of air and no significant differences were noted.

Attempts to Arrest the Reaction.—Noting that the changes occur more slowly in a weakly alkaline medium, some attempts were made to isolate intermediate compounds under these conditions. 2-β-Phenylethyl-3-hydroxy-1,4-naphthoquinone was dissolved in 0.5% alkali and treated with a solution of potassium permanganate in water. The separation of manganese dioxide was complete only in one and one-quarter hours and when this was removed a pale red filtrate was obtained. On acidification there was obtained only a small amount of the normal oxidation product, 2-benzyl-3-hydroxy-1,4-naphthoquinone. On making the filtrate alkaline the solution gradually acquired a deeper crimson color, and more of the above compound separated on acidification. It was observed that the darkening of the solution occurred at the same rate whether the alkaline solution was allowed to remain undisturbed or was shaken vigorously with air.

2-Methyl-3-hydroxy-1,4-naphthoquinone seemed well adapted to a study of the intermediate stages of the reaction because the changes occur somewhat more slowly with

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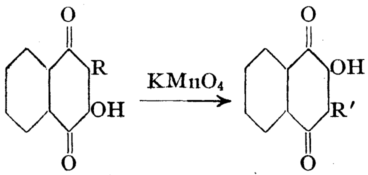
[10] Fieser, THIS JOURNAL, **49**, 857 (1927).

[11] Fieser, *ibid.*, **50**, 465 (1928); **51**, 940, 1896 (1929).

[12] The final result is the same if the manganese dioxide is removed at once and the filtrate is allowed to stand for several hours before acidifying.

TABLE I

PERMANGANATE OXIDATION OF 2-ALKYL-3-HYDROXY-1,4-NAPHTHOQUINONES



	Subst. oxidized, R =	Solution of substance: Subst., g.	Volume, concn. of NaOH soln., cc.	%	Solution of KMnO4: KMnO4, g.	2[O]+ −%	Vol., cc.	NaOH, %	Oxidation product, R =	Yield: Wt., g.	%
1	—$(CH_2)_3C_6H_5$	0.5	125	2	0.4	11	40	0	—$(CH_2)_2C_6H_5$	0.37	78
2	—$(CH_2)_2C_6H_5$	2	400	5	2	32	200	0	—$CH_2C_6H_5$	1.49	78
3	—$CH_2C_6H_5$	1	200	5	1	25	100	0	—C_6H_5	0.66	70
4	—$(CH_2)_6CH_3$	6	600	1	5.1	10	600	4	—$(CH_2)_5CH_3$	4.86	85
5	—$(CH_2)_5CH_3$	3	300	0.5	2.7	10	300	15	—$(CH_2)_4CH_3$	2.72	96
6	—$(CH_2)_4CH_3$	3	300	.5	2.85	10	300	10	—$(CH_2)_3CH_3$	2.57	91
7	—$(CH_2)_3CH_3$	6.27	630	.5	6.05	5	630	10	—$(CH_2)_2CH_3$	5.22	89
8	—$(CH_2)_2CH_3$	3.43	350	.5	3.51	5	350	10	—CH_2CH_3	2.80	88
9	—CH_2CH_3	1.72	175	.5	1.88	5	175	10	—CH_3	1.28	80
10	—CH_3	0.1	10	.5	0.12	5	10	10	—H	(0.04)	(43)

	Solvent	Crystalline form	M. p., °C. Found	Recorded	Analyses: % C Calcd.	% C Found	% H Calcd.	% H Found
1	Alcohol	Orange-yellow prisms	171.5–172.5	171.5–172.5[4]	77.67	77.46	5.07	5.02
2	Alcohol	Golden-yellow plates	176.2–177.2	175–176[5]	77.25	77.48	4.58	4.42
3	Alcohol	Orange-yellow plates	142.6–143.6	143.5–144.5[6,13]	76.77	77.02	4.03	4.12
4	Alc., pet. ether	Yellow needles	98–98.5	....	74.38	74.70	7.03	6.93
5	Alc., pet. ether	Orange-yellow needles	103.2–103.7	104–104.3[4]	73.73	73.92	6.61	6.57
6	Alc., pet. ether	Orange-yellow needles	99.2–99.7	100.3–100.7[4]	73.01	73.20	6.13	6.23
7	Pet. ether	Orange-yellow plates	100–101	100.5–101.5[4]	72.19	72.36	5.60	5.71
8	Pet. ether	Yellow plates	138.2–138.7	....	71.26	71.37	4.99	4.84
9	Pet. ether, alcohol, ether	Yellow needles	172–173	173–174[8,14]	70.19	70.14	4.29	4.20
10	Alcohol	Yellow needles, scales	187–188, dec.	About 192, dec.[15]	...	...	..	..

this compound than in other cases. Under the conditions outlined in Table I the solution could be filtered from the manganese dioxide without acquiring more than a light brownish-red color. The acidified solution was yellow and it was kept in the dark for several weeks without undergoing any apparent change. A small amount of hydroxynaphthoquinone separated, but no intermediate product could be obtained. From time to time portions of the solution were made alkaline, which caused the gradual appearance of a dark red-brown color. Hydroxynaphthoquinone was then obtained on acidification.

Test for Formic Acid.—In the attempt to establish the manner in which a single carbon atom is eliminated in the oxidation, the mother liquor remaining after acidifying the alkaline solution with sulfuric acid and collecting the reaction product was investigated for the presence of formic acid. The solution was distilled and the nearly colorless, faintly acidic distillate was heated with 5% mercuric chloride solution. There was no precipitate, although in control experiments it was found that an amount of formic acid equivalent to the quinone employed can be detected easily by this method.

Further Observation.—A number of attempts were made to obtain an oxidation product similar to those described above from 2-β-hydroxyisobutyl-3-hydroxy-1,4-naphthoquinone,[3] but the experiments were not successful. The alkalinity and the temperature were varied over a wide range, but a large part of the material was invariably converted into resinous products and 35–50% of the starting substance was recovered unchanged. There were some indications of the formation of 2-hydroxy-1,4-naphthoquinone, but the substance was not completely identified.

Color Test for Hydroxynaphthoquinones.—Volhard[13] has recorded that 2-phenyl-3-hydroxy-1,4-naphthoquinone gives with concentrated sulfuric acid and benzene containing thiophene a dark blue color. I have found that this reaction is a general one. Hydroxynaphthoquinone itself and those of its derivatives having saturated carbon chains in the quinone ring, with or without phenyl groups, respond to it.

The test can be made conveniently by dissolving a small quantity of the substance to be examined in two drops of concentrated sulfuric acid on a watch glass and adding to this 2 drops of benzene containing one drop of thiophene in 5 cc. As the sulfuric acid containing the hydroxynaphthoquinone or its derivative is thoroughly mixed with the benzene, a brown color usually first develops which passes slowly on standing through an olive green to a deep blue, the color being first observed at the edges of the solution as moisture is absorbed. Finally a blue precipitate is

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(13) Volhard, *Ann.*, **296**, 18 (1897), gives 146–147°.

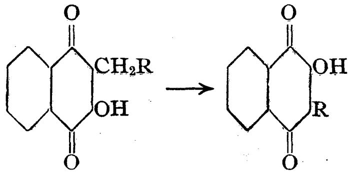
(14) J. Madinaveitia, *Anales soc. españ. fis. quim.*, **31**, 750 (1933); *Rev. acad. cienc. Madrid*, **31**, 617 (1934).

(15) Fieser, THIS JOURNAL, **48**, 2930 (1926).

formed. All of the substances listed in Table I gave the test, and this was true also of hydrolapachol and of 2-isobutyl-3-hydroxy-1,4-naphthoquinone.[3]

Summary

It is shown how alkaline potassium permanganate oxidation of hydroxynaphthoquinone derivatives can result in a general reaction involving the following change:



Thus it is possible to eliminate CH_2 adjoining the quinone ring without otherwise disturbing the structure of the chain. In the course of the oxidation the quinone ring is split and then reformed. One carbon atom of the original ring is eliminated, another from the side chain taking its place, with the result that the chain is shortened by one carbon atom and the positions of the hydroxyl and the side chain are reversed in the new ring. The steps involved are fully discussed and many examples of the reaction are given. It is also shown how the oxidation can be of assistance in determining the structure of the side chain and, if unsaturated, the position of the double bond.

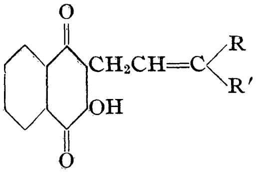
82 REMSEN STREET
BROOKLYN, NEW YORK

RECEIVED MARCH 25, 1936

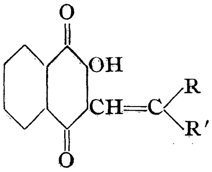
On the Oxidation of 2-Hydroxy-1,4-naphthoquinone Derivatives with Alkaline Potassium Permanganate. Part II. Compounds with Unsaturated Side Chains[1,2]

BY SAMUEL C. HOOKER AND AL STEYERMARK

It has been shown that the novel oxidation reaction described recently by one[3] of us is applicable to a large number of hydroxynaphthoquinones with saturated side chains in the quinone ring, but only one example of a substance containing a double bond in the side chain was included in the previous studies, namely, lapachol.[3a] Lapachol (I, R and R′ = CH_3) is converted by alkaline permanganate in the cold into the next lower homolog of the type II, in which CH_2 has been eliminated and the double bond shifted from the β,γ- to the α,β-position. In order to extend this observation the following additional compounds have been examined: the 2-allyl, 2-γ-methylallyl, and 2-cinnamyl derivatives of 3-hydroxy-1,4-naphthoquinone. The materials were in part kindly supplied by Dr. L. F. Fieser, who has described the preparation of all three of these quinones.[4]



I (Yellow)



II (Orange or red)

The three compounds of the type I are yellow, like lapachol, and on oxidation with permanganate they behave in an entirely similar manner yielding orange or red quinones of the type II. The product resulting from the oxidation of 2-γ-methylallyl-3-hydroxy-1,4-naphthoquinone (I, R = CH_3, R′ = H) proved to be identical with the substance prepared[5] by the condensation of propionaldehyde with hydroxynaphthoquinone, namely, 2-α-propenyl-3-hydroxy-1,4-naphthoquinone. The oxidation product of the cinnamyl compound similarly was identified by direct comparison with the compound II (R = C_6H_5, R′ = H) prepared[5] by the aldehyde synthesis.

The oxidation of the allyl compound presented some difficulties but conditions eventually were defined permitting the isolation of the sensitive reaction product, 2-vinyl-3-hydroxy-1,4-naphthoquinone (III). This compound, which is described for the first time, was fully identified by its conversion on catalytic hydrogenation into 2-ethyl-3-hydroxy-1,4-naphthoquinone (IV), a substance previously prepared[3b] in this Laboratory by the oxidation of the propyl compound (V).

These results fully confirm and extend the observations made in the case of lapachol. In all four of the examples investigated it has been found that the oxidation of a yellow alkyl hydroxynaphthoquinone having a double bond in the β,γ-position in the side chain leads to the re-

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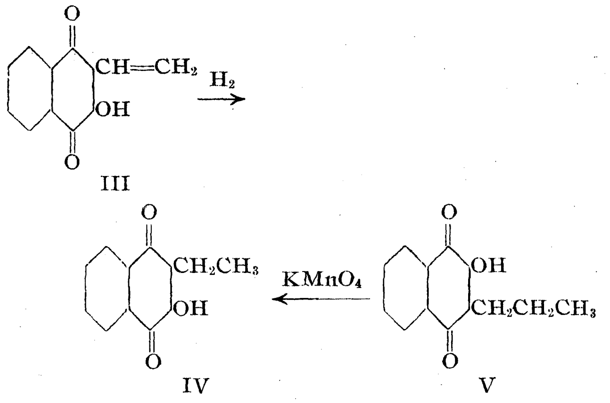
(1) See Editor's note (1), THIS JOURNAL, **58**, 1163 (1936).

(2) Dr. Hooker left no manuscript for the first part of this paper but wrote the description of the three oxidations recorded in the experimental part.—L. F. FIESER.

(3) HOOKER, THIS JOURNAL, (a) **58**, 1168 (1936); (b) **58**, 1174 (1936).

(4) Fieser, (a) *ibid.*, **48**, 3201 (1926); (b) **49**, 857 (1927).

(5) Hooker, *ibid.*, **58**, 1163 (1936).



moval of CH_2 adjacent to the quinone ring with the formation of an orange or red quinone with the double bond in the α,β-position. It appears that the reaction is a very general one and that the relationship between lapachol and its product of oxidation extends to other cases and can be used with assurance in the determination of the position of a double bond in the side chain.

Experimental Part

Conversion of 2-Allyl-3-hydroxy-1,4-naphthoquinone into 2-Vinyl-3-hydroxy-1,4-naphthoquinone.—The required starting material was prepared by the method of Fieser.[4a] In carrying out the allylation of the silver salt of hydroxynaphthoquinone considerably more benzene was employed (2.6 times that specified) and the mixture was not heated but was allowed to stand in the dark in a stoppered flask with occasional shaking for two days. The yields of the *o*-quinone ether and allylhydroxynaphthoquinone were 54 and 18%, respectively. The fraction containing the *p*-quinone ether was discarded. The *o*-quinone ether was rearranged at a temperature lower than that specified by Fieser, the material being heated in an oil-bath at 125–127° for one and one-half hours (5-g. lots). The mass was soaked with cold 0.25% alkali for two days and the solution was filtered from an undissolved resin. The precipitated material was extracted with petroleum ether in the Soxhlet apparatus (yield 61–68%), and crystallized from glacial acetic acid, m. p. 116–117°.

2-Vinyl-3-hydroxy-1,4-naphthoquinone is difficult to obtain in a pure condition. As the result of many experiments it was found that it could be best prepared as follows. To 1 g. of 2-allyl-3-hydroxy-1,4-naphthoquinone dissolved in 100 cc. of 1% sodium hydroxide solution an aqueous solution of potassium permanganate containing 1.085 g. (10% in excess of the theoretical amount for two atoms of oxygen) in 100 cc. was added quickly, both solutions previously having been cooled in ice water. The oxidation occurred rapidly. The manganese dioxide separated in one to two minutes and was filtered off immediately, this operation taking about ten minutes. The filtrate was quickly diluted with 800 cc. of water and at once *poured into* 100 cc. of dilute hydrochloric acid (1:3). After standing for about eight minutes, during which microscopic orange needles formed from the emulsion produced by the addition to the acid, the oxidation product was collected as quickly as possible by suction filtration. Any delay in conducting these operations resulted unsatisfactorily, as the substance was found to change rapidly in the alkaline solution, and as an additional compound commenced to separate from the acid solution soon after the precipitation of the oxidation product. Although somewhat impure the substance as thus obtained is probably suitable for most purposes. The yield was about 40% of the weight of the allyl compound oxidized. Complete purification for analysis presented considerable difficulty as the substance underwent partial change in all the solvents used. Crystallization from methyl or ethyl alcohol, chloroform, acetic acid, benzene, ether, ethyl acetate or acetone decreased rather than increased the purity of the substance. Purification was finally accomplished by dissolving 0.94 g. in 50 cc. of ether at the laboratory temperature and gradually adding at intervals of some hours a total of 145 cc. of petroleum ether (b. p. 35–55°). When the cloud had cleared sufficiently the deposit was filtered off and discarded. The solution was then allowed to go to dryness in an Erlenmeyer flask tilted so as to promote more rapid evaporation. The residue consisted of small, red-brown crystalline masses scattered here and there over the surface of the flask surrounded by a finely divided yellow substance undoubtedly resulting from one or other of the changes above referred to. The brown-red crystalline masses were mechanically removed and after being washed with a few drops of ether melted at 121.5–123.5°. Analysis gave figures agreeing sufficiently well with those required by **2-vinyl-3-hydroxy-1,4-naphthoquinone.**

Anal. Calcd. for $C_{12}H_8O_3$: C, 71.96; H, 4.05. Found:[6] C, 71.79; H, 4.54.

The conclusion drawn from the analysis was confirmed by conversion of the substance into ethylhydroxynaphthoquinone by hydrogenation, the identity being established beyond question by direct comparison with the product previously obtained[3b] as described above and substantiated further by a mixed melting point determination.

Conversion of 2-Cinnamyl-3-hydroxy-1,4-naphthoquinone into 2-β-Phenylvinyl-3-hydroxy-1,4-naphthoquinone.—The permanganate oxidation of cinnamylhydroxynaphthoquinone occurs most satisfactorily in a very dilute alkaline solution and even then the yield of the desired substance does not much exceed 9% of the weight of the material oxidized. As the result of a number of trials the following method was adopted. The cinnamyl compound, 0.5 g., was dissolved in 100 cc. of 0.1% alkali, and potassium permanganate, 0.4 g., in 50 cc. of water. Both solutions were cooled to about 1° and quickly mixed as above. The manganese dioxide was filtered off promptly after separation, washing of the precipitate being avoided to prevent unnecessary dilution. About 140 cc. of a 25% alkali, a volume equal to that of the filtrate, was then added and the whole set aside for five days during which the sodium salt of the oxidation product crystallized in the form of dark violet needles. These were collected on glass wool and washed with 10% alkali. The alkaline mother liquor now brown in color was discarded. The violet needles were dissolved in 40 cc. of warm water and the deep violet solution after filtration acidified with dilute hydrochloric

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(6) Microanalysis by Dr. D. Price of Columbia University.

acid. The resulting dark red precipitate consisting of microscopic needles was collected, washed with water and air dried, yielding approximately 0.045 g. The substance when crystallized from alcohol melted at 166–167°. It was compared directly with 2-β-phenylvinyl-3-hydroxy-1,4-naphthoquinone, prepared by the aldehyde condensation,[5] with which it is undoubtedly identical, the various points of similarity being further confirmed by a mixed melting point determination.

Conversion of 2-γ-Methylallyl-3-hydroxy-1,4-naphthoquinone into 2-α-Propenyl-3-hydroxy-1,4-naphthoquinone.—A solution of 0.1 g. of potassium permanganate in 10 cc. of water was cooled in an ice-bath and quickly added to a similarly cooled solution of 0.1 g. of the crotyl compound in 10 cc. of 1% alkali. Manganese dioxide separated in a few minutes leaving an almost colorless solution which rapidly became purple. After two hours the filtered solution was partially precipitated by cautiously adding dilute hydrochloric acid until the mother liquor, still alkaline, had become red. The orange, crystalline precipitate was collected, washed and air dried. The yield was 0.03 g. For purification it was dissolved in 6 cc. of a 0.5% solution of sodium hydroxide and then nearly but not completely reprecipitated with dilute acid. Washed and air dried it melted at 134–135° and gave a dark crystalline sodium salt which dissolved in water to an intensely violet solution. Comparison of its properties and a mixed melting point established its identity with the compound prepared from propionaldehyde by condensation with hydroxynaphthoquinone.[5] Oxidation in more strongly alkaline solution gave less satisfactory results.

Summary

Extending an observation regarding the oxidation of lapachol with potassium permanganate, three similarly constituted derivatives of 3-hydroxy-1,4-naphthoquinone having in the 2-position side chains of the type —CH_2CH=CHR have been converted into the corresponding compounds of the side chain —CH=CHR. The hitherto unknown vinyl derivative of hydroxynaphthoquinone has in this way been isolated.

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BROOKLYN, NEW YORK
RECEIVED MARCH 25, 1936

Lomatiol. Part II. Its Occurrence, Constitution, Relation to and Conversion into Lapachol. Also a Synthesis of Lapachol.[1,2]

BY SAMUEL C. HOOKER

In a paper published in 1895 the late Dr. Edward H. Rennie[3] showed that the yellow coloring matter with which the seeds of *Lomatia ilicifolia* and *Lomatia longifolia* are more or less surrounded is closely related to lapachol; and he succeeded in converting the lomatia coloring matter into the hydroxy-β-lapachone which I had previously prepared indirectly from lapachol.[4] The results of Dr. Rennie's work together with the study of numerous compounds which I had obtained from lapachol led me to assign to the lomatia coloring matter the constitution of an hydroxyisolapachol, instead of that of hydroxylapachol proposed by Dr. Rennie, and as at least one other hydroxyisolapachol had been isolated, the name lomatiol was suggested for the lomatia coloring matter.[5]

At the time of this later publication Dr. Rennie had already courteously announced the determination of leaving the further study of the coloring matter to me, and it was my intention to pursue the work as soon as a sufficient supply of raw material had been secured in hope of eliminating all doubts regarding the structure of lomatiol. Conditions arose subsequently which made it impossible to carry out my intentions and it was not until after an interval of many years that I was able to resume the investigation.

Occurrence of Lomatiol.—In addition to the seeds of the two species above referred to, *L. ilicifolia* and *L. longifolia*, I have also examined the seeds of *L. silaifolia* from the Sydney district, New South Wales, and of *L. tinctoria* and *L. polymorpha* from Tasmania.[6] The seeds of all

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(1) See Editor's note (1), THIS JOURNAL, **58**, 1163 (1936).

(2) The theoretical part of this paper is from an original manuscript written by Dr. Hooker and modified only to the extent of numbering the formulas and notes and making minor editorial changes. The experimental part has been constructed by consolidating, with some abridgment, descriptions of the experiments written by Dr. Hooker. The summary was supplied by the undersigned. In the experiments Dr. Hooker was assisted by Dr. G. H. Connitt.—L. F. FIESER.

(3) Rennie, *J. Chem. Soc.*, **67**, 784 (1895).

(4) Hooker, *ibid.*, **61**, 611 (1892).

(5) Hooker, *ibid.*, **69**, 1381 (1896).

(6) The seeds of *L. silaifolia* were kindly sent to me by the late Mr. J. H. Maiden, Director of the Botanical Gardens, Sydney. For one sample of *L. tinctoria* I have to thank Dr. J. K. Small, of the New York Botanical Gardens, New York City; and for another, and also for the seeds of *L. polymorpha*, I am indebted to Mr. L. Rodway, then the Government Botanist, Hobart, Tasmania. Of the seeds forwarded by Mr. Rodway, those of *L. polymorpha* were collected near Macquarie Harbour, on the west coast of Tasmania; and those of *L. tinctoria*, principally near Eaglehawk Neck, about 50 miles from Hobart. For the several specimens from Chile I am indebted to Prof. Charles Sprague Sargent of the Arnold Arboretum of Harvard University; to Lt.-Col. Sir D. Prain, F. R. S., Director of the Royal Botanical Gardens, Kew; and to Dr. J. K. Small of the New York Botanical Gardens.

the varieties mentioned were surrounded with a yellow coloring matter which was positively identified as lomatiol in every case. The seeds of three varieties of *Lomatia* growing in Chile were also examined, namely, *L. dentata*, *L. ferruginea* and *L. obliqua*, but they failed to give any indication of the presence of lomatiol, two different specimens of *L. dentata* being tested, three of *L. ferruginea* and two of *L. obliqua*. Thus all the species from Australia were found to be associated with lomatiol; whereas the coloring matter was absent in the seeds of the several species examined growing in Chile.

The greater part of the substance accumulated for investigation was extracted from seeds of *L. longifolia*, obtained near Clarence in the upper parts of the Blue Mountains, about 85 miles from Sydney. For this material I am very much indebted to the late Mr. J. H. Maiden, who, through several seasons, and in the face of a number of difficulties, most courteously arranged for its collection.

The *Lomatia longifolia* fruits when quite ripe, the follicles being open and the seeds exposed, were found when air dried to yield rather more than 3.5% of lomatiol; and the seeds when detached from the follicles slightly over 12%. Fruits subsequently received which were not quite ripe and which had not opened yielded rather less than 1.5%, the amount actually present being slightly greater as the process of extraction in the case of the unripe material was not without waste.

Extraction of Lomatiol.—Lomatiol was extracted by Rennie by boiling the seeds with water slightly acidified with acetic acid, and subsequently purifying the material by recrystallization several times from hot water also acidified. The disadvantage of this method in handling considerable quantities of seeds lies in the large volume of boiling water which must be used inasmuch as each gram of lomatiol extracted requires nearly 300 cc. for its solution; and further in the decomposition which lomatiol slowly undergoes on prolonged heating with water.

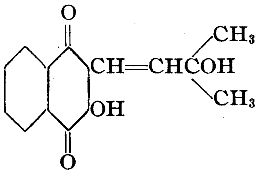
The following method of extraction will be found to give very satisfactory results: 250 g. of the seeds removed from the follicles are immersed in 3000 cc. of 0.75% sodium carbonate solution at the prevailing laboratory temperature. After digestion for about two hours, during which time the mixture is stirred frequently, the whole is transferred to a percolator and the alkaline solution drawn down to the level of the seeds and then completely displaced by cold water. Lomatiol, accompanied by a brown amorphous substance, is precipitated from the crimson alkaline extract by the gradual addition of dilute hydrochloric acid, it being desirable to add the acid at short intervals and to avoid at first a material excess, in order that a granular precipitate may be obtained which can be readily decanted, filtered off and washed with water. The mother liquor, rendered very slightly alkaline by the addition of sodium carbonate, may be concentrated in small portions at a time by evaporation on a water-bath avoiding in this way unnecessary exposure to heat. Upon the addition of hydrochloric acid to the concentrated solution a further quantity of lomatiol may be obtained in a less pure condition; the amount however is small and unless material is scarce perhaps hardly justifies the time and effort to obtain it.

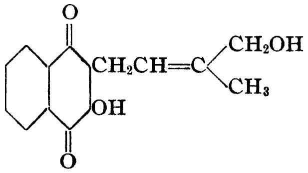
Lomatiol dissolves freely in boiling benzene and being but slightly soluble in this solvent in the cold can be very satisfactorily purified by means of it, as the accompanying brown substance above referred to, which may be present in considerable quantity in the crude material, is practically insoluble in benzene and therefore readily separated. The dried crude lomatiol should be finely pulverized and refluxed for a few minutes with about 20 cc. of benzene per gram. The addition of a small quantity of blood charcoal previous to filtration gives a brilliancy to the lomatiol which cannot be readily obtained without it. If the above directions are followed the one crystallization suffices to yield a very pure material.

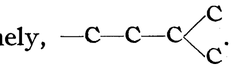
It was found necessary to modify the process of extraction in the case of unripe fruits as the opening of the follicles and the removal of the seeds proved to be a difficult matter. The air dried fruits after being ground in a pebble mill were immersed for a short time in a cold 1% solution of sodium carbonate. The solution when filtered was exposed to the air and allowed to ferment. After two weeks it was decanted off and filtered from the deposit which had formed; the deposit was discarded and the solution containing lomatiol oxidized by drawing through air, as the crimson color had been partly discharged below the surface. Lomatiol was then precipitated by the addition of hydrochloric acid at intervals, collected after several days and purified by crystallization from benzene. Whenever possible, lomatiol should be obtained from thoroughly ripe seeds, partly because of much better yields, and further because the extraction from the unripe material was found to be tedious and otherwise not fully satisfactory.

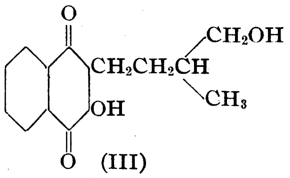
Chemical Investigations.—Since the appearance of my paper[5] in 1896 the chemistry of lomatiol and its derivatives has remained without further development. No additional facts whatever have been published regarding this coloring matter and no light has been thrown on its structure. The formula which I then suggested and indeed regarded as reasonably well fortified by experimental evidence was largely based upon the action of concentrated sulfuric acid in giving rise to hydroxy-β-lapachone. This change however, was thought to be far simpler than is actually the case for it involves a shift in the position of the double bond and also of the hydroxyl in the chain. Consequently deductions made in ignorance of this were erroneous.

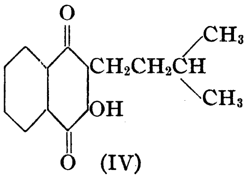
I shall show in this communication that the formula I for lomatiol as accepted in the literature must be changed to II. In the light of our present knowledge the position of the double bond in I would alone condemn the structure of the chain in this formula, as lomatiol is yellow and I would undoubtedly be deep orange to red.[7] Moreover a compound of this formula has been obtained in my laboratory in alkaline solution.[8] On liberation by acids it forms an internal anhydride and its possible existence in a free condition is doubtful. These are in themselves sufficient reasons for abandoning the formula I.


I

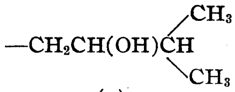

II

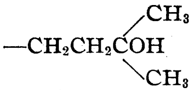
The hydrogenation of lomatiol gives rise to two substances (III and IV). Of these hydrolapachol (IV) is also obtained by the hydrogenation of lapachol. This demonstrates not only that lomatiol is a 3-hydroxy-1,4-naphthoquinone derivative but also that it has the same skeleton structure as that of lapachol, namely,  $-C-C-C\begin{matrix}C\\C\end{matrix}$. The ready absorption of hydrogen moreover proves the presence of a double bond in the lomatiol *chain* as the resulting hydrolapachol retains all the characteristics of a hydroxynaphthoquinone derivative.


(III)
Hydrolomatiol

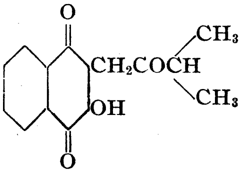

(IV)
Hydrolapachol

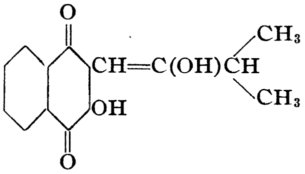
The formation of the second compound, hydrolomatiol (III), is of importance because it locates the position of the hydroxyl group in lomatiol. Of the three other possible isomeric substances in which hydroxyl is situated in the side chain two have been isolated in my laboratory and their structure determined with reasonable certainty. The location of hydroxyl in these compounds is as follows:


$-CH_2CH(OH)CH\begin{matrix}CH_3\\CH_3\end{matrix}$
(a)

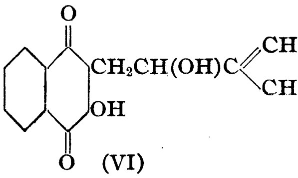

$-CH_2CH_2COH\begin{matrix}CH_3\\CH_3\end{matrix}$
(b)

The compound containing the chain (a) will be described in this paper. It is formed by the hydrogenation of hydroxyisolapachol, V, and also of isolomatiol VI, formerly regarded as a stereoisomer of lomatiol.


(Va)


(Vb)

Tautomeric forms of hydroxyisolapachol


(VI)
Isolomatiol

This conversion of isolomatiol and hydroxyisolapachol into the same hydrogenated compound determines the position of hydroxyl in isolomatiol, as the structure of hydroxyisolapachol is definitely known.[9] It is thus clear that the hydroxyl groups in lomatiol and isolomatiol are attached to different carbon atoms and that these substances cannot therefore be stereoisomers, as I previously suggested.

The chain (b) is contained in hydroxyhydrolapachol, a substance which results from the action

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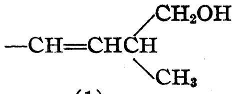
[7] Hooker, THIS JOURNAL, **58**, 1163 (1936).

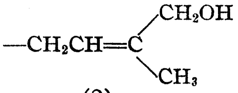
[8] The results will be communicated in a later paper.

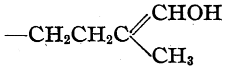
[9] Hooker, *J. Chem. Soc.*, **69**, 1355 (1896).

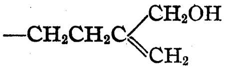
of alkalies on both α- and β-lapachone. The structure of this compound is also well established.[9] The third isomer in which hydroxyl occupies the α-position in the chain, though not isolated, is satisfactorily accounted for as it undoubtedly occurs as an intermediate product in the formation of isolapachol by the condensation of isovaleraldehyde and hydroxynaphthoquinone.[7,9] There is therefore only the δ-position available for the hydroxyl group in hydrolomatiol and consequently in lomatiol itself.

With the skeleton of the chain known, the hydroxyl located, and the existence of a double bond demonstrated, there remains only the position of the double bond to be determined in order that the constitution of lomatiol may be regarded as settled. There are four possible formulas which meet the requirements of an isoamyl skeleton and the hydroxyl in the δ-position. They are:

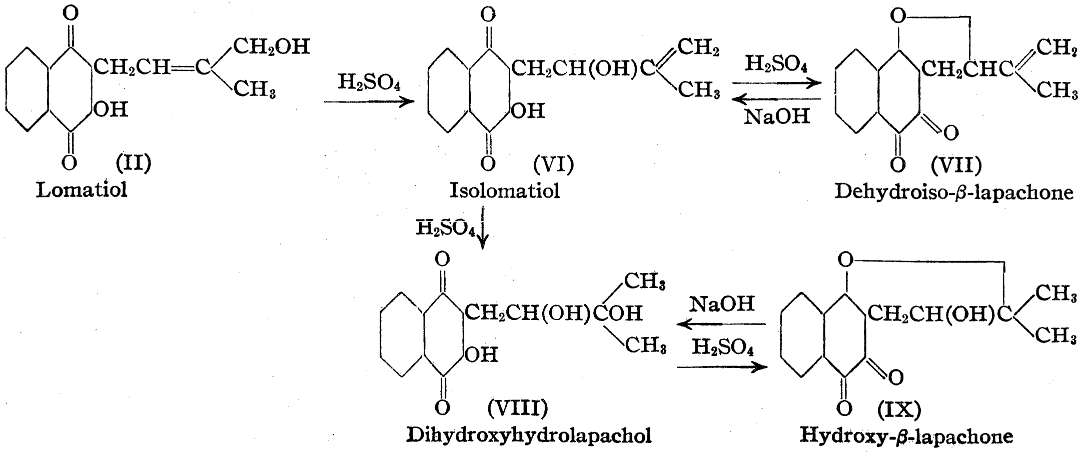

(1)


(2)


(3)


(4)

Of the above chains (1) is at once eliminated because lomatiol is yellow. Of the remainder (2) alone explains the behavior of lomatiol. The action of sulfuric acid is particularly illuminating, and is described by Rennie[3] in some detail. While recording the facts his theory fails to account satisfactorily for them. The discovery, however, that the hydroxyl group is attached to the β-carbon of the chain in isolomatiol and to the δ-carbon in lomatiol enables the reaction to be readily understood. Thus:



The intermediate compounds shown, while not isolated in the progress of the change, nevertheless can be obtained by the action of dilute alkalies on the closed ring substances and again reconverted into them by moderately concentrated sulfuric acid.

The action of concentrated sulfuric acid on lomatiol has thus brought about a change in the location of the hydroxyl group and, simultaneously, the double bond has necessarily shifted. Similar changes are already well known in compounds having like groupings (allylic rearrangement):[10] $>C{=}\underset{|}{C}CH_2OH \longrightarrow >C(OH)\underset{|}{C}{=}CH_2$. Thus these formulas for lomatiol and isolomatiol are in perfect harmony with all the experimental facts and enable satisfactory explanations to be advanced not only of the changes which these substances themselves undergo, but also of their relation to the very numerous compounds in this group which have been prepared in my laboratory.

The oxidation of lomatiol with alkaline permanganate following the general method given in recent papers[11] yields, with the elimination of CH_2, a *deep orange* compound[12] having the characteristic properties of a hydroxynaphthoquinone derivative. It can be safely inferred therefore from the color of this oxidation product that it has a double bond in the α,β-position in the chain and consequently the formula X, confirming the structure of chain (2) as that of the lomatiol chain. Chains (3) and (4) under similar circumstances, that is, with the elimination of CH_2, would have

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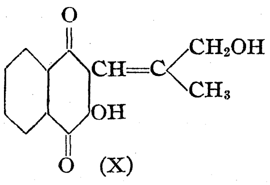
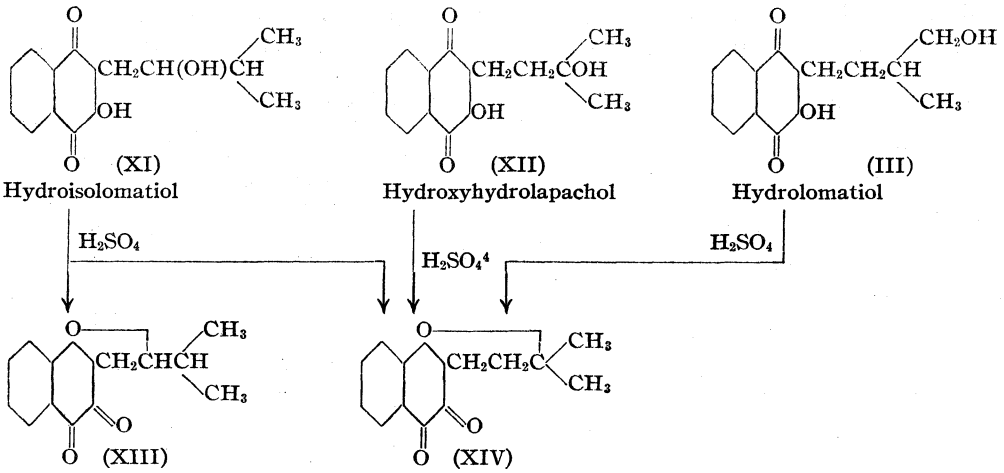
(10) Compare for instance, Burton and Ingold, *J. Chem. Soc.*, 904 (1928); Burton, *ibid.*, 759 (1931).

(11) Hooker, THIS JOURNAL, **58**, 1168, 1174, 1179 (1936).

(12) The substance formed by the oxidation of lomatiol has been studied in my laboratory in conjunction with Dr. Al Steyermark. The results obtained will be recorded in another paper.


(X)

the *yellow* color of their respective compounds left unchanged owing to the double bonds in the oxidation products being otherwise situated than in the α,β-position.



(XI) Hydroisolomatiol

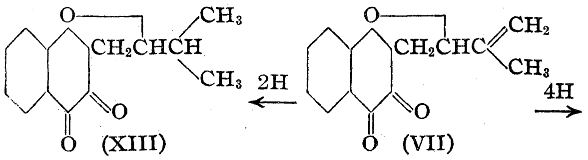
(XII) Hydroxyhydrolapachol

(III) Hydrolomatiol

(XIII) Iso-β-lapachone

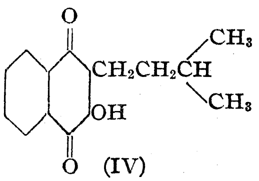
(XIV) β-Lapachone

The action of concentrated sulfuric acid on the three known hydroxy-amyl derivatives of hydroxy naphthoquinone is interesting because all give as the principal product or one of the principal products the same substance, β-lapachone, thus involving a migration of the hydroxyl group in two cases and indicating a general tendency toward the formation of a six-membered ring. Simultaneously, iso-β-lapachone is also formed from hydroisolomatiol and like β-lapachone is red and undoubtedly a β-quinone derivative. Iso-β-lapachone (XIII) is closely related to the red compound first obtained by Rennie[3] by the action of sulfuric acid on lomatiol. Rennie's compound is now recognized as dehydroiso-β-lapachone (VII), for on hydrogenation it yields iso-β-lapachone along with hydrolapachol, the latter substance arising from the cleavage of the oxide ring adjacent to the unsaturated carbon atom:

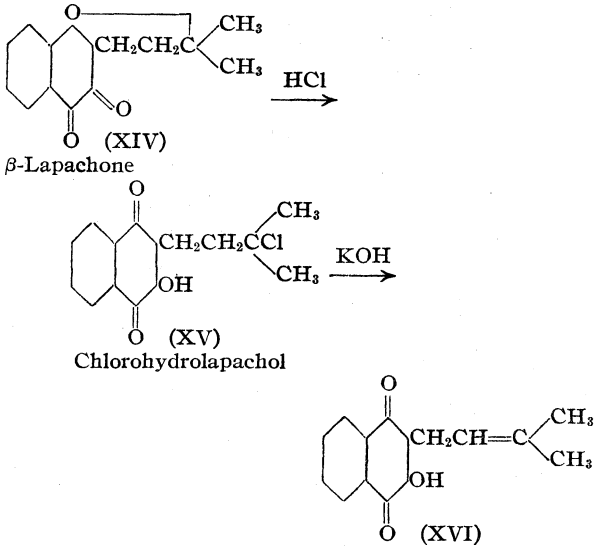


(XIII) Iso-β-lapachone

(VII) Dehydroiso-β-lapachone


(IV)
Hydrolapachol

Having converted lomatiol following hydrogenation into β-lapachone it is a simple matter to continue through to lapachol,[4] thus:



(XIV) β-Lapachone

(XV) Chlorohydrolapachol

(XVI) Lapachol

Also the conversion of hydroxyisolapachol, which has been obtained by synthesis as well as from lapachol,[9] into hydroisolomatiol by hydrogenation and then into β-lapachone completes the steps necessary for a synthesis of lapachol. A much more direct synthesis has been recorded already by Fieser.[13]

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(13) Fieser, This Journal, **49**, 857 (1927).

The formation of isolomatiol from lomatiol and of β-lapachone from hydrolomatiol, as well as from the two isomeric compounds in which the hydroxyl occupies the β- and γ-positions in the chain, indicates the difficulties and dangers which exist in drawing conclusions as to the structure of the compounds of this group from a single reaction. Moreover, my experiments demonstrate that the shifting of the double bond in lapachol and lomatiol and their derivatives must be also recognized as an ever present possibility, and, therefore, that great caution must be exercised in attributing formulas to these substances.

Still another fact must be constantly borne in mind, namely, that changes from the para to the ortho quinone grouping occur frequently and insidiously in the conversion of open to closed ring compounds and *vice versa* in opening the ring. Also similar changes from ortho to para and from para to ortho quinones may take place in the case of the closed ring compounds themselves.

In the course of my investigations, however, I have been fortunate in being able to prepare a large number of substances in the formation of which many interesting and unexpected changes have been developed and studied, and as the formulas adopted are able to explain satisfactorily the relation of these numerous compounds to each other as well as to account for all observations so far made, they may be accepted, I believe, as representing with reasonable certainty the correct structure of the compounds to which they have been assigned. The very number of these compounds and the necessity of fitting each one into the complex whole, has prevented errors which might otherwise have occurred, as with fewer substances the number of available formulas would have been greater and the chances of wrong interpretation thus increased.

Experimental Part

Identification of Lomatiol.—Lomatiol may be positively and comparatively easily identified even in very small quantity owing to its striking characteristics admirably adapted for microscopic tests. Crude lomatiol is best purified by crystallization from benzene as above described, and if only a small quantity is available for identification the benzene can be allowed to evaporate almost to dryness on a watch glass and the resulting crystals may then be washed freely with the cold solvent. The substance is thus obtained matted in fine needles often accompanied by a few microscopic groups of heavier crystals of the same compound. It melts quite sharply at 127° and may be further identified by crystallization from water in which it is but sparingly soluble and in which it fuses at the boiling temperature. If the hot aqueous solution be allowed to cool gradually it becomes somewhat turbid and yellow needles separate which are visible to the naked eye. If the solution be quickly cooled, the emulsion which first results gives rise to minute spherical clusters of very fine needles together with irregular groups of crystals with thorn-like projections. These two forms appear to be invariably present and can be recognized with the help of the microscope. Thus examined the crystals are strikingly beautiful and characteristic.

Lomatiol may be further identified by the crimson color of its solution in alkalies and particularly by means of its barium salts[3] which are extremely typical, the one *orange* and the other dark *claret red*. The test may be made by moistening a very small quantity of lomatiol in contact with an excess of barium carbonate with a few drops of cold water, and filtering off the excess barium carbonate after an hour or so. If a very small quantity of the crimson filtrate be allowed to evaporate spontaneously on a glass slide, needles of the orange salt form readily, and a careful microscopic examination will reveal in addition minute masses of the dark claret colored salt, sometimes recognizable as consisting of thread-like forms suggesting cobwebs. If the solution be very dilute microscopic clusters of needles of lomatiol may also separate. The orange salt when vigorously rubbed on a hard surface yields a dark claret red, resin-like substance, the color change being quite striking.[14]

For further identification a trace of lomatiol may be moistened with an extremely small quantity of concentrated sulfuric acid. A bromine-colored solution is obtained, and if to this a drop or two of water be immediately added an orange-red emulsion forms from which microscopic ribbon-like orange-red crystals slowly separate, many grouped in characteristic root-like forms. After standing exposed to the air in contact with the acid solution the crystals completely disappear in the course of two to three days, an orange resin remaining in their place.[14]

Conversion of Lomatiol (II) into Hydrolomatiol (III) and Hydrolapachol (IV).—Several experiments in which from 1 to 5 g. of lomatiol dissolved in alcohol (50–100 cc.) was hydrogenated in the presence of reduced platinum oxide catalyst (Adams) at ordinary pressure or at a pressure of 38 lb. (2.53 atm.) at the laboratory temperature failed to give entirely concordant results. At times mostly hydrolapachol was obtained, at others mostly hydrolomatiol, a difference presumably due to variations in the condition of the catalyst. The hydrogenation was continued in each case until a drop of the solution, evaporated to dryness, gave with concentrated sulfuric acid a somewhat bromine-colored solution yielding a *yellow* emulsion on dilution. This indicates the absence of lomatiol, as the latter dissolves more to a brown and gives an *orange* emulsion when similarly treated.

In one experiment two 1-g. lots of lomatiol were hydrogenated with the same catalyst derived from 0.2 g. of platinum oxide and the combined, filtered solutions were allowed to stand overnight for oxidation. After evaporation to about 25 cc. the solution was diluted with about an equal volume of hot water. After standing for several

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[14] Cf. Rennie, ref. 3.

hours the long needles which had formed were filtered off after chilling, washed with 30% alcohol, and dried, giving 1.14 g. of material melting at 92.5–93°. Recrystallized from dilute alcohol the substance melted at 93.5–94° and was identified as **hydrolapachol** by all the characteristics and properties previously described.[7] The melting point was not lowered by admixture with hydrolapachol from lapachol.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.77; H, 6.55. Found: C, 73.76; H, 6.64.

Hydrolomatiol was obtained in another experiment in which 5 g. of material was hydrogenated in the presence of the catalyst derived from slightly less than 0.3 g. of platinum oxide, about one-third having been used previously once and one-third twice. As attempts to obtain the substance well crystallized directly from the alcohol proved unsuccessful, the solution was allowed to go to dryness. After efforts to obtain from the residue satisfactory crystals from several solvents had failed, the larger part was dissolved in 500 cc. of 1% alkali and the substance was reprecipitated from the filtered solution by hydrochloric acid in three fractions (0.97, 1.92 and 1.08 g.), thus finally completely discharging the crimson color of the alkaline solution. In each case an emulsion was first formed and became crystalline on standing, an interval of an hour or more being allowed between the precipitations. The first fraction contained some hydrolapachol while the second and third were almost pure hydrolomatiol. The second fraction was dissolved in 14 cc. of hot benzene, filtered and allowed to stand overnight. The prismatic yellow needles of **hydrolomatiol** which separated weighed 1.75 g. and melted at 101–102°.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.23; H, 6.15. Found: C, 68.99, 69.23[15]; H, 6.07.

In other experiments fractional precipitation as above described proved generally a satisfactory method of separating the two compounds.

Hydrogenation of Hydroxyisolapachol (V).—The hydrogenation of hydroxyisolapachol has proved more uncertain than that of the other substances of this group. In two experiments the hydrogen was added readily, in others under apparently essentially similar conditions the starting material was recovered unchanged. Possibly a slight difference may have existed in the condition of the catalyst, platinum oxide-platinum black, and perhaps the fact that the stable form of hydroxyisolapachol is that having the chain —$CH_2COCH(CH_3)_2$ (since it is *yellow*) increases the difficulties of hydrogenation and renders the success of the operation dependent upon very exact conditions which have not been determined with sufficient precision. However this may be, the addition of hydrogen gives rise to hydroisolomatiol (XI), which was positively identified by direct comparison with the compound obtained from isolomatiol as described below.

In the successful experiments, using 0.1 g. of substance in 15 cc. of alcohol and 0.1 g. of catalyst, hydrogenation was complete in ten minutes. A drop of the solution, allowed to evaporate (and oxidize) on a watch glass, when tested with concentrated sulfuric acid no longer gave the dark brown almost immediately produced by hydroxyisolapachol, but an orange-red solution which held its color. The residue from another drop gave with 1% alkali a more crimson solution than hydroxyisolapachol, and on acidification the *deep* yellow cloud which formed gave way rapidly to characteristic needles, a behavior entirely different from hydroxyisolapachol, which under similar circumstances gives a *light* yellow jelly-like mass which soon becomes permeated with extremely minute bacillus-like, short crystals. These tests, which must of course be made with the help of a microscope, may be of assistance in following the progress of the hydrogenation.

After standing exposed for about forty-eight hours to ensure complete oxidation of the hydroquinone, the alcoholic solution was evaporated to about 5 cc. and an equal quantity of water was added. The yellow crystalline scales which had formed in the course of a few days weighed 0.055 g. Recrystallized first from alcohol and then from benzene the substance was obtained in fine, orange-yellow needles, m. p. 120–120.5°, identical in all properties with hydroisolomatiol described below. The melting point of the mixed substances from both sources remained the same as for the individual compounds.

Hydrogenation of Isolomatiol (VI): Hydroisolomatiol or β-Hydroxyhydrolapachol (XI).—No difficulty was found in readily obtaining hydroisolomatiol by this method. Several lots were prepared with slight variations, but the irregularities noticed in the hydrogenation of hydroxyisolapachol were not experienced. The catalyst differed slightly in amount in the several lots and possibly also in its condition, as varying amounts had been used previously. The results, however, were essentially the same. Isolomatiol (2 g.) was dissolved in alcohol (50 cc.), platinum oxide (0.4 g.) added and the whole agitated under pressure of 37–38 lb. (2.46–2.53 atm.) at laboratory temperatures. The progress of the hydrogenation can be followed by testing an evaporated drop of the solution, concentrated sulfuric acid giving, when the hydrogen absorption is complete, an orange-red solution which does not change to the brown characteristic of isolomatiol. The addition of water to the acid solution gives a yellow cloud which shortly crystallizes, whereas in the case of isolomatiol an orange-red precipitate is obtained. Ten minutes of contact with hydrogen under the above conditions was found to be sufficient.

Hydroisolomatiol was isolated from the solution essentially as described in the preceding section, 6.1 g. of material hydrogenated in four lots giving 5 g. of product. Recrystallized from alcohol the substance melted constantly at 120.5–121.5°.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.23; H, 6.15. Found: C, 69.26; H, 6.17.

Conversion of Lomatiol (II) into Dehydroiso-β-lapachone (VII).—It was found that the red compound obtained by Rennie[3] by the action of concentrated sulfuric acid on lomatiol can be prepared more satisfactorily by using acid of more moderate concentration, for further change is thus prevented. After various trials the following method was adopted.

A flask containing 10 g. of pulverized lomatiol is immersed in ice water and thoroughly cooled; 100 cc. of ice-cold acid prepared by mixing five volumes of concentrated sulfuric acid with three volumes of water is then added

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(15) In this analysis the hydrogen was lost.

and well stirred for a few minutes until the lomatiol has dissolved completely, the flask being kept throughout in ice water. The bromine-colored solution is then immediately poured into water (750 cc.). The new substance separates as an orange-red emulsion which soon crystallizes, forming a voluminous precipitate. After standing until crystallization is complete (usually thirty minutes), the material is filtered off with the aid of suction, washed, broken up under water to facilitate the complete removal of acid, and again washed on the filter. The air-dried material (8.74 g.) is crystallized from 50 cc. of alcohol. As the solution cools dehydroiso-β-lapachone sometimes forms silky, radiating, red needles and sometimes heavier prismatic crystals. If the needles are allowed to stand in contact with the mother liquor they disappear in the course of a few days and the prismatic crystals take their place. Rennie analyzed the needles and reported the melting point 110–111°. The prisms were used for the analysis reported below and the melting point found was 116–116.5°. Dehydroiso-β-lapachone appears to be somewhat sensitive to light and unnecessary exposure should be avoided in its preparation. It dissolves in concentrated sulfuric acid to an orange-red solution.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.00; H, 5.00. Found: C, 74.96; H, 5.00.

The **azine** of dehydroiso-β-lapachone (VII) was easily formed by heating the red compound with *o*-phenylenediamine in glacial acetic acid solution for a minute or two. Crystallized from alcohol the substance formed yellow needles, m. p. 157.5–158°. It dissolves in concentrated sulfuric acid with a deep green color and gives a salmon-colored sulfate.

Anal. Calcd. for $C_{21}H_{16}ON_2$: C, 80.74; H, 5.17. Found: C, 80.45; H, 5.09.

Conversion of Dehydroiso-β-lapachone (VII) into Isolomatiol (VI).—Isolomatiol was first obtained by Rennie[3] by boiling dehydroiso-β-lapachone with strong potassium hydroxide solution, but the crude material precipitated on acidification had to be crystallized four or five times before it was obtained pure. Better results are possible by immersing 1 g. of the finely ground red compound in 75 cc. of 1% sodium hydroxide solution at the laboratory temperature. In the course of some hours solution is essentially complete, and after filtering to remove any possible trace of the unaltered substance dilute hydrochloric acid is added in slight excess to the intensely crimson solution. Isolomatiol is thus precipitated as a yellow oil which slowly crystallizes in groups of branch-like flattened needles with scales attached. Rosets of scales are also sometimes obtained. After washing with water and drying, the crude substance (1 g.) is dissolved in 10 cc. of alcohol, the solution filtered, warmed and gradually diluted with 10 cc. of water. Isolomatiol usually separates in clusters of scales melting at 109–110°. It appears to be sensitive to light.

Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.77; H, 5.42. Found: C, 69.71; H, 5.39.

Action of Sulfuric Acid on Isolomatiol (VI). (a) Dilute Acid.—Finely ground isolomatiol (0.25 g.) was quickly dissolved in 7.5 cc. of dilute sulfuric acid (5 vol. concentrated acid to 3 vol. water) by stirring for about two minutes and the solution was immediately poured into 75 cc. of cold water. The resulting red emulsion slowly became crystalline and the product (0.12 g.) after crystallization from alcohol was obtained as red needles, m. p. 116–116.5°, and fully identified as dehydroiso-β-lapachone.

(b) Concentrated Acid.—Isolomatiol (0.25 g.) was dissolved in concentrated sulfuric acid (5 cc.) and after four minutes the dark red-brown solution was poured into 65 cc. of cold water. The turbid solution after standing overnight was filtered from a small amount of resinous material and after standing four to five days the filtrate deposited orange-red prisms of hydroxy-β-lapachone (0.04 g.). After recrystallization from alcohol the product melted at 203–205°. The resinous material on further treatment with concentrated acid yielded a trace of yellow needles of what, most probably, was isopropylfurano-1,4-naphthoquinone,[9] but it was not fully identified.

Hydrogenation of Dehydroiso-β-lapachone (VII) and its Conversion into Iso-β-lapachone (XIII).—A solution of 1 g. of dehydroiso-β-lapachone in 100 cc. of alcohol containing 10 drops of acetic acid was agitated with 0.2 g. of platinum oxide catalyst at 38 lb. pressure of hydrogen for twenty minutes at 18°. Dehydroiso-β-lapachone dissolves in concentrated sulfuric acid to an orange-red solution which rapidly darkens on slight warming, and this property enables the end of the hydrogenation to be satisfactorily determined, as the new compound under similar circumstances gives an apricot color which is not darkened by slight heat. In preliminary experiments a drop or two of the solution was removed from time to time, evaporated and tested, and thus the time required was determined. When completely hydrogenated the colorless solution was filtered and exposed to the air until oxidation was complete, as indicated by no further increase in color. The solution was evaporated to 20 cc. and diluted with 10 cc. of water. Slight turbidity ensued and the following morning a red crystalline crust had formed on the bottom of the flask, and after another day the crystals of iso-β-lapachone were filtered off and washed with 50% alcohol; yield, 0.44 g. The mother liquor and washings were further diluted with 2.5 cc. of water and after standing overnight yellow crystals of hydrolapachol were found to have separated; yield 0.13 g. On further dilution a small additional amount of iso-β-lapachone was obtained in a somewhat resinous condition. This was digested with 1% alkali to remove resin and hydrolapachol and crystallized from alcohol.

Iso-β-lapachone crystallizes in dark orange-red plates or scales and melts at 124.5–125.5°. It has also been obtained in voluminous masses of tufts of needles materially lighter in color. The sample for analysis was recrystallized from dilute alcohol without unnecessary exposure to light.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.38; H, 5.78. Found: C, 74.32; H, 5.81.

I have not been successful in attempts to transform isopropylfurano-1,2-naphthoquinone[9] directly into iso-β-lapachone by hydrogenation. Using alcohol as the solvent the starting material was recovered unchanged; in ethyl acetate only a red oil was obtained.

Conversion of Iso-β-lapachone (XIII) into Hydroisolomatiol (XI).—This change was quantitatively effected by boiling powdered iso-β-lapachone (0.1 g.) for a minute or two with 1% sodium hydroxide solution (20 cc.). The deep crimson solution was filtered to remove possible traces of the unchanged substance, cooled and acidified with dilute hydrochloric acid, avoiding an undue excess. The oily, yellow suspension soon gave place to fine yellow needles which were filtered off on the following day. Crystallized from benzene the substance separated as needles and prisms melting at 121–122°.

Action of Concentrated Sulfuric Acid on Hydroisolomatiol (XI).—A solution of 0.5 g. of hydroisolomatiol in 10 cc. of concentrated sulfuric acid was allowed to stand for one hour in a corked vessel and poured into water (500 cc.). The emulsion first formed soon gave place to fine orange-red needles which were filtered off on the following morning and recrystallized a number of times from 50% alcohol (3 cc. at first and finally 2 cc.). Although the substance appeared to be pure under the microscope, the rise of the melting point with each crystallization from an initial 135–142° to eventually 153–154° clearly suggested the presence of more than one compound.

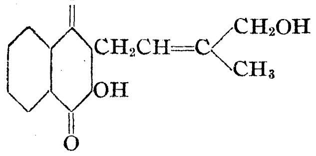
The crystals finally obtained pure were identified as β-lapachone by a mixed melting point and by conversion into γ-hydroxyhydrolapachol and its characteristic barium salt. The second substance, which proved to be iso-β-lapachone, was not itself isolated but its presence was proved by reconversion into hydroisolomatiol. In order to demonstrate the presence of iso-β-lapachone in the mixture another lot was prepared from 0.1 g. of hydroisolomatiol as before and collected one and one-half hours after pouring the acid solution into water. Microscopic examination of the material both while still wet and after being air dried definitely established the absence of yellow crystals of unchanged hydroisolomatiol. The material (0.07 g.) was immersed in cold 1% alkali which in the course of two hours had dissolved the greater part of the iso-β-lapachone, leaving 0.02 g. of β-lapachone unattacked. To the filtered crimson solution an excess (2.5 cc.) of dilute (1:3) hydrochloric acid was added. This gave a yellow suspension which soon crystallized in spherical groups of light needles characteristic of hydroisolomatiol. The crystals were allowed to stand in contact with the acid liquor so that any hydroxyhydrolapachol derived from the action of alkali on β-lapachone might be reconverted into β-lapachone. After a day or so microscopic examination revealed a very small quantity of orange-red crystals (assumed to be β-lapachone) which did not appear to increase on further standing (fifteen days). The mixture of crystals was then filtered off and immersed in a very dilute solution of sodium hydroxide to dissolve and thus separate the hydroisolomatiol from the orange crystals. Hydrochloric acid reprecipitated the yellow substance from the filtered solution and this was twice crystallized from benzene and identified by direct comparison with hydroisolomatiol by melting point (120–121°) and other characteristics.

Conversion of Hydrolomatiol (III) into β-Lapachone (XIV).—A small quantity of hydrolomatiol (0.1 g.) was dissolved in concentrated sulfuric acid (3 cc.) in a test-tube which was then corked to prevent the absorption of water and allowed to stand at the laboratory temperature. Action was slow. A drop of the solution was diluted from time to time and the color of the resulting emulsion taken as indicating the progress of the change. After one hour this was still yellow; subsequent tests tended more and more toward orange, and on the following morning the acid solution was poured into water (75 cc.). The resulting deep orange-red emulsion soon crystallized into root-like forms, which were thoroughly washed, dried (yield, 0.07 g.) and crystallized four times from alcohol, as, although the brilliant orange-red needles obtained appeared to be pure from the first, each crystallization resulted in a higher melting point. Identification was made as β-lapachone by direct comparison with this substance, by melting point (153–154°), mixed melting point and by conversion into hydroxyhydrolapachol and the characteristic barium salt of the latter. Owing to the repeated crystallizations necessary to obtain β-lapachone melting correctly, the presence of a second substance as the result of the action of concentrated sulfuric acid would seem to be indicated.

Summary

Various species of *Lomatia* from Australia have been found to be associated with lomatiol, whereas the coloring matter was absent in the seeds of several species examined growing in Chile. Methods of extracting lomatiol from both ripe and unripe fruits are described.

Lomatiol was found by Rennie to have the same skeletal structure as lapachol, from which it differs only in the character of the side chain. In the present investigation it is shown that the alcoholic hydroxyl group of hydrolomatiol is located in the δ-position in the chain ($-CH_2CH_2CH(CH_3)CH_2OH$) because substances having the other three possible structures have been obtained or characterized by synthesis or from lapachol. The double bond present in the lomatiol side chain is recognized as occupying the α,β-position with respect to the primary alcoholic group ($-CH_2CH{=}C(CH_3)CH_2OH$) by the observation that an allylic shift occurs in the conversion of lomatiol into isolomatiol, a substance having the chain $-CH_2CH(OH)C(CH_3){=}CH_2$. It is thus proved that lomatiol has the constitution of 2-[δ-hydroxy-β-isopentenyl]-3-hydroxy-1,4-naphthoquinone:



The formula is in perfect harmony with all the experimental facts and enables satisfactory explanations to be advanced of many changes which the compounds of the lomatiol series undergo and of their relationship to substances of the lapachol series. The transformations described in this paper include the conversion of lomatiol into lapachol through a series of intermediate substances, and since one of these can be prepared also from synthetic isolapachol, the work reported constitutes a synthesis of lapachol.

82 REMSEN STREET
BROOKLYN, N. Y.

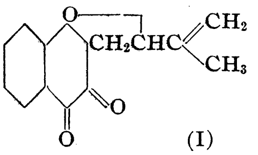
RECEIVED APRIL 3, 1936

The Constitution of Lapachol and its Derivatives. Part V. The Structure of Paternò's "Isolapachone"[1,2]

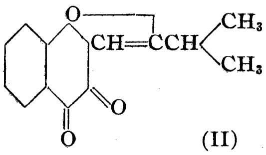
BY SAMUEL C. HOOKER

"Isolapachone" was first referred to by Paternò[3] in 1882 in his "Ricerche sull'acido lapacico" (lapachol). It was obtained by the removal of two acetyl groups, followed by spontaneous oxidation, from a compound formed by the action of acetic anhydride and sodium acetate upon lapachol. Seven years later the compound was studied by Paternò and Minunni[4] and the conclusion reached that the substance is similar to and isomeric with lapachone (β), the compound resulting from the action of concentrated sulfuric acid on lapachol. This view was shown by me to be untenable,[5] for in investigations published in 1892 it was found that the so-called "isolapachone" and also the diacetyl compound from which it had been obtained had each two atoms of hydrogen less than required by the formulas assigned by Paternò and Minunni. At that time I suggested a structural formula for the diacetyl compound which twenty-three years later received additional support from the experiments of L. Monti.[6] The matter was discussed by Monti apparently in ignorance of the revised and now generally accepted formula[7] for lapachol which necessitated a corresponding modification in "isolapachone" and all the compounds derived from lapachol studied previous to 1896.

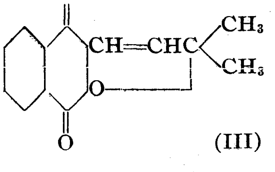
In the course of the study of the action of concentrated sulfuric acid upon lomatiol, the discovery by Rennie[8] of a compound isomeric with and in some respects similar to Paternò's "isolapachone" gave rise to uncertainties and errors of interpretation both as to its own structure and that of "isolapachone."[9] This was mainly due to misconceptions regarding the structure of lomatiol. In a recent paper[10] evidence has been presented which fully establishes the structure of lomatiol, and in the course of this work it was shown that Rennie's compound has the formula I and can be regarded as a dehydroiso-β-lapachone. An isomeric dehydro derivative of iso-β-lapachone was obtained in an earlier investigation[7] both from lapachol and by synthesis and it was assigned the structure II. The corresponding para quinone was also fully characterized. In this paper it will be shown that the preponderance of the facts now known favors formula III, or possibly IV, for "isolapachone." The equivalent of formula IV, based upon what was then believed to be the structure of lapachol, was previously suggested by me[5] but afterward aban-



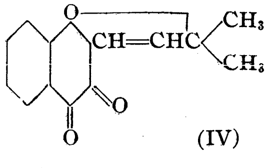
(I)
Rennie's Compound



(II)
Isopropylfurano-1,2-naphthoquinone



(III)



(IV)

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(1) See Editor's note (1), THIS JOURNAL, **58**, 1163 (1936).

(2) Dr. Hooker wrote a preliminary version of the introductory part of this paper in April, 1931, but he did not find time subsequently to incorporate in the manuscript certain modified views and new interpretations growing out of his more recent work on this and related problems. I was informed of his views throughout this period, however, through correspondence and conversations, and from the letters and from the notes of his assistant Dr. A. Steyermark, I have been able to revise the paper in accordance with Dr. Hooker's wishes and in large part in his own words. The experiments recorded were carried out with the collaboration of Mr. H. W. Shepard and Mr. J. G. Walsh, Jr., in 1891–1896, and of Dr. G. H. Connitt and Dr. A. Steyermark in the more recent period.—L. F. FIESER.

(3) Paternò, *Gazz. chim. ital.*, **12**, 337 (1882).

(4) Paternò and Minunni, *ibid.*, **19**, 607 (1889).

(5) Hooker, *J. Chem. Soc.*, **61**, 611 (1892).

(6) Monti, *Gazz. chim. ital.*, **45**, II, 58 (1915).

(7) Hooker, *J. Chem. Soc.*, **69**, 1355 (1896).

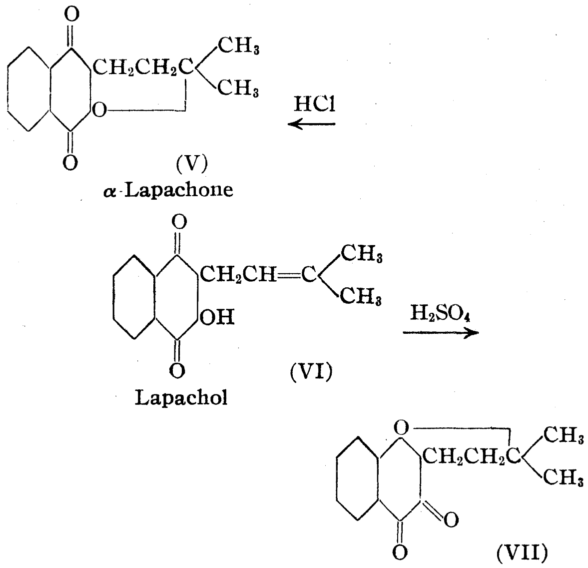
(8) Rennie, *ibid.*, **67**, 786, 792 (1895).

(9) Hooker, *ibid.*, **69**, 1362, 1370, 1377, 1382 (1896).

(10) Hooker, THIS JOURNAL, **58**, 1181 (1936).

doned[9] for the reasons stated above, the compound thereafter being referred to as pseudodehydrolapachone. On the basis of the present work the name dehydrolapachone may be assigned to the compound.

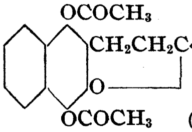
When lapachol is submitted to the action of mineral acids it can be converted quantitatively into either α-lapachone or β-lapachone according to the conditions under which the experiment is made.[5,7,11] By the action of acetic anhydride in the presence of zinc dust and sodium acetate the lapachones yield the diacetyl derivatives of their hydroquinones, VIII and IX.[4,6] I shall show that no fundamental change has occurred under the influence of acetic anhydride, as the removal of the acetyl groups followed by spontaneous oxidation enables the respective lapachones to be again obtained. Now Monti has found[6] that the diacetyl compound from which dehydrolapachone ("isolapachone") was obtained by Paternò can be converted by hydrogenation into VIII, thus substantiating the theory advanced by me.[5] Similarly I have since converted into IX the isomeric diacetyl compound which H. W. Shepard working in my laboratory observed was simultaneously formed when following Paternò's directions for the preparation of the diacetyl compound which he described. Shepard's experiments, mentioned briefly in an earlier communication,[5] are recorded in detail in the experimental part of the present paper. The second diacetyl compound was possibly overlooked by Paternò and by Monti on account of the melting points of both derivatives being almost identical. These compounds can, however, be readily distinguished by their color reactions with concentrated sulfuric acid.



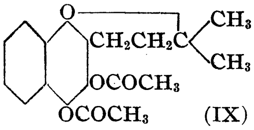
(V) α-Lapachone

(VI) Lapachol

(VII) β-Lapachone

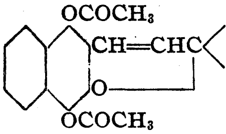


(VIII)

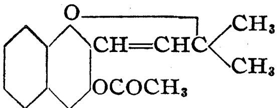


(IX)

It is evident from the results of the hydrogenations that the isomeric diacetyl compounds must bear the relations to α- and β-lapachone, respectively, which the formulas X and XI indicate.



(X)
Paternò's diacetyl compound



(XI)
Shepard's isomeric compound

The double bond must occupy the α,β-position in the chain, since no other location is available. It would be natural to expect that these diacetyl derivatives would yield in weak acid solution, followed by spontaneous oxidation, the α- and β-quinones III and IV, respectively, but this is not the case. Only one and the same substance, namely, dehydrolapachone (Paternò's "isolapachone"), has been obtained from each, notwithstanding that the conditions of the experiment have been varied materially. This change, however, is not entirely without precedent as α-lapachone can be converted by the action of sulfuric acid into β-lapachone, and the reverse action can be readily effected with hydrochloric acid.[5] The changes involve the conversion of the α-quinone into the β-quinone group as well as the opening and closing of the side ring. Similarly isopropylfurano-1,2-naphthoquinone (II) can be converted into the corresponding 1,4-naphthoquinone derivative by the action of hydrochloric or sulfuric acid,[7] and still other examples could be cited from my work. Since isomers of this type are not infrequently interconvertible by acids it is not possible to deduce from the above recorded experiments whether dehydrolapachone is a derivative of α- or β-naphthoquinone. Neither does hydrolysis of the diacetyl derivatives in alkaline solution lead to any definite

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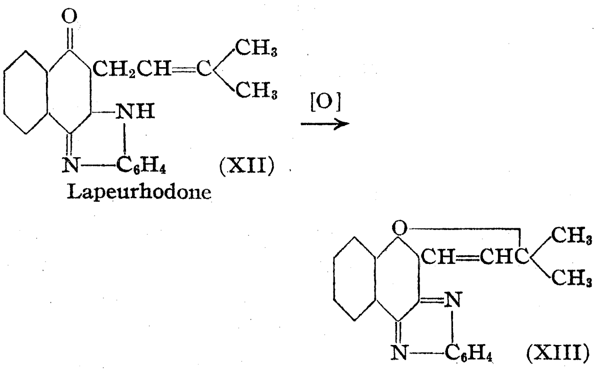
(11) Monti[6] states that when lapachol is treated with either concentrated sulfuric or hydrochloric acid in the cold β-lapachone is formed, while at higher temperatures α-lapachone is the product, it being entirely a matter of temperature and not of the acid used as was recorded by me.[5] Monti's statements are totally incorrect. On repeating the experiments with lapachol hydrochloric acid was found to give α-lapachone both at room temperature and at 55–60°, while with sulfuric acid β-lapachone was obtained at either 25 or 100°.

conclusion, as the side ring of compounds of the lapachone type is invariably more or less readily opened by alkalies, leading to the same hydroxynaphthoquinone derivative in both cases.[5]

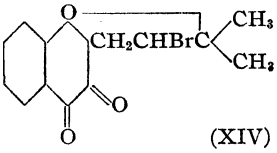
Since Paternò has showed that dehydrolapachone can be reconverted into the diacetyl compound X from which it was obtained, it is clear that in the removal of the acetyl groups no fundamental change has occurred. This is further demonstrated by the ready conversion, described in the present paper, of dehydrolapachone into α-lapachone by hydrogenation. The following facts therefore would seem to furnish very strong arguments in favor of dehydrolapachone being an α-quinone derivative with the formula III: 1. The diacetyl derivative X can be again obtained from dehydrolapachone. 2. The derivative X can be readily converted by hydrogenation into the diacetyl compound VIII derived from α-lapachone. 3. Dehydrolapachone can be converted directly into α-lapachone (V).

The evidence however is subject to some uncertainty because experiments can be advanced apparently proving almost equally satisfactorily that we are dealing with a derivative of β-napthoquinone. For instance dehydrolapachone gives with o-phenylenediamine in good yield an azine (XIII) which can be converted by hydrogenation into the azine of β-lapachone. Also, from lapachol and o-phenylenediamine a dark red compound with a metallic reflex can be obtained which has most probably the structure XII,[12] and this compound, which when treated with concentrated sulfuric acid yields the azine of β-lapachone, is converted into the azine of dehydrolapachone (XIII) by spontaneous oxidation when its ethereal solution is allowed to remain some days in contact with a moderately strong alkaline solution. The change is practically quantitative under proper conditions.


(XII) Lapeurhodone

(XIII) Dehydrolapazine

The formation of dehydrolapachone in small quantity in addition to dihydroxyhydrolapachol by the action of dilute sodium hydroxide solution on bromo-β-lapachone (XIV) has already been recorded.[5] At first sight this last method of formation also would seem to suggest the presence of the β-quinone group, but as the transformation occurred in alkaline solution it is probable that the side ring was opened and again closed on acidifying, but possibly in a different direction.


(XIV)
Bromo-β-lapachone

The several reactions by which dehydrolapachone itself or its derivatives have been obtained lead either to uncertain conclusions or to positively contradictory ones, and the question of whether the compound is an α- or a β-quinone must perhaps remain somewhat uncertain until the isomeric compound has been discovered. The very smooth conversion of dehydrolapachone directly into α-lapachone and also indirectly into the diacetyl derivative of α-lapachone, however, seem to outweigh its conversion into the azine of β-lapachone, as the yield of the intermediate azine of dehydrolapachone, notwithstanding that it is good, nevertheless falls materially below that obtained from other β-quinones in this group. This lower yield may perhaps be due to a preliminary and more or less imperfect change of the α- into the β-quinone before the azine formation occurs.

Perhaps slightly in favor of the α-group, but certainly not at all conclusively so, may also be mentioned the reduction potential determined by Fieser.[13] While this figure varies materially from that of more or less similar heterocyclic α-naphthoquinone substances examined, it falls on the whole better in line with the α-quinones than the β-quinones. The difference, however, is not convincing. The comparison was made by separately averaging the figures given by Fieser for α- and β-naphthoquinone derivatives containing an heterocyclic ring, omitting however the furan derivatives which vary considerably from the other.

It was formerly thought[5] that the orange-red color of dehydrolapachone distinctly favored its

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[12] Hooker, *J. Chem. Soc.*, **63**, 1376 (1893).

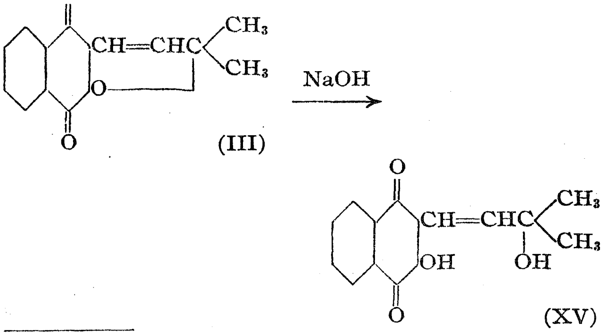
[13] Fieser, THIS JOURNAL, **50**, 450 (1928).

classification as a β-quinone, but in view of the recent recognition that hydroxy-α-naphthoquinone derivatives are usually red or orange-red when they contain a double bond in the α,β-position in the side chain,[14] as is the case with the compound in question, this argument is no longer valid. It would seem, therefore, that the most reliable evidence favors the α-quinone structure III for Paternò's compound and that all of the other observations are capable of being reconciled with this formula.[15]

In regard to the formation of the diacetyl derivatives from which dehydrolapachone is obtained, I am inclined to believe that the first step involved is the closing of the ring through oxidation, the quinone group itself acting as the oxidizing agent. There seems to be a pronounced tendency to form the six-membered ring[10] present in dehydrolapachone, and this can occur only by a shifting of the double bond. The actual mechanism involved must remain in doubt.

Lapachol itself on long standing appears to undergo a corresponding change by spontaneous oxidation and without help from the acetic anhydride. Crude lapachol which had been precipitated from an alkaline extract of Surinam greenheart in 1894 and kept in a wooden box was found after thirty years to be more or less covered with well-formed orange crystals of dehydrolapachone. The crude lapachol after drying had been broken up in moderate sized lumps, and it was in the cavities of these that the crystals had principally formed. In this case there is no positive proof that the dehydrolapachone was really produced directly from lapachol, as it may have had its origin in some other substance present in the crude material, or, as samples of pure lapachol have not been observed to undergo this change, it is also possible that the reaction may have been brought about through the agency of some impurity present. However, in view of the fact that oxidation also occurs in the compound obtained from lapachol and *o*-phenylenediamine (XII) when dissolved in ether and exposed to the air in contact with an alkaline solution, resulting in the azine of dehydrolapachone (XIII), it would seem likely that the orange crystals on the crude lapachol were really derived from lapachol itself.

In addition to this type of oxidation, it has been shown in another paper[16] that lapachol is converted by alkaline permanganate in the cold into 2 - β,β - dimethylvinyl - 3 - hydroxy - 1,4 - naphthoquinone (XVI, below), a compound having one less methylene group in the side chain. In the course of the present studies this same substance has been encountered as a product of the oxidation of dehydrolapachone by the air in alkaline solution. As mentioned above, it was found in the earlier work[5] that bromo-β-lapachone is converted by very dilute alkali in part into dehydrolapachone. In repeating the experiment it has now been found that with more concentrated alkali there is formed in place of dehydrolapachone a small amount of the orange-red compound resulting from the permanganate oxidation of lapachol. It seemed likely that dehydrolapachone is formed in all cases along with the main product, dihydroxyhydrolapachol, but that in the more strongly alkaline solution it undergoes further change and is converted by oxidation into the dimethylvinyl compound, and this was established by treating dehydrolapachone directly. When this substance is allowed to stand in contact with cold 10% sodium hydroxide it slowly dissolves to a dark red solution containing the salt of the acidic substance XV. The material which precipitates on acidification consists chiefly of the original substance III in an unchanged condition, but there is present a small percentage of the dimethylvinylhydroxynaphthoquinone XVI. When dehydrolapachone is treated with sodium hydroxide



(III)

(XV)

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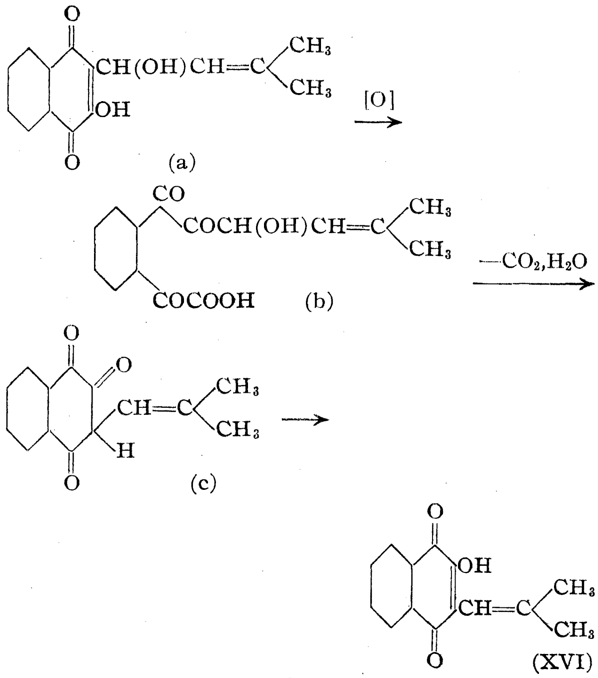
[14] Hooker, THIS JOURNAL, 58, 1163 (1936).

[15] At Dr. Hooker's request in 1931 I tested dehydrolapachone for its ability to form an addition product with sodium bisulfite, a property characteristic of most, if not all, β-quinones. In recently repeated tests it was found that β-lapachone, bromo-β-lapachone and iso-β-lapachone dissolve easily in cold, saturated sodium bisulfite solution when the crystals are crushed to a powder. A colorless, crystalline addition product subsequently separates in each case, and when a dilute solution of the addition product is treated with sodium carbonate the original β-quinone is reprecipitated. Rennie's compound also dissolves in cold bisulfite solution but on adding soda a red solution is obtained, indicating hydrolysis of the side ring. Treated with bisulfite under similar conditions, dehydrolapachone remains undissolved after several hours. The observation supports Dr. Hooker's most recent conclusion (1934) that the substance "almost undoubtedly" is an α-quinone.—L. F. F.

[16] Hooker, THIS JOURNAL, 58, 1168 (1936).



in the presence of zinc dust, followed by air oxidation of the filtered solution, its conversion into XVI is completed within one hour and a yield of more than 80% can be obtained. The rapidity of the reaction may be due to the fact that the closed ring compound easily passes into solution in the form of the hydroquinone whereas it dissolves very slowly in the absence of the zinc dust.

In the course of this remarkable reaction the double bond migrates to a new position in the chain and a carbon atom is eliminated in the oxidation. In analogy with the recently described[10] conversion of lomatiol into isolomatiol, it appears possible that the migration of the double bond is due to an isomerization of the acidic substance XV to an intermediate of the structure (a). The remaining stages may be accomplished through the opening of the quinone ring (b) and its subsequent closing by oxidation (c), as in the formation of the final product (XVI) in the permanganate oxidation of lapachol.[16,17]

Experimental Part

Preparation of the Diacetyl Compounds X and XI from Lapachol.—A mixture of 40 g. of lapachol, 40 g. of anhydrous sodium acetate and 125 cc. of acetic anhydride was refluxed for fifteen minutes and the resulting green solution was poured into about 1 liter of water. A green oil separated and in the course of a few days it had solidified. After being thoroughly washed and dried, the crude material was fractionally crystallized from alcohol, using 5–6 cc. per gram and employing a liberal quantity of animal charcoal. Needles of Paternò's compound (X) separated first, followed by small crystalline balls of Shepard's compound (XI), the pure, colorless materials being obtained in the following amounts: 20 g. of X and 14 g. of XI. Paternò's compound melted at 131–132°, Shepard's at 128–129°. The first substance (X) dissolves in concentrated sulfuric acid to a light yellowish-green solution which immediately darkens to a deep green with a brownish tinge, while XI gives a garnet color on first contact with the acid and this changes to indigo, or to a very dark green, and finally becomes brown.

Anal. Calcd. for $C_{19}H_{18}O_5$: C, 69.93; H, 5.52. Found: (X) C, 69.55; H, 5.71; (XI) C, 69.74, 69.73; H, 5.53, 5.57.

Conversion of the Diacetyl Compounds X and XI into α- and β-Lapachone.—Monti[6] hydrogenated Paternò's diacetyl derivative (X) in the presence of palladium and found the product identical with the diacetyl compound VIII, which she prepared by the reductive acetylation of α-lapachone. In the present work Adams catalyst was used for the hydrogenation and the product, obtained in quantitative yield, melted at 169.8–170° and was fully identified by comparison with a sample of VIII prepared according to Monti. Shepard's compound (0.25 g.), XI, hydrogenated in alcoholic solution (35 cc.) using Adams catalyst (thirty minutes), gave colorless crystals (0.21 g.), m. p. at 162–162.6°, which did not depress the melting point of the diacetyl compound IX from β-lapachone prepared according to Monti.

The hydrolysis and oxidation of the saturated diacetyl derivatives VIII and IX was accomplished by dissolving 0.1 g. of the material in 8 cc. of glacial acetic acid, adding to the cooled solution 15 drops of a mixture of 1 cc. of sulfuric acid and 2 cc. of glacial acetic acid, and allowing the solution to stand in an open flask at room temperature for about ten days. On adding 25–60 cc. of water the product was precipitated as an emulsion which became crystalline on standing. The substance obtained from VIII, after recrystallization, melted at 117°, that from IX at 153.5–154°, and these compounds were found identical, by mixed melting point determinations, with α-lapachone and β-lapachone, respectively.

Conversion of the Diacetyl Compounds X and XI into Dehydrolapachone (III).—The hydrolysis and spontaneous oxidation of the unsaturated diacetyl compounds was studied under three sets of conditions, the first of which is the most satisfactory for preparative purposes.

(a) Sulfuric and Acetic Acids.—A solution of 2 g. of Shepard's compound (XI) in 25 cc. of warm glacial acetic acid was transferred to a flat dish so as to expose a large surface to the air and 5 cc. of a mixture of one volume of concentrated sulfuric acid with two volumes of water was added to the cooled solution. The solution was allowed to stand uncovered for five days, 40 cc. of glacial acetic acid being added to replace that which evaporated. A small amount of the starting material crystallized at first and later dissolved. Dehydrolapachone was slowly deposited and at the end of the period specified this was collected and purified by crystallization from 80% alcohol, giving 0.44 g. of orange prisms, m. p. 142.5–143°. An additional 0.13 g. of the product was obtained on diluting the acid liquor. The above crystallization of the

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(17) Hooker, THIS JOURNAL, **58**, 1174 (1936).

crude material removed a dark brown, granular substance which is insoluble in alcohol and very sparingly soluble in glacial acetic acid. It appears to form a yellow azine with *o*-toluylenediamine.

Treated in the same way, 2 g. of Paternò's diacetyl derivative (X) gave 0.6 g. of dehydrolapachone and none of the brown by-product.

(b) **Aqueous Sodium Hydroxide.**—One gram of either X or XI was finely ground and boiled for about fifteen minutes with 200 cc. of 0.5% sodium hydroxide solution. The solution was filtered from an oily residue (0.23 g.) and on cooling it deposited a reddish oil which soon formed a resinous solid. This was dissolved in hot alcohol and on the addition of water dehydrolapachone was deposited as orange needles. The yields were poor.

(c) **Alcoholic Potassium Hydroxide.**—Ten grams of Shepard's compound (XI) was dissolved in 60 cc. of hot alcohol and the solution was cooled under the tap while 7 g. of solid potassium hydroxide was slowly added and dissolved. A current of air was drawn through the solution for fifteen minutes to ensure complete oxidation to the quinone and the alkali was neutralized with dilute hydrochloric acid (150 cc.). A red oil separated and after several hours it had partially crystallized. The material was removed and allowed to soak with 50 cc. of 1% alkali at room temperature for two days and the solution was poured off and replaced by a fresh portion. The crude residue (4.7 g.) was thoroughly washed with water and crystallized from alcohol, yielding 2.3 g. of pure dehydrolapachone. The combined alkaline extracts on acidification yielded a small amount of 2-β,β-dimethylvinyl-3-hydroxy-1,4-naphthoquinone, which formed orange needles, m. p. 119–120°, from alcohol.

The hydrolysis of Paternò's diacetyl compound (5 g.) by this method proceeded in much the same way, yielding 2.3 g. of crude dehydrolapachone. In the purification small amounts of a colorless and a yellow by-product were observed, but these were not investigated.

Reduction and Hydrogenation of Dehydrolapachone.—Paternò reported[3,4] the conversion of dehydrolapachone by reductive acetylation into the diacetyl derivative X from which he had obtained it, but since he was unaware of the existence of the isomeric compound of Shepard of essentially the same melting point it appeared advisable to repeat the experiment. On boiling for ten minutes a mixture of 0.25 g. of dehydrolapachone, 2.5 g. of zinc dust and 5 cc. of acetic anhydride and pouring the filtered, colorless solution into 30 cc. of water, there was obtained 0.33 g. of product which formed colorless needles, m. p. 130–130.5°, from alcohol. It was found by mixed melting point determination and by the color reaction with sulfuric acid to be identical with Paternò's diacetyl compound X, and there was no indication of the presence of Shepard's compound.

The hydrogenation of dehydrolapachone was conducted in alcoholic solution with Adams catalyst at room temperature for thirty minutes. The filtered solution after exposure to the air was concentrated and the product allowed to crystallize. The material, obtained in 73–80% yield, formed yellow needles, m. p. 117.5–118°, and it was identified as α-lapachone by direct comparison with a known sample. In one experiment the purified product melted at 124.5–125.5° but gave no depression when mixed with a known sample, m. p. 117°, the highest melting point recorded in the literature.

Reductive Acetylation of Isopropylfurano-1,2- and 1,4-naphthoquinone.—Since the isopropylfurano-naphthoquinones[7] such as II are isomeric with dehydrolapachone, they were converted into the diacetyl derivatives of their hydroquinones for comparison with the diacetyl compounds of Paternò and of Shepard. In each case 1 g. of the quinone was refluxed with 20 cc. of acetic anhydride and 10 g. of zinc dust for thirty minutes and the filtered solution was poured into 125 cc. of water. The product crystallized after a few hours and was obtained in each case in quantitative yield. Diacetyl isopropylfurano-1,4-naphthohydroquinone (a) formed colorless needles, m. p. 167–168° from alcohol. It also crystallizes well from glacial acetic acid or benzene. The solution in concentrated sulfuric acid is at first brown, then orange-red and finally a greenish precipitate forms as moisture is absorbed from the atmosphere. Diacetyl isopropylfurano-1,2-naphthohydroquinone (b) crystallizes from alcohol as colorless plates, m. p. 135.5–136.5°. In concentrated sulfuric acid it gives a greenish brown solution changing to dull red on exposure to the air.

Anal. Calcd. for $C_{19}H_{18}O_5$: C, 69.94; H, 5.52. Found. (a) C, 70.03; H, 5.49; (b) C, 69.34, 69.91; H, 5.37, 5.53:

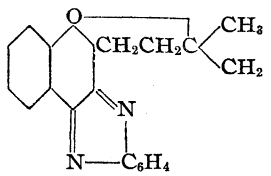
Dehydrolapazine (XIII).—A mixture of 2 g. of dehydrolapachone, 1.8 g. of *o*-phenylenediamine hydrochloride, 5.4 g. of crystalline sodium acetate and 40 cc. of glacial acetic acid was brought to the boiling point, the solution was filtered to remove salt, and allowed to cool. Dark, shield-shaped crystals of the reaction product separated and were collected after twenty-four hours and washed with alcohol and water and again with alcohol; yield 1.03 g. As examination of the mother liquor showed that it contained unchanged dehydrolapachone it was treated with more of the diamine, yielding an additional 0.4 g. of the azine. The product was purified by crystallization from alcohol and was obtained as brownish yellow scales, m. p. 156.5–157°. The substance imparts to concentrated sulfuric acid a green color which changes to cerise on slight dilution. Its ethereal solution has a strong green fluorescence.

Anal. Calcd. for $C_{21}H_{16}ON_2$: C, 80.76; H, 5.12; N, 8.97. Found (Hooker): C, 80.73; H, 5.43; N, 8.98.

Lapeurhodone (XII).—This was prepared from lapachol (20 g.) by essentially the method described above except that less solvent was employed (200 cc.) and the mixture was heated for two hours on the steam-bath. To this was then added 100 cc. of hot water and on cooling the solution deposited dark prisms of the reaction product. The collected material was washed successively with 50% acetic acid, with water, with 150 cc. of cold 1% alkali to remove unchanged lapachol and with water. The yield was 25.6 g. (97%). The substance crystallized from alcohol in the form of small, diamond-shaped scales with a metallic dark green reflex, m. p. 161.5–162.5°. From acetic acid it crystallizes both in the above form and as wooly, dark magenta colored needles. Cold 1% alkali dissolves the diamond-shaped crystals slowly and the needles more rapidly, giving a bright crimson colored solution. The solution in concentrated sulfuric acid is bright green, and water precipitates orange crystals of the sulfate.

Anal. Calcd. for $C_{21}H_{18}ON_2$: C, 80.25; H, 5.73; N, 8.91. Found (Hooker): C, 79.86; H, 5.80; N, 9.09.

Lapazine.—



The azine was prepared by each of the following methods and the samples were all compared and found to be identical.

(a) **From β-Lapachone.**—A mixture of 5 g. of the quinone, 13 g. of crystalline sodium acetate, 5 g. of *o*-phenylenediamine hydrochloride and 90 cc. of glacial acetic acid was heated on the steam-bath for two hours and the red-brown solution was diluted with water and allowed to stand overnight, the resulting oil slowly crystallizing during this time. The yellow globular masses of micro scales were washed with 50% acetic acid and with water; yield, quantitative. Crystallized from alcohol, lapazine was obtained either as yellow scales melting at 130.5–131.5°, or as yellow needles which melt at 121.5–122.5° to a clear liquid which then becomes opaque as the temperature rises and finally clears again at 130.5–131.5°. Either variety can be obtained by merely dissolving the crystals in hot alcohol and seeding with the type desired. No difference could be detected in the action of concentrated sulfuric acid on the two varieties, both dissolving to a deep green solution which became orange on slight dilution.

Anal. Calcd. for $C_{21}H_{18}ON_2$: N, 8.91. Found: N, 8.94.

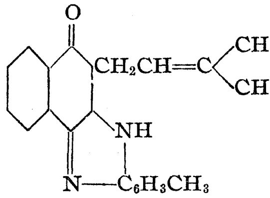
(b) **From Lapeurhodone (XII).**—A solution of 0.1 g. of lapeurhodone in 5 cc. of cold concentrated sulfuric acid was allowed to stand at room temperature for ten minutes and poured into 100 cc. of cold water. A brownish-red, flocculent precipitate formed and on being washed with water it became more crystalline and changed to a yellow color. The yield of lapazine was quantitative.

(c) **From Dehydrolapazine (XIII).**—Dehydrolapazine (0.05 g.) was hydrogenated in alcoholic solution (35 cc.) with Adams catalyst (forty-five minutes) and the filtered solution after exposure to the air was concentrated to a volume of 10 cc. The product, identified as lapazine, was deposited as extremely fine yellow needles mixed with yellow scales, the two forms having the properties recorded above.

Oxidation of Lapeurhodone (XII) to Dehydrolapazine (XIII).—A solution of 5 g. of lapeurhodone in 600 cc. of ether was transferred to a separatory funnel containing 250 cc. of 5% sodium hydroxide. The funnel was plugged with cotton and the mixture let stand at room temperature for eight days. The aqueous layer at the outset gradually turned red in color due to the presence of dissolved lapeurhodone. At the end of the period both layers had become lighter in color, the ether layer developing a strong green fluorescence and depositing some yellow crystals. The aqueous layer was discarded and the ethereal solution on evaporation yielded 3.4 g. of dehydrolapazine. The substance crystallized from alcohol in the form of brownish-yellow scales melting at 156.5–157°. It gave no depression when mixed with the azine from Paternò's dehydrolapachone and gave the same color reactions.

The above change also occurred when a solution of 0.1 g. of lapeurhodone in 20 cc. of 1% sodium hydroxide solution was refluxed for about twenty-four hours, the dehydrolapazine depositing from the alkaline solution as a yellow oil which solidified on cooling. The yield was good but the product was less satisfactory than that obtained by the other method.

Oxidation of Methyllapeurhodone.—Six grams of methyllapeurhodone (from lapachol and *o*-toluylenediamine)[12] was dissolved in 500 cc. of ether, 500 cc. of 5%



sodium hydroxide solution was added and the mixture was allowed to stand in a loosely stoppered flask for two days. Evaporation of the ether layer yielded 4.5 g. of a mixture of yellow needles and yellow scales. The two substances, which appear to be isomers differing in the location of the methyl group, were separated by fractional crystallization from alcohol, the needle-form separating first. The needles melted at 149–151.5°, the scales at 169.5–171.5°. Both substances give a green solution in concentrated sulfuric acid, the solution becoming carmine on dilution and depositing red needles of a salt.

Anal. Calcd. for $C_{22}H_{18}ON_2$: C, 80.98; H, 5.52; N, 8.59. Found: (needles) C, 80.74; H, 5.45; N, 8.55; (scales) C, 81.12; H, 5.60; N, 8.56.

By condensing dehydrolapachone with *o*-toluylenediamine in the usual way and fractionally crystallizing the product from alcohol, two methyldehydrolapazines were obtained having properties identical with those of the compounds described above and giving no depression in melting point when mixed with these substances.

Action of Sodium Hydroxide on Bromo-β-lapachone (XIV). (a) **1% Alkali.**—Finely ground bromo-β-lapachone was allowed to stand at room temperature with 1% sodium hydroxide solution for ten days and the crimson colored solution was filtered from unattacked material and acidified. Orange-yellow crystals of dihydroxyhydrolapachol,[5] m. p. 184–185°, were deposited, and the aqueous mother liquor slowly yielded an additional crop of crystals which were found to consist chiefly of dihydroxyhydrolapachol and an extremely small amount of material insoluble in cold dilute alkali and identified as dehydrolapachone.

(b) **5% Alkali.**—Treated as above, but with stronger alkali, the substance was attacked more rapidly. After one week the alkaline solution was filtered from unchanged material and acidified. The crystalline product consisted of a mixture of dihydroxyhydrolapachol (60–65% by weight) and the lapachol oxidation product XVI (5% by weight), m. p. 119–120°. A separation was accomplished by reprecipitation from an alkaline solution, the oxidation product separating rapidly while dihydroxyhydrolapachol is deposited slowly.

Conversion of Dehydrolapachone (III) into 2-β,β-Dimethylvinyl-3-hydroxy-1,4-naphthoquinone (XVI). — (a) Finely ground dehydrolapachone was allowed to stand in contact with 10% sodium hydroxide solution at room temperature and after one day the alkaline solution was filtered from unattacked material and acidified. The precipitate consisted largely of dehydrolapachone, but a small amount of an acidic substance was isolated by soaking the crude material with dilute alkali, which leaves the dehydrolapachone largely, if not entirely, undissolved, and reprecipitating with acid. The dimethylvinyl compound XVI was identified by melting point (119 – 120°), mixed melting point, and by its reaction with concentrated sulfuric acid.

(b) Ten grams of dehydrolapachone was ground to a paste with 200 cc. of water, this was treated with a solution of 50 g. of sodium hydroxide in 300 cc. of water, 50 g. of zinc dust was added and the container was stoppered and shaken at intervals. The substance dissolved within a few minutes owing to its rapid conversion to the hydroquinone, as indicated by the change in the color of the solution from crimson to yellow. After one hour the mixture was poured into 2.5 liters of water, the color changing at once to red and the dilute alkaline solution was filtered to remove the zinc. Air was drawn through the solution for a few minutes to ensure complete oxidation and the solution was then acidified by pouring it into dilute hydrochloric acid (a better product was obtained than when the acid was added to the alkaline solution). The crude material contained some unchanged dehydrolapachone, but this was largely left as a residue on extracting the product with 700 cc. of 0.5% alkali and filtering immediately. On acidification the reddish-purple filtrate yielded 6.7 g. of 2-β,β-dimethylvinyl-3-hydroxy-1,4-naphthoquinone in the form of red prismatic needles. Extraction of the mother liquor gave 1.3 g. more of the material. The purified product melted at 119–120° and was identical with that obtained by the permanganate oxidation of lapachol.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.26. Found: C, 73.49; H, 5.54.

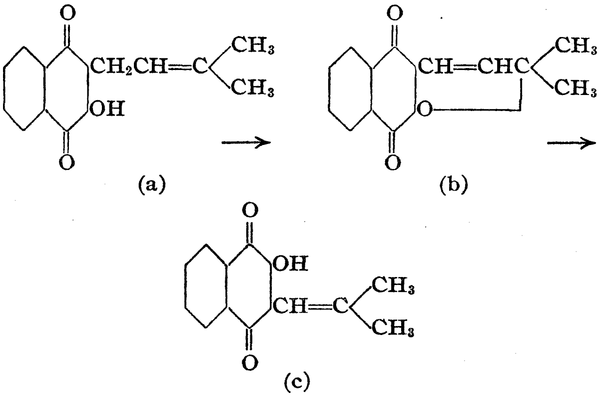
Action of Acetic Anhydride and Sodium Acetate on 2-Allyl-3-hydroxy-1,4-naphthoquinone.—It was observed by Fieser[18] that the allyl compound behaves in the acetylation reaction like lapachol, and he reported the isolation of a substance of m. p. 220–221°, dec., analogous to Paternò's diacetyl compound X. A further investigation of the reaction was undertaken with Dr. Steyermark in the hope of obtaining the parent quinone of which dehydrolapachone (III) is the dimethyl derivative, but the work was not completed. A second isomer, probably corresponding to Shepard's compound XI, was isolated from the reaction mixture by fractional crystallization from alcohol. From 1 g. of the allyl compound there was obtained 0.5 g. of Fieser's diacetyl compound, which after recrystallization melted at 223.5–224.5°, dec., and 0.4 g. of the new compound. The latter formed feather-shaped needles, m. p. 178.5–179.5°.

Anal. Calcd. for $C_{17}H_{14}O_5$: C, 68.43; H, 4.73. Found: C, 68.71; H, 4.70.

Fieser's compound on acid hydrolysis and exposure to the air gave a red quinone resembling dehydrolapachone, but the substance was not fully characterized.

Summary

It is shown in this paper that Paternò's "isolapachone" is in reality a dehydro derivative of α-lapachone in which the double bond occupies the α,β-position in the chain. Under certain conditions lapachol (a) or its derivatives can be transformed both directly and indirectly into Paternò's compound (b), or the corresponding derivatives of this substance. The actual mechanism of the change is still in doubt. Conditions also have been defined under which dehydro-α-lapachone (b) can be transformed by air oxidation in the presence of alkali into a substance (c) previously obtained by the oxidation of lapachol with alkaline potassium permanganate.



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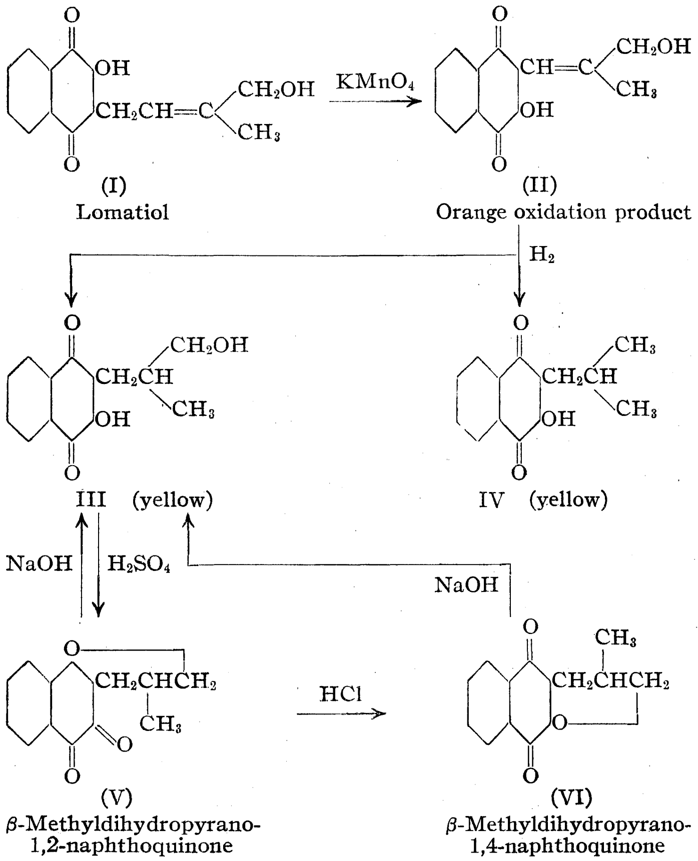
[18] Fieser, THIS JOURNAL, **48**, 3201 (1926).

Lomatiol. Part III. Oxidation with Alkaline Potassium Permanganate[1,2]

BY SAMUEL C. HOOKER AND AL STEYERMARK

In a previous paper[3] evidence was presented indicating that lomatiol has the constitution represented by formula I, and it was reported that on oxidation with alkaline potassium permanganate the yellow substance yields an orange compound of the formula II, a change of the type observed[4] in the case of lapachol and related hydroxynaphthoquinone derivatives. The present paper includes a full account of the reaction and a description of a second substance which is formed in small amounts in the course of the oxidation.



The structure of the orange compound (II) is established by the following observations. On hydrogenation two substances are formed concurrently, one by the saturation of the double bond in the side chain (III), the other by the simultaneous replacement of hydroxyl by hydrogen and the addition of hydrogen to the double bond (IV). As such a reaction is characteristic of an allylic system, the original hydroxyl group must occupy a position adjacent to the double bond. The compound in which the hydroxyl has been removed from the side chain was found to be identical with a quinone previously described[4a] and known to have the structure of IV, and consequently the allylic system must be arranged either in the manner indicated in II or with the hydroxyl group in the α-position and the double bond at the end of the chain. A choice between the two possibilities is easily made, for it can be inferred from other observations[5] that if the latter structure were correct the alcoholic hydrogenation product (III) would readily lose water to form a substance with an unsaturated side chain. Instead it is converted by sulfuric acid into an orange closed-ring compound (V) very similar in properties to β-lapachone. That this is a β-quinone is shown by its ability to form an azine and by its conversion by means of hydrochloric acid into a yellow α-quinone, VI. Consequently the hydroxyl group must be at the end of the chain in the saturated alcohol III and in the oxidation product (II) itself.

The observations thus lend further support to the structure assigned to lomatiol and the oxidation is shown to proceed, as in the examples already studied, by the removal of CH_2 from the position adjacent to the quinone group. The change is all the more remarkable because both the primary alcoholic group and the double bond remain unattacked. Comparing the orange oxidation product II with the compounds which it yields on hydrogenation (III and IV) and with lomatiol, all of which are yellow, it is seen that

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(1) See Editor's note (1), THIS JOURNAL, **58**, 1163 (1936).

(2) The orange oxidation product from lomatiol and the interesting red closed ring compound obtained from it were isolated by Dr. Hooker as early as 1917, but as the nature of the oxidation was not at the time understood the matter was dropped for the time being. After the course of the reaction of lapachol with alkaline permanganate had been established, work on the present problem was later resumed in conjunction with Dr. Steyermark. Dr. Hooker wrote no manuscript describing the investigation and the paper has been constructed from his notes and from the notes and reports of his assistant.—L. F. FIESER.

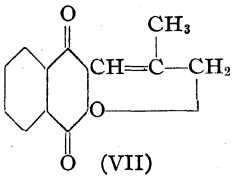
(3) Hooker, THIS JOURNAL, **58**, 1181 (1936).

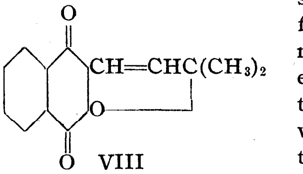
(4) Hooker, *ibid.*, **58**, (a) 1168; (b) Hooker and Steyermark, *ibid.*, **58**, 1174; (c) 1179 (1936).

(5) Hooker, THIS JOURNAL, **58**, 1163 (1936).

the presence of a double bond in II in the α,β-position of the chain could be safely inferred from the orange color.

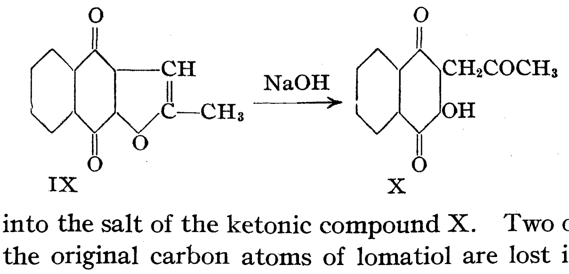
The orange compound II easily loses a molecule of water under various conditions, for example when it is gently heated, or when the aqueous solution is boiled. The anhydride, which forms dark red needles, has been recognized as a para quinone of the structure VII by its conversion on hydrogenation into the yellow α-quinone VI.


(VII)
β-Methylpyrano-1,4-naphthoquinone


VIII
Dehydrolapachone

The compound has the type of unsaturated, six-membered ring characteristic of Paternò's dehydrolapachone,[6] VIII, and it closely resembles this substance in its red color, which no doubt is due to the conjugation of the double bond with the quinone ring, in its behavior when treated with sulfuric acid, and its ready formation from the open chain compound. The substance has been found to undergo a number of additional changes, which will be described in a later paper.

As in the oxidation of other quinones having unsaturated side chains,[4a,c] the action of alkaline potassium permanganate is not limited to a single reaction and the quantity of the orange compound II produced amounts to no more than about one-third of the lomatiol used. As another product of oxidation there was isolated a small quantity of a yellow substance which was fully identified, by direct comparison with a sample prepared by a method which will be described in a later paper, as β-methylfurano-1,4-naphthoquinone, IX. On treatment with alkali the substance is converted



IX X

into the salt of the ketonic compound X. Two of the original carbon atoms of lomatiol are lost in the formation of this oxidation product, one probably being that next to the quinone ring and the other the carbon atom carrying the hydroxyl group at the end of the chain. The course of the reaction is not known.

Experimental Part[7]

Orange Oxidation Product, II (2-β-Methyl-γ-hydroxy-α-propenyl-3-hydroxy-1,4-naphthoquinone).—Four grams of lomatiol was dissolved in 400 cc. of 1% sodium hydroxide solution and this was cooled in ice water and treated quickly with a similarly cooled solution of 4 g. of potassium permanganate in 400 cc. of water. The solution turned green, then brown, and the manganese dioxide had largely separated within a minute or two. The solution was filtered at once from the precipitate and very carefully neutralized with dilute hydrochloric acid, avoiding an excess as this promotes the conversion of the material into the red anhydride (VII). The resulting orange solution was transferred to four flat dishes and evaporated at room temperature with the aid of electric fans to a volume of 45–140 cc. (four and one-half hours to five and one-half hours). By this time a considerable amount of crystalline, orange material had separated and this was collected and washed with a small volume of cold water. A small quantity of the red anhydride can be obtained by boiling the mother liquor.

The crude product (1.2–1.4 g.) was contaminated with a small amount of the red anhydride, but it was easily separated from this material by extraction with cold 1% sodium carbonate solution (33 cc. per g.), which does not attack the red compound on short contact. The orange material reprecipitated from the soda solution was crystalline and nearly pure (recovery, 86%). The substance separates from benzene or from benzene–ligroin as orange, crystalline masses, while from petroleum ether it forms woolly orange needles. It has no true melting point for it is rapidly converted into the red anhydride on being heated. Loss of water also occurs on boiling the aqueous solution for a few minutes or treating the compound with sulfuric or hydrochloric acid at room temperature. The change occurs on prolonged boiling of the solution in alcohol, in which the orange compound is very soluble, and even in the solid state the hydroxy compound undergoes slow, spontaneous cyclization.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.82; H, 4.96. Found: C, 68.79; H, 5.37.

The Red Anhydride, VII (β-Methylpyrano-1,4-naphthoquinone).—For the preparation of this substance in quantity it is convenient to effect the dehydration of the oxidation product II directly in the reaction mixture, rather than to first isolate it. In a typical experiment 10 g. of lomatiol was oxidized exactly as described above and the filtered alkaline solution was neutralized with dilute (1:3) hydrochloric acid and treated with an additional 50 cc. of the dilute acid. The orange solution was boiled gently for twenty minutes, avoiding any appreciable decrease in the volume, as the product is then contaminated with other substances. During this time the solution became red and crystals of the red anhydride were deposited from the hot solution. After cooling to room temperature, the product was collected and washed with water; yield 3 g. The crude material usually contains a small amount (2–3%)

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(6) Hooker, THIS JOURNAL, **58**, 1190 (1936).

(7) Analyses by Dr. D. Price, Columbia University.

of the second oxidation product, β-methylfurano-1,4-naphthoquinone, IX, which was recognized in separate experiments by its greater resistance to alkaline hydrolysis. The substance is eliminated in the course of the crystallization.

The anhydride VII is sparingly soluble in alcohol and crystallizes from this solvent as fiery red, prismatic needles melting at 196.5–197.5°. It dissolves readily in benzene or glacial acetic acid and is very sparingly soluble in water, from which it is deposited as very fine, bright red needles.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.30; H, 4.45. Found: C, 73.93; H, 4.45.

Very characteristic of the red anhydride, as well as of Paternò's dehydrolapachone, is the following color reaction. The compound dissolves in concentrated sulfuric acid to give a clear, deep green solution and if this is exposed on a watch glass it gradually absorbs moisture from the atmosphere, acquires a plum pink color, and finally deposits the unchanged substance in the form of red needles, sometimes curved, leaving the solution colorless. The same changes are noted with Paternò's compound.

Heated for six hours with *o*-phenylenediamine in glacial acetic acid solution, the red anhydride was in part resinified and in part recovered unchanged. There was no evidence of azine formation.[8]

β-Methyldihydropyrano-1,4-naphthoquinone (VI).—A suspension of 4 g. of the red anhydride (VII) in 200 cc. of alcohol was agitated with hydrogen at 40 lb. (2.66 atm.) pressure in the presence of Adams catalyst. The red compound soon went into solution in the form of the hydroquinone and this gradually added hydrogen to the double bond. The course of the reaction was followed by removing a drop of the solution, allowing it to evaporate and oxidize on a watch glass, and adding a drop of concentrated sulfuric acid. The starting material gives a green color with the acid while the dihydro derivative gives a red color. The hydrogenation was found to be complete in forty-five minutes. After filtering and allowing time for oxidation, a part of the reaction product crystallized from the solution and further crops were obtained after concentration of the mother liquor; yield, 3.8 g. The product was purified by crystallization from alcohol, using animal charcoal, and it was obtained as bright yellow, elongated plates, m. p. 170.5–171°.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.65; H, 5.30. Found: C, 73.74; H, 5.74.

The red solution of the quinone in concentrated sulfuric acid on exposure to the air deposits long yellow needles of the unchanged compound on absorption of moisture. The action of boiling alkali on the substance and its formation from the isomeric ortho quinone are described below.

2-γ-Hydroxyisobutyl-3-hydroxy-1,4-naphthoquinone (III).—This compound is most conveniently prepared by the saponification of the dihydropyrano-*p*-quinone VI, described immediately above. This material (2.9 g.) was finely ground and boiled with 1% sodium hydroxide solution (400 cc.) for about ten minutes, when it had completely dissolved. The resulting crimson colored solution was carefully treated with dilute hydrochloric acid and left faintly alkaline, as in the presence of excess acid the product is readily dehydrated to the dihydropyrano-*o*-quinone V. The crude product which precipitated (2.8 g.) contained in addition to the desired acidic compound a small amount of a neutral, yellow substance not identical with the starting material. The two were easily separated by extraction with cold 1% alkali, the hydroxy quinone III being recovered from the filtered solution by careful neutralization; yield, 2.6 g. The substance crystallizes from benzene or from benzene–ligroin in the form of yellow needles, m. p. 147.5–148.5°. It is very soluble in alcohol, but crystallizes well from dilute alcohol as needles.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.26; H, 5.73. Found: C, 68.25; H, 5.99.

The compound was obtained by the action of alkali on the isomeric *o*-quinone V in exactly the same manner.

β-Methyldihydropyrano-1,2-naphthoquinone (V).—A solution of 1.6 g. of the hydroxyquinone III in 20 cc. of concentrated sulfuric acid was prepared at room temperature and after standing for forty-five minutes the red solution was poured into 100 cc. of water. The reaction product separated in the form of orange needles and in a very pure condition; yield 1.5 g. The product, purified by crystallization from alcohol, was obtained either as orange prismatic needles or as elongated orange plates, m. p. 148–148.5°.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.65; H, 5.30. Found: C, 73.32; H, 5.37.

The compound is also formed when the hydroxyquinone III is allowed to stand for one to two days in contact with dilute hydrochloric acid. It is insoluble in cold dilute alkali, but on boiling it soon dissolves with opening of the oxide ring. The conversion of the substance into the isomeric para quinone VI was accomplished by heating a solution of 0.1 g. of the material in 3 cc. of concentrated hydrochloric acid at 55–65° for one and a half hours. The red solution on cooling deposited yellow needles (0.09 g.) of the para quinone in a very pure condition.

The azine of the ortho quinone V was prepared by heating a solution of the substance and *o*-phenylenediamine in glacial acetic acid at the boiling point for a few minutes. The yellow product separated in part from the boiling solution. Recrystallized from alcohol (fluorescent solution), it formed yellow needles, m. p. 160–161°. The solution in concentrated sulfuric acid is deep green and deposits an orange sulfate on dilution.

Anal. Calcd. for $C_{20}H_{16}ON_2$: C, 79.97; H, 5.37. Found: C, 80.11; H, 5.25.

Hydrogenation of the Orange Oxidation Product II.—The two compounds III and IV, which are formed simultaneously in the hydrogenation of the unsaturated alcohol II, are not both easily separated as such from the reaction mixture, but on treatment with acids the saturated alcohol III is converted into its ortho quinone anhydride and IV can then be removed from it by extraction with alkali. The following procedure gave satisfactory results. A solution of 0.2 g. of the oxidation product II in 4 cc. of alcohol was submitted to hydrogenation (Adams catalyst) for forty-five minutes and on filtering and concentrating the solution to a small volume a small crop (0.06 g.) of 2-iso-

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[8] Similarly, the quinone does not dissolve in cold sodium bisulfite solution.—L. F. F.

butyl-3-hydroxy-1,4-naphthoquinone (IV) was deposited. After allowing the mother liquor to evaporate to dryness the residue was dissolved in 0.25% alkali and the solution was filtered from a small amount of resin and acidified with dilute (1:3) hydrochloric acid, adding 5 cc. excess. The crystalline yellow precipitate, consisting of a mixture of the two products of hydrogenation, was allowed to stand in contact with the acid liquor for two days, during which time the alcohol III was converted into its ortho quinone anhydride. The collected material was then shaken with cold 0.25% alkali for one to two minutes and the solution was quickly filtered from unchanged orange needles of V (0.03 g.) and acidified, giving 0.04 g. of the yellow isobutyl compound IV. After recrystallization the orange substance melted at 148–148.5° and the yellow one at 132.5–133.5°. Identifications with known samples were made by mixed melting point determinations and by microscopic examination of the character of the precipitates resulting on the acidification of the solutions in alkali.

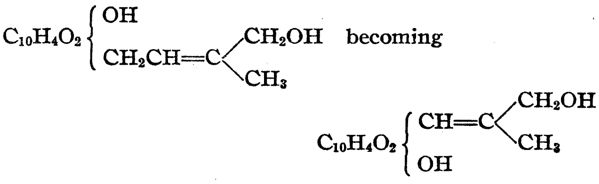
The Second Oxidation Product, IX (β-Methylfurano-1,4-naphthoquinone).—This compound is produced only in small quantities in the oxidation of lomatiol, but by the following procedure it is possible to free the substance from other products of the reaction and to obtain it in a very pure condition. The new compound was isolated from the acid mother liquor remaining from the oxidation of 10 g. of lomatiol, after removing the orange product in the form of its red anhydride as described above for the preparation of the latter substance. The acid filtrate was boiled down to a volume of about one liter and allowed to cool to room temperature, when about 0.6 g. of crude material was deposited. This contained, in addition to the new compound, some material easily soluble in alkali and some of the red anhydride, VII. It was first ground with 40 cc. of cold 0.25% alkali, and after standing for three hours the undissolved material was collected and boiled for about three minutes with 20 cc. of 1% alkali. This treatment left the new compound largely unattacked, but a small amount of the red anhydride also escaped the action of the alkali, and the orange residue (0.2 g.) was still impure. In order to remove the red anhydride, the crude product was submitted to hydrogenation in alcoholic solution, it having been established that the new compound is converted only into its hydroquinone under these conditions. This procedure removed the red color due to anhydride (VII), for the latter was converted into its yellow dihydro derivative VI, which is more soluble in alcohol and which can be removed by crystallization. After agitation with hydrogen the filtered alcoholic solution was exposed to the air and on standing it slowly deposited yellow needles of the purified product (IX). On further crystallization the substance was obtained as yellow needles or prisms, m. p. 246–247°.

Anal. Calcd. for $C_{13}H_8O_3$: C, 73.58; H, 3.57. Found: C, 73.75; H, 3.73.

The substance did not depress the melting point of a sample prepared by a method which will be described in a forthcoming paper. Both samples were converted into the same acidic substance X (m. p. 176.5–177.5°) by boiling sodium hydroxide solution.

Summary

The oxidation of lomatiol with alkaline potassium permanganate proceeds exactly as in the case of other examples studied in this Laboratory:



There is formed in addition a very small amount of a substance having one less carbon atom, but although the structure of the compound has been established the manner in which it is formed is still obscure. The principal product of the oxidation yields two substances simultaneously on hydrogenation, and it gives rise to an interesting red ring compound which has been recognized as an α-quinone of a type analogous to Paternò's dehydrolapachone.

82 Remsen Street
Brooklyn, New York

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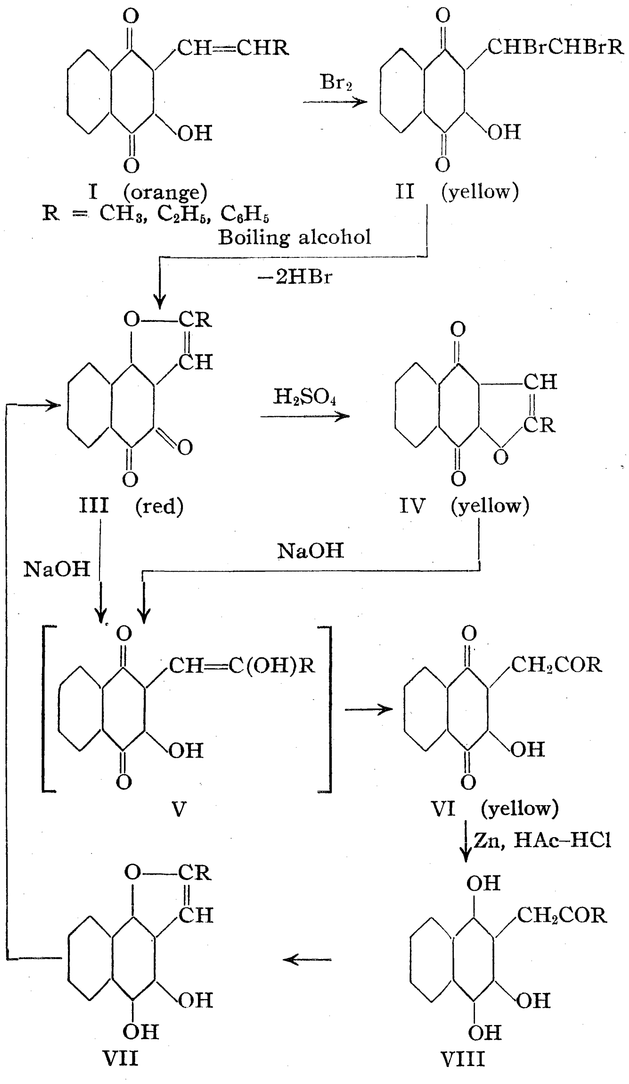
Conversion of Ortho into Para, and of Para into Ortho Quinone Derivatives. Part IV.[1] Synthesis of Furan Derivatives of α- and β-Naphthoquinones[2,3]

By Samuel C. Hooker and Al Steyermark

The ready conversion of isolapachol into isopropylfurano-1,4- and 1,2-naphthoquinone was described many years ago in connection with experiments on the structure of lapachol,[4] and the belief was then expressed that the reaction would prove to be a general one. This is abundantly substantiated by the experiments recorded in this paper. The accompanying table shows graphically the formation of the furan derivatives and some of the important reactions studied involving changes from para to ortho quinones and *vice versa*. In some instances the changes take place practically quantitatively, in others modifications occur with the formation of additional substances, but in general the table records the reactions common to the substances examined.



The parent compound of this group of furanonaphthoquinones, IX, was first obtained by Scholl and Zincke[5] from X by a series of changes following the formation of X by alkaline ferricyanide oxidation of alizarin. The furan compound was described as crystallizing in red needles, but in spite of this very characteristic property of ortho naphthoquinones of this type, to which attention has been called repeatedly in former papers,[1a,1b,6] Scholl and Zincke preferred to assign to their compound the formula XI which would be yellow. We shall show that they erred in this respect and that the substance is not a para quinone. In dealing with this subject of quinone change, it may again be emphasized that many compounds are now known of the general formulas XII, XIII and XIV, and that in the course of minor chemical changes of naphthoquinone derivatives *of this type* whenever a red compound passes into a yellow one or *vice versa* it may almost be taken for granted that a change corresponding to this change of color has occurred in the quinone groups.

Errors in the chemical literature have already been corrected[1a,b] where this change in color has been disregarded. There are, however, some known exceptions to the general rule, the causes of which have been fully discussed and explained in recent papers.[7] For instance, in compounds of the type I we have one of these exceptions. These substances, which served as the starting materials for the present syntheses,

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(1) Previous papers: (a) Hooker and Carnell, *J. Chem. Soc.*, **65**, 76 (1894); (b) Hooker and Walsh, *ibid.*, **65**, 321 (1894); (c) Hooker and Wilson, *ibid.*, **65**, 717 (1894).

(2) See Editor's note (1), This Journal, **58**, 1163 (1936).

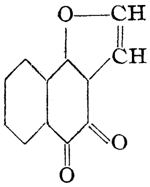
(3) Dr. Hooker wrote the first three paragraphs of this paper and the remainder has been constructed from the notes and reports of the junior author.—L. F. Fieser.

(4) Hooker, *J. Chem. Soc.*, **69**, 1355 (1896).

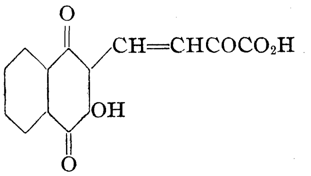
(5) R. Scholl and A. Zincke, *Ber.*, **52**, 1142 (1919).

(6) Hooker, *J. Chem. Soc.*, **61**, 611 (1892); **63**, 1376 (1893); **65**, 15 (1894); **69**, 1355 (1896); Hooker and Gray, *ibid.*, **63**, 424 (1893).

(7) (a) Hooker, This Journal, **58**, 1163; (b) 1168; (c) 1181; (d) Hooker and Steyermark, **1179**; (e) **1198** (1936).



IX



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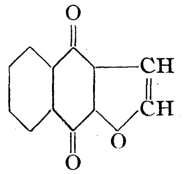
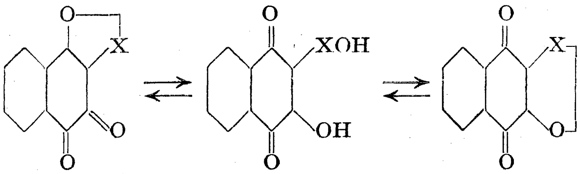


XI



(XII) Red or deep orange (XIII) Yellow (XIV) Yellow

were prepared for the most part by the condensation of aldehydes with hydroxynaphthoquinone.[7a] The simplest member of the series, 2-vinyl-3-hydroxy-1,4-naphthoquinone, has not been obtained by this method, possibly because of its unusually sensitive nature, but it has been prepared by the oxidation of the allyl compound.[7d] The compounds in question (I) are not yellow as the para naphthoquinone grouping ordinarily requires, but are deeply colored, usually orange or brick red. This is due to the presence of a double bond in the α,β-position of the side chain. They add bromine readily in chloroform solution forming compounds of the general formula II which with the elimination of the double bond become *yellow*.

The bromine addition compounds (II) are comparatively unstable, being readily converted into furano-1,2-naphthoquinone derivatives, III, which are red. This change takes place gradually with loss of hydrogen bromide even in the dry, purified substances. The bromine compounds can be purified by crystallization from benzene or chloroform but even at ordinary temperatures there is usually slight decomposition. Solution in alcohol containing small amounts of water, sometimes even in the cold, brings about almost quantitative conversion into the corresponding deep red III, due to the passage of the para quinone group of the yellow dibromide into the ortho quinone group of the furan derivative.

In the case of the methyl, ethyl and phenyl derivatives, the red ortho quinones (III) can be isomerized to the yellow para quinones (IV) by the action of sulfuric acid. By boiling the quinones of either type with alkali the furan ring is opened and the same acidic substance is obtained from the two isomers III and IV. Since the resulting compound invariably is *yellow*, the structure must be that of VI, for the unsaturated compound of formula V would be orange or red. The ketonic compounds of the type VI on direct cyclization give mixtures of the ortho and para quinones, but after reduction to the hydroquinones (VIII) ring closure occurs selectively in a single direction and on oxidation the ortho quinones (III) can be obtained in a pure condition.

While the methyl and ethyl substituted compounds of the type IV are pure yellow in color and stand in marked contrast to the corresponding red quinones (III) of the ortho series, β-phenylfurano-1,4-naphthoquinone can be obtained both as golden yellow plates and as bright red needles. The red form is the less stable modification and changes into the yellow form when heated. Although it is unusual that a para quinone of this type should exist in any but a yellow condition, even as a metastable form, there is still a considerable contrast between the bright red color of this modification and the dark, purplish-red of the ortho isomer. The latter substance combines with *o*-phenylenediamine to form an azine, and the same characteristic property of an ortho quinone is shared by the methyl and ethyl derivatives, which from their red color alone would be regarded as ortho quinones.

The preparation and characterization of the parent quinone of the furan group presented some difficulties, probably because the general instability of the vinyl derivative of hydroxynaphthoquinone is shared by the other open-chain compounds resulting from it. Only one of the two possible furanonaphthoquinones was isolated, namely, a deep red compound corresponding to the description of Scholl and Zincke. From its color and from the fact that it was obtained by the general method which in other cases leads to the formation of ortho quinones, it can be inferred that the substance is an ortho quinone of the formula IX, a conclusion which is convincingly established by the formation of a characteristic azine in good yield.[8] The quinone is unusually

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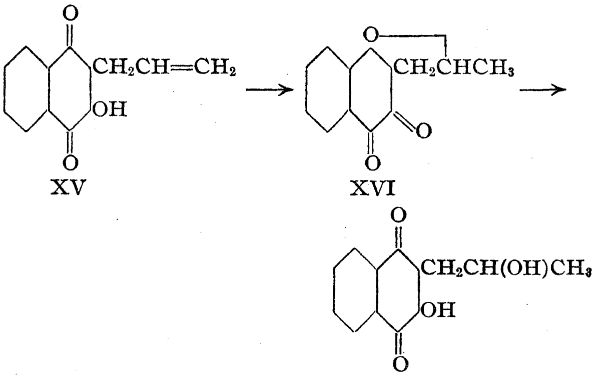
[8] A further confirmation of the structure is that the substance dissolves in cold sodium bisulfite solution. The action is slower than in the case of the methyl and ethyl derivatives, as might be expected from the much higher melting point of the parent substance, but as with these compounds the quinone is precipitated unchanged on the addition of sodium carbonate.—L. F. F.

stable in concentrated sulfuric acid solution and, although some change occurs after the solution has stood for several weeks, no substance corresponding to a para quinone has been isolated. Attempts to open the furan ring by alkaline hydrolysis indicated that the aldehydic substance first formed undergoes further change in the course of the reaction.

The substituted furanonaphthoquinones of both the ortho and para series are converted by alkalies in good yield into the ketonic compounds of the formula VI. Although the properties of these substances have not been investigated extensively it has been found in one case that the carbonyl group of the side chain is easily reduced by hydrogen in the presence of platinum catalyst, and probably the reaction is a general one. The compound studied was 2-acetonyl-3-hydroxy-1,4-naphthoquinone (R = CH_3), and the alcoholic reduction product (XVII) proved to be identical with a substance obtained by Fieser[9] by cyclizing 2-allyl-3-hydroxy-1,4-naphthoquinone (XV) with sulfuric acid and opening the ring by treatment with alkali. The identity of the products verifies



the structures assumed by Fieser for XVI and XVII on the basis of the known rule of addition, and it is of interest that the rule holds for the allyl compound as well as for lapachol[4] although the former substance gives rise to the formation of a five-membered ring while with the latter a six-membered internal anhydride is produced.

Experimental Part[10]

Reaction of the Unsaturated Compounds (I) with Bromine

The bromine addition products were prepared by dissolving the unsaturated compound in chloroform (10–20 cc. per gram of material) at room temperature and either quickly treating this with, or adding it to, a solution of somewhat more than one equivalent of bromine in the same solvent (5 cc. per gram). The bromine was absorbed at once, following which the solvent was removed completely, except in the case of the less soluble phenyl compound, by distillation from a water-bath, avoiding unnecessary heating. The residual oil usually crystallized after standing for several hours, and this crude material was quite suitable for use in the next step in the synthesis. The substances were not all obtained in a completely pure condition.

In the case of 2-vinyl-3-hydroxy-1,4-naphthoquinone the chloroform solution of the crude material was filtered from some insoluble residue, cooled to 0°, and poured into the bromine solution. The crude reaction product was very unstable and it was converted at once into the furano-1,2-naphthoquinone. From 1 g. of the 2-α-propenyl compound and 0.65 g. of bromine there was obtained, after washing the crystalline reaction mass with 1 cc. of cold benzene to remove adhering resin, 1.5 g. of crude dibromo compound. It crystallized from benzene (5 cc. per gram) as yellow plates, m. p. 156–157°, dec., but the sample decomposed before an analysis could be made.

2 - α,β - Dibromo - *n* - butyl - 3 - hydroxy - 1,4 - naphthoquinone (II, R = C_2H_5) was prepared from 2 g. of the unsaturated compound and 1.3 g. of bromine. Recrystallized from 5 cc. of benzene, the substance formed yellow prisms, m. p. 133–134°; yield, 2.5 g.

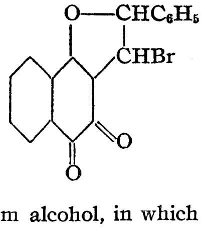
Anal. Calcd. for $C_{14}H_{12}O_3Br_2$: C, 43.31; H, 3.11; Br, 41.19. Found: C, 43.60; H, 3.00; Br, 40.51.

2 - α,β - Dibromo - β - phenylethyl - 3 - hydroxy - 1,4 - naphthoquinone (II, R = C_6H_5).—A solution of 2 g. of 2-β-phenylvinyl-3-hydroxy-1,4-naphthoquinone in 25 cc. of chloroform was treated gradually at room temperature with 1.6 g. of bromine in 6 cc. of chloroform. After standing one to four days the solution deposited 1.1–1.4 g. of yellow prisms of the addition product, and after concentrating the mother liquor to one-half its volume an additional crop amounting to 0.3–0.4 g. was obtained. A second substance was obtained from the mother liquor as described below. The dibromide was crystallized from chloroform, taking care to avoid undue heating as this results in cyclization to the ortho quinone with the elimination of hydrogen bromide, and the compound was obtained as yellow prisms, m. p. 172.5–173.5°, dec.

Anal. Calcd. for $C_{18}H_{12}O_3Br_2$: C, 49.55; H, 2.78; Br, 36.66. Found: C, 49.84; H, 2.92; Br, 37.79, 35.99.

The substance is slowly attacked by concentrated sulfuric acid giving a bluish-green solution; hydrogen bromide is evolved and there is some sulfonation. Cold 1% alkali converts the compound into 2-benzoylmethyl-3-hydroxy-1,4-naphthoquinone, but this is contaminated with other products.

α - Bromo - β - phenyl - dihydrofurano - 1,2 - naphthoquinone was obtained from the mother liquor remaining after the removal of two crops of the dibromide as described above. The substance separated in admixture with some dibromide after further concentration of the chloroform solution. The dibromide was removed by immersion in cold 1% sodium hydroxide solution, and the undissolved material (0.3 g.) was crystallized from alcohol, in which



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(9) Fieser, THIS JOURNAL, 48, 3201 (1926).

(10) Microanalyses by Dr. D. Price of Columbia University.

it is sparingly soluble. The compound first separates as voluminous red needles, which change, on standing in contact with the mother liquor, into dark red plates, m. p. 218–219°. It is readily soluble in benzene or chloroform, it forms an emerald-green solution in concentrated sulfuric acid, and on prolonged boiling with 1% sodium hydroxide it is converted into benzoylmethylhydroxynaphthoquinone, identified by melting point and mixed melting point determinations. During the latter process a part of the material is converted into a greenish-black, alkali-insoluble substance which is oxidized to the starting material by air when in a moist condition.

Anal. Calcd. for $C_{18}H_{11}O_3Br$: Br, 22.50. Found: Br, 22.48, 21.80.

Preparation and Properties of the Ortho Quinones (III)

Furano-1,2-naphthoquinone (IX).—The crude dibromide from 0.4 g. of 2-vinyl-3-hydroxy-1,4-naphthoquinone was dissolved in 25 cc. of cold alcohol and the solution was allowed to stand in the dark in a loosely stoppered flask for one to two months, during which time the solution had evaporated to a volume of about 8 cc. and dark red masses of the reaction product had been deposited. After being washed well with alcohol and dried, the crude material (0.17 g.) was crystallized from alcohol, giving 0.08 g. of product melting at 207°. After two more recrystallizations it was obtained as deep red needles, m. p. 209.5–210°. There was no depression in the melting point when the substance was mixed with a sample prepared by the method of Scholl and Zincke,[5] and both samples gave the identical azine and showed the same behavior in the following test: the solution in concentrated sulfuric acid is blackish-green; on the absorption of moisture from the atmosphere it becomes blue, then purple and finally red needles of the unchanged material are deposited. The substance is more stable in sulfuric acid solution than its homologs, and although some change occurs after the solution has stood for several weeks, a pure transformation product has not been isolated. No change occurred when a solution of the compound in glacial acetic acid was treated with a few drops of concentrated sulfuric acid and boiled for several hours.

The above method of preparation gave better yields than more rapid processes. Thus on boiling the same amount of dibromide with 50 cc. of water for five minutes, filtering the hot solution from resinous material and allowing it to cool, there was deposited 0.015 g. of the quinone, m. p. 206°. The yield was about the same when the dibromide was allowed to stand in contact with water for ten days at room temperature.

β-Methylfurano-1,2-naphthoquinone (III, R = CH_3) was prepared by refluxing for one-half hour a solution of 1.4 g. of the dibromopropyl derivative in 25 cc. of alcohol. The solution became deep red and on cooling deposited 0.5 g. of red needles of the reaction product. Recrystallized from alcohol the substance formed small red needles melting at 164–164.5°.

Anal. Calcd. for $C_{13}H_8O_3$: C, 73.58; H, 3.57. Found: C, 73.44; H, 3.71.

On concentrating the mother liquor remaining after collecting the ortho quinone there was obtained 0.1 g. of the isomeric para quinone. This probably arises from the action of the hydrogen bromide liberated in the reaction on the ortho compound, for the latter substance can be converted in part into the yellow isomer by the action of boiling alcoholic hydrochloric acid.

β-Ethylfurano-1,2-naphthoquinone (III, R = C_2H_5) was obtained by allowing a solution of 2 g. of the dibromide in 10 cc. of alcohol to stand at room temperature for two days; 0.6 g. of the product crystallized from the solution and 0.8 g. more was obtained on concentration of the mother liquor. The compound forms red needles, m. p. 143.5–144°, from alcohol.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.31; H, 4.46. Found: C, 73.97; H, 4.75.

The mother liquor was found to contain a mixture of substances from which cold 1% alkali extracted an acidic compound probably having before hydrolysis the side chain $—CH{=}CBrCH_2CH_3$, for on acidifying the solution the ketonic compound of the type VI was obtained.

β-Phenylfurano-1,2-naphthoquinone (III, R = C_6H_5).—A solution of 2 g. of the dibromide in 100 cc. of alcohol was refluxed for one and one-half hours, during which time dark red plates of the ortho quinone separated from the boiling solution. After cooling, this material was collected (1.1 g.) and recrystallized from alcohol, in which it is sparingly soluble; dark red plates or needles, m. p. 219.5–220.5°.

Anal. Calcd. for $C_{18}H_{10}O_3$: C, 78.81; H, 3.68. Found: C, 78.87; H, 3.74.

The mother liquor yielded a mixture (0.1 g.) of the quinones III and IV with a small amount (0.02 g.) of a substance which could be extracted with cold alkali. The material recovered on acidifying the deep blue filtrate crystallized from alcohol in the form of purple-bronze needles melting with decomposition at about 275°. The substance forms a crystalline, blue sodium salt and gives a purple solution in concentrated sulfuric acid. From the analysis it appears to be a **hydroxyphenylfurano-1,2-naphthoquinone.**

Anal. Calcd. for $C_{18}H_{10}O_4$: C, 74.49; H, 3.45. Found: C, 74.04; H, 3.80.

Azines of the Ortho Quinones.—These derivatives were obtained in nearly quantitative yield by heating a mixture of the quinone, *o*-phenylenediamine hydrochloride, crystalline sodium acetate and glacial acetic acid at the boiling point for a few minutes. Most of the material separated in a crystalline condition on cooling and the remainder was obtained on dilution. The melting points and analyses of the compounds are recorded in Table I. These azines are all yellow and they crystallize well from alcohol or glacial acetic acid, usually as needles.

TABLE I

AZINES OF FURANO-1,2-NAPHTHOQUINONES

Substituents	M. p., °C.	%C Calcd.	%C Found	%H Calcd.	%H Found
None	195–196	79.97	79.14	3.73	4.01
β-Methyl	209.5–210.5	80.25	80.26	4.26	4.19
β-Ethyl	159–160	80.51	80.65	4.73	4.64
β-Phenyl	237–238	83.21	83.06	4.08	3.96
α-Bromo-β-phenyl-α,β-dihydro-	237–238	67.44	67.36	3.54	3.29

The Para Quinones (IV)

The methyl and ethyl derivatives were obtained in quantitative yield by dissolving one part of the ortho quinone in 50 parts by volume of cold concentrated sulfuric acid and allowing the solution to stand at room temperature for twenty-four hours, during which time the initially blue-green solution after passing through intermediate stages became crimson. On pouring the solution into water the yellow product separated in a microcrystalline condition. The compounds crystallize well from alcohol, acetic acid, or benzene. The properties are given in Table II.

TABLE II

FURANO-1,4-NAPHTHOQUINONES

Substituents	M. p., °C.	Description	% C Calcd.	% C Found	% H Calcd.	% H Found
β-Methyl	246–247	Yellow needles	73.58	73.64	3.57	3.79
β-Ethyl	145–145.5	Yellow needles	74.31	74.46	4.46	5.03
β-Phenyl	246.5–247.5	Yellow plates	78.81	78.40	3.68	3.90
	......	Bright red needles	78.81	79.02	3.68	3.97

Since the phenyl derivative of the ortho series is rather easily sulfonated the procedure was in this case modified as follows: 1 g. of the quinone was dissolved in 200 cc. of a mixture of 5 volumes of concentrated sulfuric acid with 1 volume of water, and the solution was heated in a boiling water-bath for one hour. The initially deep blue-green solution gradually became deep violet in color and on pouring the solution into water the product was obtained as a flocculent orange precipitate in about 80% yield. Crystallized from benzene, alcohol, glacial acetic acid or chloroform, the compound separated either as slender, bright red needles or as golden-yellow plates. On standing in contact with the mother liquor for a few days the red variety usually changes into the yellow form. Both forms show the same melting point, for when the red needles are heated at about 195° they soon become yellow while retaining the original form of crystal, and the melting point is that of the yellow modification.

The isomerization of the phenylated ortho quinone can be accomplished also by boiling an acetic acid solution of the substance containing a very small amount of sulfuric acid. The phenylated para quinone dissolves in concentrated sulfuric acid with an intense blue color which slowly changes; the methyl and ethyl compounds give crimson solutions which are more stable. The para quinones sublime readily without charring, while the ortho isomers undergo some decomposition.

The para quinones were obtained in small amounts by allowing solutions of the unsaturated compounds of the type I in concentrated sulfuric acid to stand at room temperature for twenty-four hours, but the yields were poor. No pure product was obtained from the vinyl compound by this method.

The Ketonic Compounds (VI)

The cleavage of the furan ring of the quinones of both the ortho and para series usually was effected by boiling under the reflux a suspension of one part of the finely powdered material in 100 parts of 1% sodium hydroxide solution until the material had completely dissolved. The phenylfurano-1,2-naphthoquinone is very resistant to attack and in this case the heating was interrupted at two-hour intervals, the solution was filtered, and the residual material, which had become blue as the result of a reduction process, was exposed to the air for re-oxidation and then boiled with a fresh portion of alkali. The isomeric phenylfurano-1,4-naphthoquinone was attacked with still greater difficulty and successive fresh portions of alkali were used; in this case, however, no insoluble blue substance was noticed. The alkaline solutions were orange-brown, and on acidification the reaction product separated as a buff-colored, crystalline precipitate. The pure substances were obtained by crystallization from alcohol or benzene, using animal charcoal. They are all yellow and usually crystallize in the form of needles. The yields, properties and analyses are given in Table III.

TABLE III

KETONIC DERIVATIVES OF 3-HYDROXY-1,4-NAPHTHOQUINONE

		Time and yield from *p*-Quinone		Time and yield from *o*-Quinone		% C		% H	
Substituent	M. p., °C.	Hrs.	%	Hrs.	%	Calcd.	Found	Calcd.	Found
2-Acetonyl	176.5–177.5	5	71	0.5	75	67.87	67.89	4.35	4.47
2-γ-Methylacetonyl	165–165.5	3	70	0.25	80	68.83	68.94	4.96	5.19
2-Benzoylmethyl	182.5–183.5	10–12	15	6	70	73.94	73.73	4.14	4.32

Concentrated sulfuric acid converts these substances first into the ortho furano-1,2-naphthoquinones which then undergo rather rapid transformation into the para isomers. Consequently mixtures of the two compounds are usually obtained on pouring the solutions into water. The orthoquinone can be obtained as the sole product by the method previously[4] used in the lapachol series and indicated in the chart. Thus one part of either of the three compounds listed in Table III was dissolved in 70–100 parts of warm, dilute (55–80%) acetic acid, depending on the solubility, one part of zinc dust was added followed by 16–20 parts of dilute (1:3) hydrochloric acid, and the solution was refluxed for five minutes. Reduction occurred rapidly and the solution of the hydroquinone was filtered to remove the zinc dust, reheated if necessary to bring all of the material into solution, and treated with a solution of 0.25 part of chromic anhydride in 10 parts of water. Red needles of the ortho quinone began to deposit almost immediately, and the material which did not separate on cooling was obtained by diluting the mother liquor. The substances were obtained in practically quantitative yield and in a very pure condition.

2 - β - Hydroxypropyl - 3 - hydroxy - 1,4 - naphthoquinone (XVII).—2-Acetonyl-3-hydroxy-1,4-naphthoquinone (0.05 g.) was hydrogenated in alcoholic solution using Adams catalyst, and the solvent was removed from the filtered solution by distillation and evaporation in warm air. The oily residue was taken up in 1% alkali and on acidifying the crimson solution the product separated as a yellow oil which slowly solidified (0.04 g.). Crystallized from benzene or benzene–ligroin the substance melted at 115.5–116.5° and gave no depression when mixed with a sample prepared according to the method of Fieser,[9] although Fieser gave the melting point as 108–110°. In a number of determinations with highly purified samples from both sources the melting point 108–110° was sometimes observed, and after allowing the melt to resolidify it then melted sharply at 115.5–116.5°. At other times the higher melting point was reached without previous melting. Microscopic examination of the samples prepared by the two methods also indicated their identity. The oil which first separates on acidifying the alkaline solution rapidly crystallizes in the form of very characteristic clusters of yellow needles.

Summary

The methods developed in 1896 for the synthesis of furan derivatives of β-naphthoquinone, and for the conversion of these substances into the corresponding α-naphthoquinones and open-chain compounds, have been studied in additional cases and found capable of rather general application. The parent compound of this group of furanonaphthoquinones has the ortho quinone structure and is not a para compound as assumed in the literature. The usual relationship between the color and the structure of the quinone group is maintained among the compounds investigated.

82 REMSEN STREET
BROOKLYN, NEW YORK

RECEIVED APRIL 7, 1936

Lomatiol. Part IV. A Violet Quinone from the Oxidation Product[1,2]

BY SAMUEL C. HOOKER AND AL STEYERMARK

It has been shown[3] that the quinone I resulting from the oxidation of lomatiol easily loses water with the formation of a red ring compound of the formula II. When this is boiled with alkali the pyran ring opens and there is produced a deep crimson solution resembling that formed by the oxidation product I. While I can be recovered without great difficulty by the careful neutralization of its alkaline solutions, the solution prepared from II contains a very unstable hydroxy compound (III) which when in the free condition undergoes cyclization so readily that it has not been possible to isolate the substance. Evidently some change occurs in the side chain of I when the pyran ring is closed and subsequently opened, but it is not known whether the difference is in the spatial arrangement of the groups attached to the double bond, in the respective positions of the hydroxyl group and the double bond in the allylic system, or in other modifications of the original structure. The unstable substance III on liberation from its salts changes into a beautiful, deep violet quinone isomeric with the red anhydride II. The violet compound forms a characteristic azine, indicating the presence of an ortho quinone group, and on catalytic hydrogenation two atoms of hydrogen are added to the unsaturated ring with the formation of the known[3] β-methyldihydropyrano derivative V, and on the basis of these observations the violet substance is assigned the structure of β-methylpyrano-1,2-naphthoquinone, IV.[4]

The new compound differs from the red anhydride II only in the nature of the quinone group, and it is interesting that with this pair of isomers the ortho compound has the deeper color, as in other cases, although on account of the presence of an active double bond in the side ring both quinones are deeper in color than the corresponding naphthoquinones more commonly encountered. The violet ortho quinone (IV) is a highly reactive substance and in aqueous or alcoholic solution it is unstable, particularly in the presence of hydrochloric acid, and undergoes isomerization to the red quinone II. Perhaps it is because of a

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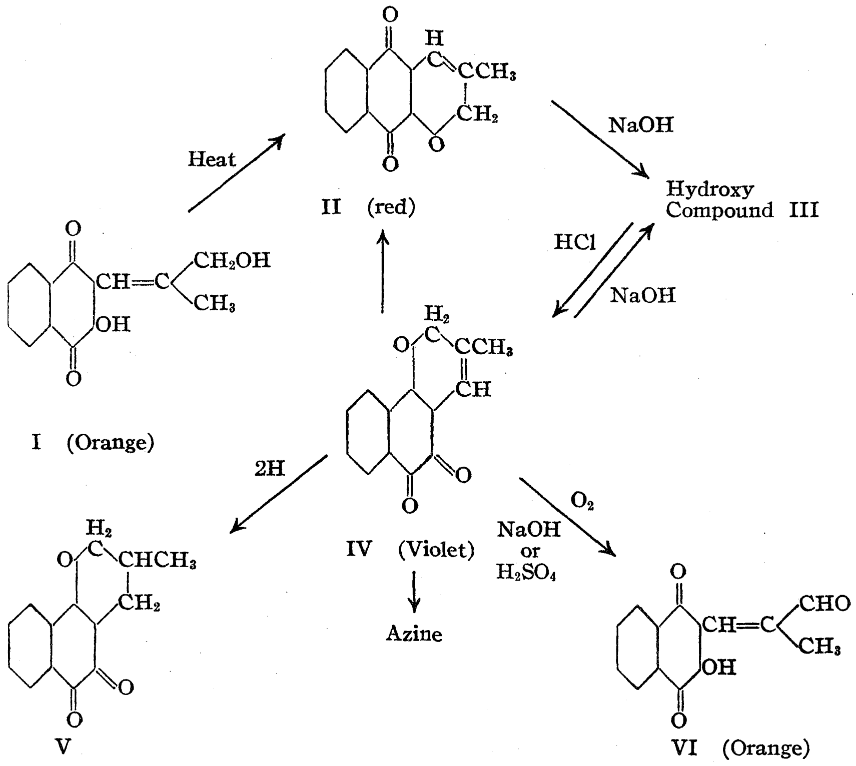
(1) See Editor's note (1), THIS JOURNAL, **58**, 1163 (1936).

(2) Although the violet compound was discovered by Dr. Hooker in 1917, most of the experiments described in this paper are of recent date (1934–1935) and no manuscript was left for the paper. At the time of his death Dr. Hooker was undecided as to the exact nature of the key compound and he was uncertain regarding the interpretation to be placed on its various transformations. He thought that a potentiometric analysis might settle the major point of uncertainty, and in a recently completed experiment I have found this to be the case (see footnote 4), although the result is the opposite of that which Dr. Hooker was inclined to anticipate. Seen from this fresh point of view the observations become less puzzling than before, and since I am sure that Dr. Hooker would have modified his early and incomplete views in the light of the later evidence, I have decided to present the theoretical interpretation which appears to be indicated by the facts now available and for which I assume full responsibility. —L. F. FIESER.

(3) Hooker and Steyermark, THIS JOURNAL, **58**, 1198 (1936).

(4) Because of the unusual color of the substance and the peculiar changes occurring in its solutions in acids and bases, and in consideration of early analyses with material later found to be impure, Dr. Hooker at the time of his death was inclined to regard the violet compound as a quinhydrone. He recognized, however, that further evidence was required to settle the matter, and I believe that the following experiment, carried out in my laboratory after his death, provides a sound basis for decision. In an electrode vessel connected to a hydrogen half-cell containing 50% alcoholic 0.1 *N* hydrochloric acid a sample of the substance was introduced to a portion of the same buffer which had been swept free from oxygen by a stream of nitrogen, and the potential was followed from the start. A fairly steady value (0.480 v.) was soon reached and after the material had dissolved a titration with titanous chloride gave a curve of the usual form for a quinone in the completely oxidized condition. The normal potential, E_0 = 0.435 v., is consistent with the ortho quinone structure, for it is 70 mv. higher than that of Paternò's dehydrolapachone, a similarly constituted pyrano compound of the para quinone series.—L. F. F.



similar instability that the ortho isomer of Paternò's dehydrolapachone[5] has eluded isolation.

The violet quinone dissolves easily in concentrated sulfuric acid and if the solution is promptly diluted with water the compound is precipitated in an unchanged condition. Likewise, after the quinone has been brought into solution by the action of boiling alkali, the original compound can be recovered if the solution of the hydroxy quinone III is at once acidified. If, however, either solution is allowed to stand for several hours a series of rather remarkable changes occurs which can be summarized briefly as follows. When exposed to the air in an open dish the alkaline solution in a few days deposits red needles of the para quinone II, and the sulfuric acid solution slowly deposits the same substance as it absorbs moisture from the atmosphere. When the freshly prepared solutions are placed in an evacuated system and allowed to stand for some time in the absence of air no red needles are deposited. Changes nevertheless occur under these conditions, for on subsequently exposing the alkaline solution to the air the red compound soon begins to separate and after this material has been removed the alkaline filtrate is found to contain 2-hydroxy-1,4-naphthoquinone, an oxidation product. Under more drastic conditions, as when the alkaline solution is refluxed for several hours, or when air is passed through the solution for a prolonged period, there is produced as a second product of oxidation an orange substance which appears to be an aldehyde of the formula VI. When the sulfuric acid solution of the violet quinone is allowed to stand *in vacuo* for several days and then poured into water, the precipitated material seems to consist largely of the hydroquinone of the orange aldehyde, for when it is dissolved in alkali or in ether in the presence of air there is a rapid color change and the solution is found to contain the aldehydic quinone VI.

The following interpretation of the changes seems to accord with all of the observations. It may be assumed that the pyran ring is opened by sulfuric acid as it is by alkali, and that in any case it is the unknown hydroxy compound III, in the form of the sodium salt or the sulfuric acid ester, which undergoes reaction. The essential change appears to consist in a disproportionation involving the reduction of the quinone group and the oxidation of the side chain. In the early stages of the process the solution contains a considerable amount of the hydroquinone of the hydroxy compound III and this undergoes partial, reversible cyclization to the hydroquinone of the red anhydride II, ring closure occurring more readily with the phenolic reduction product than with the more strongly acidic hydroxy quinone. In the presence of air the hydroquinone is oxidized and the red anhydride is deposited, even from the alkaline solution. In the absence of air the reaction proceeds in the same way at the outset, but when hydroxynaphthoquinone and the aldehyde VI tend to accumulate as oxidation products they are largely reduced by the hydroquinone of the starting material and the latter substance (III) eventually is completely consumed.

The orange aldehyde VI can be obtained in 40–

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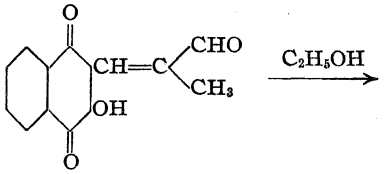
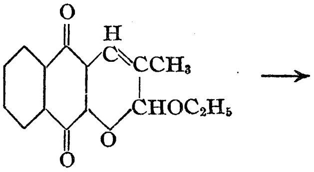
(5) Hooker, THIS JOURNAL, 58, 1190 (1936).

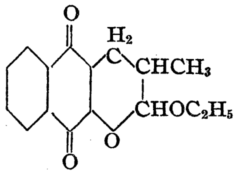
45% yield by boiling a solution of the violet compound in alkali for several hours, and in this case it is considered that the hydrogen atoms removed from the side chain reduce the quinone group and that the hydroquinone produced throughout the reaction is reoxidized by the air. The structure of the aldehydic substance has not been established rigidly, but the formula suggested accords with the analysis, with the acidic nature of the compound, with evidence indicating the presence of a double bond in the side chain, and with the observation that the substance easily forms derivatives resembling hemiacetals on reaction with various alcohols. In attempting to crystallize the orange compound from methyl, ethyl or butyl alcohol it was found that on mere boiling of the solution a reaction with the alcohol occurs and a yellow, non-acidic product separates on cooling. The reaction products can be reconverted into the starting material by dissolving them in concentrated sulfuric acid or by the action of boiling alkali. The hemiacetal structure VII would account well for the formation of such a compound from VI, for its neutral character, and for its conversion into a dihydro derivative (VIII) on hydrogenation. There is some further support for the hemiacetal structure in the qualitative observation that while the orange compound yields a crystalline, yellow derivative on reaction with aqueous ammonia the alkylated compounds remain unchanged on similar treatment. The yellow color is not easily explained on the basis of this formula, however, for in analogy with the red anhydride II, for which the structure of a pyrano-1,4-naphthoquinone is well established, a compound of the formula VII would be expected to be orange or red, unless the ethoxyl group has an effect opposite to that of the double bond in the side ring. On the other hand, it seems very unlikely that a compound of the formula VI could yield a normal hydroxy quinone ether under the conditions of the experiments or even in the presence of an esterification catalyst. Thus alkyl substituents in the quinone ring of 2-hydroxy-1,4-naphthoquinone effectively hinder a reaction with alcohol and hydrogen chloride, hydrolapachol, for example, being unaffected by such treatment. The hemiacetal formula appears to be the more probable, but further evidence will be required before a final decision can be reached.



VI (Orange)



VII (Yellow)



VIII (Yellow)

For the orange compound the open-chain structure VI is indicated by the fact that the substance dissolves easily in cold alkalies, and the formula is consistent with its color. In organic solvents such as benzene or petroleum ether there may be an equilibrium with a cyclic form. In boiling glacial acetic acid the compound is partially converted into a non-acidic substance having the composition of a bimolecular anhydride. Since such a reaction has not been encountered with other 2-alkyl-3-hydroxy-1,4-naphthoquinones, it seems likely that the elimination of water occurs between two molecules of the cyclic form of the orange compound.

Experimental Part[6]

The Violet Compound: β-Methylpyrano-1,2-naphthoquinone (IV).—It was found convenient to use for the preparation of this compound the crude β-methylpyrano-1,4-naphthoquinone (II) resulting from the oxidation of lomatiol.[3] Five grams of this material was finely ground and boiled with 500 cc. of 1% sodium hydroxide solution for two to four minutes, which sufficed to dissolve the red compound, and the bluish-crimson solution was quickly cooled to room temperature and filtered from about 0.1 g. of the yellow by-product[3] (β-methylfurano-1,4-naphthoquinone). On carefully acidifying the alkaline filtrate there was obtained a yellow emulsion which immediately darkened to violet and began to deposit brownish-violet needles of IV in a fairly pure condition; yield 4–4.5 g. On evaporating the mother liquor to one-tenth its volume, extracting the material which then separated with cold 1% alkali, and crystallizing the extracted substance from alcohol there was obtained about 0.015 g. of a by-product which forms red needles, m. p. 239–240°, dec. (Found: C, 70.52; H, 4.56.)

The violet compound is best purified by crystallization from alcohol, avoiding undue heating of the solution, and it separates either as needles or as diamond-shaped plates of an intense violet color with a somewhat brownish metallic luster, m. p. 156–158°, dec. The substance is also soluble in benzene and in glacial acetic acid, but changes appear to occur when the solutions are boiled.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.31; H, 4.46; mol.

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[6] Microanalyses and molecular weight determinations by Dr. D. Price of Columbia University.

wt., 226.1. Found: C, 74.62; H, 4.62; mol. wt., 238.0, 236.5.

The **azine**, prepared in good yield by heating a solution of the components in glacial acetic acid for a short time, forms gold-yellow needles melting at 163–163.5°. It forms a yellow-green solution in concentrated sulfuric acid and bronze-purple needles of the sulfate separate on dilution.

Anal. Calcd. for $C_{20}H_{14}ON_2$: C, 80.51; H, 4.73. Found: C, 80.34; H, 4.87.

On applying the method[7] found useful for the preparation of other ortho quinones, which in this case consisted in heating the lomatiol oxidation product I with a mixture of zinc dust, hydrochloric and acetic acids, followed by oxidation with chromic acid, there was obtained a mixture of the isomeric violet and red compounds IV and II.

The violet quinone can be converted quantitatively into the red isomer by boiling a solution of the substance in 95% alcohol for four hours, by boiling the material with water for about one hour, or by boiling it with very dilute hydrochloric acid for ten to fifteen minutes. (The violet quinone dissolves easily in cold sodium bisulfite solution, but no precipitate appears when the reagent is neutralized with soda solution.—L. F. F.)

For hydrogenation 0.1 g. of the violet quinone was dissolved in 20 cc. of warm (not boiling) ethyl alcohol and agitated with hydrogen and Adams catalyst for forty-five minutes. The end of the reaction was determined by evaporating a drop of the solution and adding a drop of concentrated sulfuric acid: initial color, blue; final color, red. There was obtained in all 0.07 g. of product which, when recrystallized, was identified by melting point and mixed melting point determinations as β-methyl-dihydropyrano-1,2-naphthoquinone, V.[3]

Action of Alkali on the Violet Compound.—By the action of boiling alkali the violet quinone is soon dissolved, giving a deep red solution. When the solution was at once cooled and neutralized with either hydrochloric acid or carbon dioxide the violet compound was reprecipitated. Allowed to stand exposed at room temperature, the alkaline solution began to deposit red needles of II within two to three days and the amount continued to increase for ten to fourteen days, the total conversion being about 55% of the starting material. During this period a test portion of the alkaline filtrate remaining after the removal of the red needles was shaken with ether, but no color was imparted to the ether layer and consequently the red anhydride was not simply present in solution. The alkaline mother liquor remaining after the final collection of the separated product gave a precipitate of impure 2-hydroxy-1,4-naphthoquinone on acidification. In another experiment the freshly prepared alkaline solution was allowed to stand in a vacuum desiccator, and no red needles appeared after seven days. On then exposing the solution to the air the red anhydride soon separated in 20% yield and the mother liquor yielded a quantity of hydroxynaphthoquinone amounting to about 20% of the weight of the starting material. When air was bubbled through a freshly prepared alkaline solution for fifteen hours and the solution was then allowed to stand in a loosely stoppered flask for three months, none of the red compound was observed but on fractionally precipitating the material in the alkaline solution with dilute acid there was obtained about 15% by weight of the orange compound VI, followed by 65% by weight of hydroxynaphthoquinone, the substances being fully identified by comparison with known samples.

The Orange Compound (VI).—This substance is best prepared by the action of alkali and air on the red anhydride II, the crude material being conveniently employed. A suspension of 1 g. of the powdered substance in 200 cc. of 0.25% sodium hydroxide solution was boiled under the reflux for fifteen minutes and the resulting deep red solution was cooled and filtered to remove the yellow by-product. The refluxing was then continued for a total of seven hours. The brownish-red solution was cooled, filtered from some mineral matter, and acidified. The crude product separated as a buff-colored precipitate which soon became crystalline and from which the sometimes cloudy mother liquor was best removed by decantation. After thorough washing, the crude product was shaken with 100 cc. of cold 0.25% alkali and the resulting solution was quickly filtered and acidified, the material separating as a brownish-orange microcrystalline mass; yield 0.4–0.45 g.

For analysis the substance was crystallized from benzene, in which it is sparingly soluble, and it was obtained in the form of bright orange needles, m. p 229–230°, dec.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.42; H, 4.13. Found: C, 69.44, 69.24; H, 4.42, 4.06.

The compound gives an orange solution in concentrated sulfuric acid. It dissolves readily in cold dilute alkali giving a crimson solution. When this evaporates on a watch glass the dark red sodium salt is deposited in branch-like forms or as interlacing hair-like needles which begin at the edges of the solution and grow inward. Attempts to obtain an acetate by the action of acetic anhydride or acetyl chloride on the orange compound were unsuccessful. A reaction with ammonia was observed as follows: the orange compound was obtained in a fine suspension by re-precipitation from dilute alkali and in this condition it dissolved at once on adding concentrated ammonium hydroxide solution, giving a deep red solution which soon became yellow and deposited bright yellow needles of a substance melting at 136–137°. Having used filtered solutions, the material was analyzed without further purification with the following results: C, 76.11; H, 4.42; N, 13.02. The compound can be crystallized from benzene or alcohol; it is not soluble in cold alkali but on boiling it yields a light brown-red solution which on cooling deposits nearly colorless needles. The study of the compound was not completed.

Hemiacetals (or Ethers?) of the Orange Compound.—The **ethyl** derivative of the probable formula VII was prepared by refluxing for one and one-half hours a solution of 1 g. of the orange compound in 50 cc. of ethyl alcohol. On cooling about 0.7 g. of the ethyl hemiacetal was deposited in the form of yellow prisms and a further 0.3 g. was obtained on concentrating the solution. The substance is somewhat sparingly soluble in ethyl alcohol and melts at 184.5–185.5°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.11; H, 5.18; mol. wt., 270.1. Found: C, 70.72, 70.70; H, 5.09, 5.19; mol. wt., 268.3.

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[7] Hooker, *J. Chem. Soc.*, **69**, 1376 (1896).

The compound appears to be partially converted into the methyl derivative on crystallization from methyl alcohol. It is insoluble in dilute alkali in the cold but dissolves slowly on boiling and the orange compound is precipitated when the red alkaline solution is acidified. The hydrolysis is more easily accomplished with the use of alcoholic alkali, followed by dilution with water and acidification. The substance dissolves easily in cold concentrated sulfuric acid and the orange compound precipitates when the solution is poured into water.

The dihydro derivative (VIII) of the ethyl hemiacetal was obtained by hydrogenation of the substance (0.5 g.) in ethyl alcoholic solution (125 cc.) in the usual way; yield, 0.4 g. The reaction product crystallizes slowly but very well from ethyl alcohol, forming yellow crystals melting at 185–186°.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.59; H, 5.88; mol. wt., 272.1. Found: C, 70.57; H, 5.35; mol. wt., 279.2.

Although the melting point is nearly the same as that of the unhydrogenated substance, a mixture of the two compounds melted about 20° lower. The dihydro derivative gives a red solution in concentrated sulfuric acid, but in contrast to the starting material water precipitates a mixture of alkali-soluble and alkali-insoluble material.

The *n*-butyl hemiacetal was prepared by refluxing for thirty minutes a solution of 0.2 g. of orange compound in 20 cc. of *n*-butyl alcohol; yield 0.18 g. The substance forms yellow rectangular plates, m. p. 121.5–122°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.48; H, 6.04; mol. wt., 298.1. Found: C, 72.21; H, 6.31; mol. wt., 292.8.

The **methyl hemiacetal** is similar in properties and melts at 160–161°.

Anhydride of the Orange Compound.—This was obtained by dissolving 1 g. of the material in 70 cc. of glacial acetic acid and refluxing the solution for one-half hour. The reaction proceeds only to the point of an equilibrium, and on cooling the solution deposited 0.7 g. of a mixture of orange needles of the starting material and yellow plates of the anhydride. (A mixture was also obtained on adding water to the mother liquor.) A separation of the two compounds was easily effected by treatment with 70 cc. of cold 0.25% alkali, which rapidly dissolved the orange needles. The solution was quickly filtered and the undissolved yellow plates were washed well with water. By using filtered solutions the anhydride was in this way obtained in a form suitable for analysis, the yield being about 0.1 g. The substance melts with decomposition at 243–244°.

Anal. Calcd. for $C_{28}H_{18}O_7$: C, 72.10; H, 3.86. Found: C, 72.21, 71.79; H, 4.05, 4.11.

The anhydride can be obtained equally well by using propionic or *n*-butyric acid. That an equilibrium is established is shown by the fact that on redissolving the anhydride in any of the solvent acids it is converted into a mixture of the two compounds. The orange compound can be obtained by boiling the anhydride with dilute alkali or by dissolving it in concentrated sulfuric acid and pouring the solution into water.

Action of Sulfuric Acid on the Violet Compound.—The violet quinone gives a deep, rich blue solution in concentrated sulfuric acid, but the color changes to red in one to two hours. When the solution was exposed to the air in an open dish it began to deposit red needles of II within two to three days. The changes occurring in the absence of air are illustrated by the following experiment.

A solution of 1 g. of the violet compound in 100 cc. of concentrated sulfuric acid was allowed to stand in a stoppered flask for two days at room temperature and the solution, which had become red after the first two hours but which deposited no red needles, was poured into 1500 cc. of cold water. The resulting blue-red solution deposited a brown flocculent precipitate which was collected after twenty-four hours and set aside (0.46 g.). On extracting the wine-red filtrate with ether it was noted that on contact with the solvent the aqueous layer generally changed in color from red to yellow and at times orange-yellow microcrystals separated and then dissolved in the ether. It appeared that an oxidation was involved. Evaporation of the ether extract left a residue of yellow crystals mixed with brown resin. On digesting this with 100 cc. of cold 0.25% alkali most of the material quickly dissolved and usually the solution was initially yellow and then rapidly darkened to a crimson color, evidently as the result of the oxidation of a hydroquinone. On filtering the alkaline solution there was a slight residue consisting of yellow plates (0.02 g.) identified as the ethyl hemiacetal of the orange compound, which probably had arisen from reaction with ethyl alcohol present in small amounts in the ether used. After allowing time for oxidation to proceed to completion, the alkaline filtrate on acidification gave a precipitate which was no longer resinous but which consisted of crystalline groups of the orange compound in a nearly pure condition; yield, 0.26 g. Somewhat better yields were obtained in further experiments using less material.

Summary

β-Methylpyrano-1,2-naphthoquinone, a violet colored quinone of a hitherto unknown structural type, has been obtained from the substance resulting from the oxidation of lomatiol. The most interesting and unusual properties of the compound, aside from the striking color, are its ready isomerization to the corresponding para quinone and its conversion, probably through a disproportionation mechanism, into a quinone having an aldehydic side chain. The latter substance also displays novel properties, combining readily with alcohols without the assistance of catalysts, and yielding a bimolecular anhydride.

82 REMSEN STREET
BROOKLYN, NEW YORK

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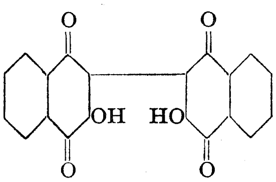
The Action of Light on β-Hydroxy-α-naphthoquinone[1,2]

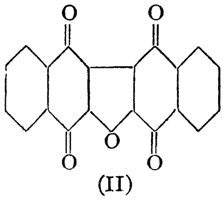
BY SAMUEL C. HOOKER

In this paper an account will be given of an interesting substance (I) which was first obtained in the author's laboratory by Mr. J. T. Walsh, Jr., in 1893–1894 from mother liquors in the preparation of 2-hydroxy-1,4-naphthoquinone. It was subsequently established that neutral and acid aqueous solutions in which small quantities of pure hydroxynaphthoquinone are dissolved deposit on standing minute globular masses (dots) of a compound readily distinguished from hydroxynaphthoquinone by the much more crimson color of its solution in alkalies. The substance may be observed floating on the surface of the solution in the course of a few days, or it may not separate for two or three weeks. After standing a number of months, however, unchanged hydroxynaphthoquinone is still present in the solution. The substance is also formed when a small quantity of hydroxynaphthoquinone is dissolved in concentrated sulfuric acid and the acid solution allowed to stand exposed. As water is absorbed crystals of hydroxynaphthoquinone first separate and then eventually give way in part to microscopic globular masses of the condensation product. After observing the phenomenon many times under various conditions it was concluded that the ("dot") compound is formed by the action of light, and as a result of a number of experiments a satisfactory method of preparation was found in exposing an aqueous solution of hydroxynaphthoquinone to ultraviolet light at 70°. The reaction product was obtained in a very good condition in yields of over 40%. When pure it consists of orange-yellow microcrystals melting at 270–275°, dec. It displays various characteristic color reactions and gives a very distinctive pattern when fused on a cover glass and examined under the microscope. Considering the source and acidic character of the material, the composition found for the compound and the observation that it is sparingly soluble in most organic solvents strongly suggested the formula of di-β-hydroxy-α-naphthoquinone, I. A substance regarded as having this structure was prepared many years ago by Chattaway[3] and described as a dark red powder melting at about 215°. Some of the original sample was kindly supplied to the author by Dr. Chattaway in 1922 for purposes of comparison, and it was examined carefully and tested by a number of methods. The material did not appear to be homogeneous, however, and although in some respects it behaved as though it contained the compound described in the present work, attempts to purify the small sample to an extent sufficient to permit a positive identification were not successful.



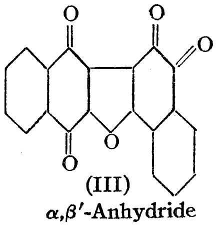
I

Independent evidence that the oxidation product of hydroxynaphthoquinone has the structure I was found in its behavior under the influence of dehydrating agents. Theoretically a substance of this formula should be capable of yielding in addition to the normal internal anhydride (II) two isomeric anhydrides, III and IV, correspond-



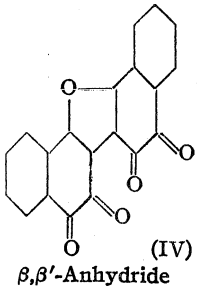
(II)

α,α'-Anhydride



(III)

α,β'-Anhydride



(IV)

β,β'-Anhydride

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(1) See Editor's note (1), THIS JOURNAL, **58**, 1263 (1936).

(2) Following the initial observation of 1893–1894 (see text), Dr. Hooker devoted considerable time in the period 1918–1926 to a study of the formation and properties of the "dot" compound, assisted in part by Dr. G. H. Connitt and by Mr. A. F. Sullivan. Apparently the work was interrupted before it was quite complete, and the observations had been summarized only partially. In repeating some of the experiments in order to comprehend fully the original notes, I was fortunate enough to find a method of preparing in a pure condition the third (red) anhydride, which Dr. Hooker had observed only as an unpurified by-product. The substance was identified by comparison with Dr. Hooker's original, well-preserved slides, and it was thus possible to supply the completing details of the investigation.—L. F. FIESER.

(3) Chattaway, *J. Chem. Soc.*, **67**, 662 (1895).

ing to the conversion of one or both para quinone groups into ortho quinone groups in the course of the dehydration. Analogous changes have been abundantly illustrated in previous work in this Laboratory. Actually it was possible to obtain three such anhydrides, using sulfuric acid as the active dehydrating agent in each case but operating under different conditions. The pure, crystalline compounds are, respectively, orange-yellow, orange and red in color, and although the distinction between the first two is but slight the relationship, in analogy with known cases, is such as to suggest that they have the α,α'-, the α,β'- and the β,β'-structures, in the order named. This was fully confirmed by the behavior of the compounds when boiled with *o*-phenylenediamine in glacial acetic acid solution or suspension. The orange-yellow anhydride, although its solubility in the medium is more than adequate to permit a reaction, was recovered unchanged, as would be expected for the α,α'-quinone II. A mono-azine was obtained from the orange anhydride (III), and the red isomer, in spite of its extremely slight solubility, yielded a diazine (m. p. 409–410°), corresponding to the two β-quinone groups of IV. These observations establish with certainty the structure of the substance formed from 2-hydroxy-1,4-naphthoquinone by the action of light, and it appears that the process involves the oxidative coupling of two molecules at the 3-position.

The occurrence of a second reaction was revealed on investigating the aqueous liquor remaining after removing the main product from the hot solution. This usually deposited in the course of twenty-four hours a brick red crystalline substance amounting to about 15% of the starting material. The material dissolved in 1% alkali to a browner solution than pure hydroxynaphthoquinone, but on exposure on a watch glass the solution soon became lighter in color and eventually corresponded in shade to that of the sodium salt of hydroxynaphthoquinone and on evaporation yielded crystals of this salt. The red color of the substance suggested a β-quinone structure, and its behavior the possibility that the hitherto unknown α-hydroxy-β-naphthoquinone had been discovered. For this reason considerable study was devoted to the matter. By varying the conditions under which the brick red substance was obtained, however, it was found that the color of its alkaline solution was not constant and in some lots this even approached a dark olive green. As the individual crystals of each lot when dusted on the surface of the alkaline solution gave a perfectly uniform color, it seemed probable that the red substance consisted mainly of ordinary hydroxynaphthoquinone modified in its properties by another substance which crystallized with it in varying proportions. This was found to be the case. Starting with 5 g. of the red substance repeated crystallizations from benzene eventually yielded as the less soluble fraction crystals which gave a dark blue solution in alkali. Further purification of these crystals from acetone resulted in their resolution into two substances. The one present in by far the larger quantity dissolved in alkali to a bright blue solution and the other, obtained in exceedingly small amount, gave a dull cherry red solution. The former substance melted at 280°, its blue solution in sodium hydroxide became colorless on exposure, with dilute sodium carbonate a violet solution was obtained, and with concentrated ammonia the substance gave a sparingly soluble, dark violet salt. These properties correspond with those of isonaphthazarin,[4] and a direct comparison with a known sample of this quinone fully established the identity.

Under the influence of light and air in aqueous solution, hydroxynaphthoquinone is partly dehydrogenated and partly hydroxylated, the attack in each case occurring at the free position in the quinone ring.

Experimental Part

Preparation of 2-Hydroxy-1,4-naphthoquinone.—In preparing large quantities of 1,2,4-triacetoxynaphthalene from samples of β-naphthoquinone of various degrees of purity by the method of Thiele and Winter,[5] the crude material precipitated by water was invariably found to contain a by-product which was separated by the following method. The crude material, which varied from orange to brown in color, was boiled with alcohol (10 cc. per gram) until the bulk of the solid had dissolved and the solution was filtered from a small amount of the less soluble by-product. The solution on cooling at first remained clear and deposited heavy crystals of the triacetate. After an hour or so, simultaneously with the commencement of the separation of the by-product, the solution became cloudy and at or before this point the mother liquor was quickly poured off from the heavy crystals. After allowing time for a mixture of the two substances to crystallize from the decanted solution, this was heated to boiling. The triacetate largely dissolved while the second substance passed into solution so slowly that a considerable amount of the material could be collected on filtration. By continuing this process a

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(4) Zincke and Ossenbeck, *Ann.*, **307**, 11 (1899).

(5) Thiele and Winter, *ibid.*, **311**, 345 (1900).

fairly complete separation was possible and the pure triacetate was obtained in about 46% yield from a mixed lot of β-naphthoquinone.

The by-product, which amounted to about one-tenth part of the quinone used, was identified as the tetraacetyl derivative of dinaphthyldihydroquinone by analysis and by direct comparison with a known sample of this substance.[6]

Anal. Calcd. for $C_{28}H_{22}O_8$: C, 69.14; H, 4.56. Found: C, 69.07, 68.92; H, 4.62, 4.80.

On being heated in the capillary tube both samples, as well as the mixture, exhibited the peculiar behavior essentially as described by Straus, Bernoully and Mautner.[7]

For the hydrolysis of the triacetate and oxidation to hydroxynaphthoquinone the following method was found more satisfactory than any described in the literature. A 10-g. portion of the triacetate was immersed in 200 cc. of 5% sodium hydroxide solution in a flat dish and allowed to stand at the laboratory temperature. The solution darkened considerably as the triacetate gradually dissolved and in three to four hours the red sodium salt of hydroxynaphthoquinone commenced to separate. In four to five days the solution became much lighter and cleaner and ultimately approximated in shade that of the sodium salt of pure hydroxynaphthoquinone, indicating that the oxidation was complete. The salt was collected, washed with 5 cc. of water, dissolved in 600 cc. of water at the laboratory temperature, and the filtered solution was acidified, giving a pale yellow crystalline precipitate of hydroxynaphthoquinone in a very pure form and in over 90% of the theoretical yield.

Identification of 2-Hydroxy-1,4-naphthoquinone.—This can be very satisfactorily accomplished with an exceedingly small quantity of the substance even when it is comparatively impure, by first subliming it in a test-tube or on a cover slip. Irregular microscopic yellow crystals are formed, sometimes also needles easily visible to the naked eye. A drop or two of 1% sodium hydroxide is used for dissolving the sublimed crystals and a small portion of the solution allowed to evaporate spontaneously readily yields characteristic red crystals of the sodium salt. To the remainder of the alkaline solution one or more drops of 0.25% hydrochloric acid is added, when with aid of the microscope characteristic needles changing in the course of a few hours to irregular crystals can be observed. The pyridine compound is also characteristic for on evaporation of a drop of the solution in pyridine clusters of bright red needles of the salt are deposited and then the pyridine is spontaneously lost and the crystals lose their red color and their luster but retain their form.

Di-β-hydroxy-α-naphthoquinone (I).—Pulverized hydroxynaphthoquinone (4 g.) was dissolved in 3 liters of boiling tap water and the hot solution was transferred to a 28-cm. crystallizing dish set on a slab of copper heated by a jet burner adjusted to maintain a temperature of about 70°. A Uviarc lamp was so placed that the center of radiation was about 29.2 cm. above the surface of the solution and the exposure was continued for two hours in all. At intervals of thirty minutes three successive 0.5-g. portions of hydroxynaphthoquinone, each dissolved in 400 cc. of boiling water, were added to the main solution, the last addition thus being made thirty minutes before the conclusion of the exposure. Shortly after the commencement of the experiment the compound began to separate on the surface of the solution as a yellow-brown, microcrystalline powder, and at the close of the exposure the substance was immediately filtered off and washed with water. By carefully following the above directions 2.4 g. of di-β-hydroxy-α-naphthoquinone will be obtained in a condition of satisfactory purity. By allowing the temperature to drop materially not only is the action retarded but the compound may be mixed with crystals of hydroxynaphthoquinone. Should this be the case the hydroxynaphthoquinone may be removed by extracting the substance with boiling water (500 cc. per gram).

Di-β-hydroxy-α-naphthoquinone does not dissolve to any appreciable extent in boiling benzene and it is only sparingly soluble in alcohol. The substance dissolves slowly in glacial acetic acid (100 cc. per g.) at the boiling point and the solution on cooling deposits an orange-yellow sandy powder consisting of small crystalline tablets which appear under the microscope to be almost rectangular. The presence of a persistent impurity often gives a brown appearance to the crystals, but this can be removed with the use of blood charcoal. The compound is fairly soluble in nitrobenzene and crystallizes well from this solvent. It is readily soluble in cold pyridine, and it also dissolves in cold dilute alkali and imparts a characteristic, bright crimson color to the solution.

Anal. Calcd. for $C_{20}H_{10}O_6$: C, 69.35; H, 2.91. Found: C, 69.16; H, 3.00.

When heated in a melting point capillary the compound begins to sublime at about 250° and melts with decomposition at about 270–275°. When heated on a cover glass it fuses, simultaneously giving a faint sublimate. When withdrawn from the source of heat the fused material crystallizes to a highly characteristic striated mass of yellow needles frequently suggestive of a map of city streets. The fused material appears to be an anhydride, as it is insoluble in dilute alkali but dissolves slowly on boiling.

α,α′-Anhydride (II).—This compound is the chief product resulting from the action of a mixture of acetic acid and dilute sulfuric acid on di-β-hydroxy-α-naphthoquinone, but it is invariably accompanied by a small amount of the α,β′-anhydride. In preparing the compound the heating should not be prolonged beyond the time necessary to effect the dehydration, as this results in a darker, less pure product. The following method was found most satisfactory. One-half gram of finely powdered di-β-hydroxy-α-naphthoquinone was suspended in 40 cc. of glacial acetic acid and 5 cc. of a solution of equal parts by volume of concentrated sulfuric acid and water, and the mixture was rapidly brought to the boiling point. Within five minutes the starting material had completely passed into solution and in another five minutes the anhydride began to separate. After continuing the boiling for a total of fifteen minutes the mixture was cooled and the crystalline product collected and washed; yield 0.39 g. The material so obtained varies in color from deep golden yellow to dark brown, and it sometimes contains traces of unchanged starting material which can be removed by

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(6) The identification was made by Mr. J. T. Dunn in my laboratory. Microanalyses by Mrs. G. M. Wellwood.—L. F. F.

(7) Straus, Bernoully and Mautner, *Ann.*, **444**, 188 (1925).

digestion with cold 1% alkali. The product was purified by crystallization from glacial acetic acid, using about 230 cc. to the gram and clarifying the solution with animal charcoal. The originally yellow or brown material then acquires a definitely orange cast, the substance separating as well-formed, detached needles of a clear orange-yellow color. The recovery amounted to about 60%, and the mother liquor on spontaneous evaporation deposited first yellowish needles of the same substance, followed by orange tufts of the α,β′-anhydride. After further recrystallization the α,α′-anhydride melted at 349–350°[8] with some decomposition.

Anal. Calcd. for $C_{20}H_8O_5$: C, 73.16; H, 2.46. Found: C, 73.06; H, 2.50.

The substance gives an orange-red solution in concentrated sulfuric acid and the reprecipitated material is pure yellow. The compound was recovered unchanged after being heated for one hour with *o*-phenylenediamine and glacial acetic acid. The anhydride gives a very characteristic fusion test (microscope) strongly resembling that obtained from di-β-hydroxy-α-naphthoquinone. On hydrolysis with boiling alkali the compound is converted into di-β-hydroxy-α-napthoquinone.

α,β′-Anhydride (III).—Five grams of di-β-hydroxy-α-naphthoquinone was dissolved in 250 cc. of cold concentrated sulfuric acid and after standing at room temperature for thirty minutes the deep red solution was poured into 3 liters of water. The flocculent orange-red precipitate was washed and dried; yield 4.35 g. This material proved to consist largely of the α,β′-anhydride mixed with a small amount of the red β,β′-isomer. The latter is much the less soluble in organic solvents and its complete removal is not easily accomplished. The α,β′-anhydride can be obtained in a pure condition by repeated crystallization from glacial acetic acid, using each time a quantity of solvent insufficient to dissolve all of the material (250 cc. per gram), but the process is tedious for the β,β′-anhydride dissolves to a very slight but definite extent in acetic acid. A better method was found in the use of dilute (2:1) nitric acid. It was found that the α,β′-anhydride crystallizes very well from the acid while the β,β′-isomer does not appear to dissolve at all in acid of this concentration. When boiled with stronger acid it slowly passes into solution but it apparently is oxidized, for the colorless solution on spontaneous evaporation leaves a residue of colorless crystals. As a result of these tests the following method was adopted. One-tenth gram of the anhydride mixture was added to a mixture of 50 cc. of concentrated nitric acid and 25 cc. of water, heated just below the boiling point. There was a lively evolution of gas and a large part of the material rapidly dissolved. The solution was cooled slightly, filtered through a suitable paper supported by a platinum cone from some undissolved, crimson red material (largely β,β′-anhydride), reheated, and allowed to cool. The α,β′-anhydride crystallized in fine hair-like needles forming a bright orange silky felt. This material was very pure, and the mother liquor yielded a further quantity of equally pure α,β′-anhydride and there was no indication of the presence of the isomer. About half of the weight of the mixture was recovered as pure α,β′-anhydride. Material which had been crystallized twice from glacial acetic acid dissolved nearly completely in the nitric acid solution.

The pure α,β′-anhydride closely resembles the α,α′-isomer in appearance except that it has a brilliant, pure orange color with no suggestion of yellow. It is fairly readily soluble in boiling nitrobenzene and crystallizes as short orange needles. It is more soluble in glacial acetic acid than the α,α′-isomer. The solution in concentrated sulfuric acid is deep red and the reprecipitated material is orange-yellow. The anhydride is slowly attacked by boiling alkali to give a red solution from which di-β-hydroxy-α-naphthoquinone is precipitated on acidification. The α,β′-anhydride melts at 317–318°[8] with some decomposition. It gives a good fusion test.

Anal. Calcd. for $C_{20}H_8O_5$: C, 73.17; H, 2.44. Found: C, 73.28; H, 2.64.

Azine of the α,β′-Anhydride.—One-half gram of the anhydride was dissolved in 200 cc. of glacial acetic acid by boiling and to this was added a filtered solution prepared from 0.6 g. of *o*-phenylenediamine hydrochloride, 2.5 g. of crystalline sodium acetate, and 50 cc. of glacial acetic acid. Heated on the water-bath for forty-five minutes the hot solution deposited yellow crystals of the azine in a good condition, the yield of the washed and dried material being 0.44 g. Crystallized from glacial acetic acid (500 cc.) the substance formed golden yellow plates melting at 329–330°.[8]

Anal.[9] Calcd. for $C_{26}H_{12}O_3N_2$: N, 7.00. Found: N, 6.86.

β,β′-Anhydride (IV).[10]—This bright red, sparingly soluble quinone appears to be the sole anhydride formed when di-β-hydroxy-α-naphthoquinone is treated with acetic anhydride in combination with either sulfuric acid or sodium acetate. The substance was satisfactorily prepared by dissolving 0.5 g. of the dihydroxy quinone in 50 cc. of nitrobenzene, cooling the solution to 50°, and adding a solution prepared by dissolving 5 cc. of concentrated sulfuric acid in 20 cc. of acetic anhydride with cooling. The solution became cherry red and almost immediately began to deposit glistening, bright red plates of the β,β′-anhydride. After cooling the material was collected and washed thoroughly with alcohol and benzene; yield 0.43 g. The substance thus obtained was entirely homogeneous and appeared to be directly pure. Recrystallized from nitrobenzene (about 200 cc.) it formed fiery red plates of great beauty.

Anal.[9] Calcd. for $C_{20}H_8O_5$: C, 73.16; H, 2.46. Found: C, 72.68; H, 2.46.

The exceedingly slight solubility of the compound in glacial acetic acid and the action of nitric acid on the substance have been mentioned above. In a capillary tube the anhydride decomposes at about 335–345° without showing signs of melting. When heated on a cover glass and examined microscopically the compound does not seem to melt but strikingly beautiful, deep red scales having a high luster collect on top of the substance heated. When boiled with dilute alkali it becomes green at first, due to a reduction, and then it dissolves to a red solution of the salt of di-β-hydroxy-α-naphthoquinone.

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[8] Determined with a Berl–Kullmann copper block (uncorr.) by L. F. F.

[9] Analysis by Mrs. G. M. Wellwood.

[10] Preparative experiments by L. F. F.

Di-azine of the β,β'-Anhydride.[10]—The anhydride (0.2 g.) was suspended in glacial acetic acid (200 cc.) and refluxed with a solution of *o*-phenylenediamine prepared as above. The red plates were rapidly replaced by hair-like yellow needles of the reaction product, and after refluxing the mixture for two hours the conversion was nearly complete. As microscopic examination revealed the presence of a few unchanged plates of the anhydride, the material was digested for a short time with alkaline hydrosulfite solution containing some alcohol. The unattacked material was crystallized twice from nitrobenzene, in which it is only moderately soluble, clarifying the solution with animal charcoal. The compound was obtained as small, somewhat dull yellow needles, m. p. 409–410°.[8]

Anal.[9] Calcd. for $C_{32}H_{16}ON_4$: N, 11.86. Found: N, 11.70.

Summary

Exposed to the light in aqueous solution, hydroxynaphthoquinone is largely converted into a diquinone by a process of dehydrogenation, and to a lesser extent it is hydroxylated in the quinone ring. A method is described for the preparation of the main reaction product in quantity, and by the isolation of three isomeric internal anhydrides it is established that the substance has the structure of di-β-hydroxy-α-naphthoquinone.

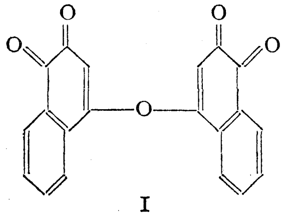
82 REMSEN STREET
BROOKLYN, NEW YORK

RECEIVED MAY 1, 1936

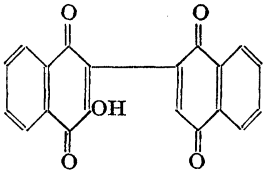
Concerning Wichelhaus' "Di-β-naphthoquinone Oxide"[1,2]

BY SAMUEL C. HOOKER AND LOUIS F. FIESER

In 1897 Wichelhaus[3] discovered that β-naphthoquinone is converted by warm aqueous ferric chloride solution into a substance which evidently is formed from two molecules of the starting material and which Wichelhaus regarded as having the structure of an oxide, I. Although this formula seems inconsistent with Wichelhaus' own observation that the substance dissolves in cold alkali or even soda solution and may be recovered unchanged from the red solutions, the matter does not appear to have received any further attention. On repeating the preparation it was found in the present work that the reaction is very smooth and that the oxidation product can be obtained in a good condition in nearly quantitative yield. The precipitated material first obtained is pure yellow, but it forms orange-red needles when crystallized from acetic acid. That it contains a free hydroxyl group, as suggested by the marked acidic properties, was established by the formation of a monoacetyl derivative. Clearly the oxide structure is inadmissible, and the substance is more properly regarded as a hydroxy dinaphthyldiquinone.


I

The yellow color of the precipitated compound at first suggested the structure of an α-naphthoquinone, and it seemed that the substance could possibly be accounted for by assuming the formation of hydroxynaphthoquinone by oxidation and the condensation of two molecules of this oxidation product with the elimination of water, giving II. This might have been confirmed by the formation of the compound from hydroxynaphthoquinone, but under the above experimental conditions the hydroxyquinone was largely unchanged and yielded none of the condensation product. It was thought also that if the Wichelhaus compound has the structure II it might be expected to yield di-β-hydroxy-α-naphthoqui-


II

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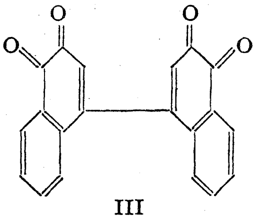
(1) See Editor's note (1), THIS JOURNAL, 58, 1163 (1936).

(2) In a letter written to me a few weeks before his death Dr. Hooker commented as follows on a prospective extension of experiments which he had started in 1926–1927 and continued with Dr. G. H. Connitt in 1927–1928 on the structure of the so-called di-β-naphthoquinone oxide: "A number of interesting compounds and reactions resulted from my work with this substance which I shall be glad to see satisfactorily explained." His hope to resume work on the problem was not realized, and the notes which subsequently came to my hand included a formula for the "oxide" which was regarded as purely provisional. The acetyl derivative was described and methods were given for the preparation of the "oxide" and of compounds A, B (first method), C (first method), and D, for the oxidation of A, and for the conversion of D into B, but no formulation was suggested for the new compounds. Following a course which I believe to be in accordance with Dr. Hooker's wishes, I have attempted to carry the work to completion.—L. F. FIESER.

(3) Wichelhaus, *Ber.*, **30**, 2199 (1897).

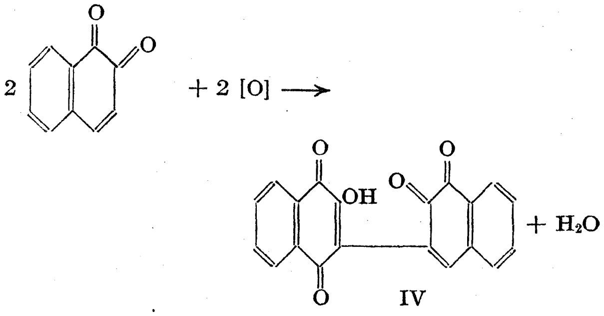
none[4] on oxidation in alkaline solution. This does not seem to be the case, for although oxidation occurs on exposing the alkaline solution to the air the product has quite different properties, as will be described below.

Another hypothesis regarding the formation of the "oxide" was suggested by the observation that on crystallization of the crude product there was isolated a small quantity of the dinaphthyldiquinone III. Although this may arise merely by the oxidation of a trace of dinaphthyldiquinhydrone present in the starting material, it seemed possible that III is an intermediate in the reaction. Experiment showed, however, that the diquinone is practically unchanged even when boiled with aqueous ferric chloride solution. The possibility of the formation of hydroxynaphthoquinone and its immediate condensation with unchanged β-naphthoquinone was similarly eliminated in test experiments, and the problem was then attacked by degradation.



III

On submitting the Wichelhaus compound to zinc dust distillation there was obtained a hydrocarbon which was fully identified as β,β-dinaphthyl by comparison with samples prepared by the zinc dust distillation of di-α-naphthoquinone[5] and by synthesis. Since there is considerable uncertainty in the literature as to the identity of a substance described by Watson Smith[6] as α,β-dinaphthyl, this hydrocarbon was prepared for comparison by synthesis from α-tetralone and β-naphthylmagnesium bromide. The properties of the compound are precisely those reported by Smith and the hydrocarbon is quite different from the above degradation product. The isolation of the β,β-compound provides a significant clue to the structure of the hydroxy dinaphthyldiquinone. Since there is no reason to believe that four of the oxygen atoms do not occupy their original positions in the naphthalene rings, as for example in formula II, and since the pronounced acidity of the compound indicates that the hydroxyl group is situated in a quinone ring, the substance very probably has the structure IV. The presence of a β-quinone group accounts for the orange-red color of the crystalline material, while the color of the alkaline solution is that expected for a β-hydroxy-α-naphthoquinone derivative. The mechanism of the remarkable oxidation reaction is still obscure.



IV

As mentioned above the hydroxy dinaphthyldiquinone is easily oxidized by air in alkaline solution, and an investigation of the reaction product has furnished additional support for the formula IV. The oxidation was accomplished by allowing an alkaline solution of Wichelhaus' compound to go to dryness in an open dish at room temperature, and there was obtained from the residue in over 50% yield a yellow compound ($C_{20}H_{12}O_7$) which gives an orange solution in alkali. This substance, which will be designated A, is quite susceptible to other changes in the presence of acids and bases and even in neutral solvents. In the course of purifying the yellow substance it was discovered that in boiling acetic acid a rather rapid isomerization takes place giving a more stable, yellow compound B which dissolves in alkali with a crimson color. When A is boiled for some time with alcohol it also yields some of the isomer B, but there is formed in addition another yellow compound, C, which differs in composition from the starting material by the elements of carbon dioxide. Compound C can be obtained in good yield by heating A in pyridine with a small amount of copper powder. This decarboxylation clearly shows that the oxidation of the hydroxydinaphthyldiquinone in alkaline solution involves the opening of one of the rings. A similar oxidation can be accomplished with the use of hydrogen peroxide in glacial acetic acid solution, but in this case isomerization also occurs and the product is B.

There are definite indications that the hydroxynaphthoquinone grouping of IV remains intact in the course of the oxidation, one being that on ex-

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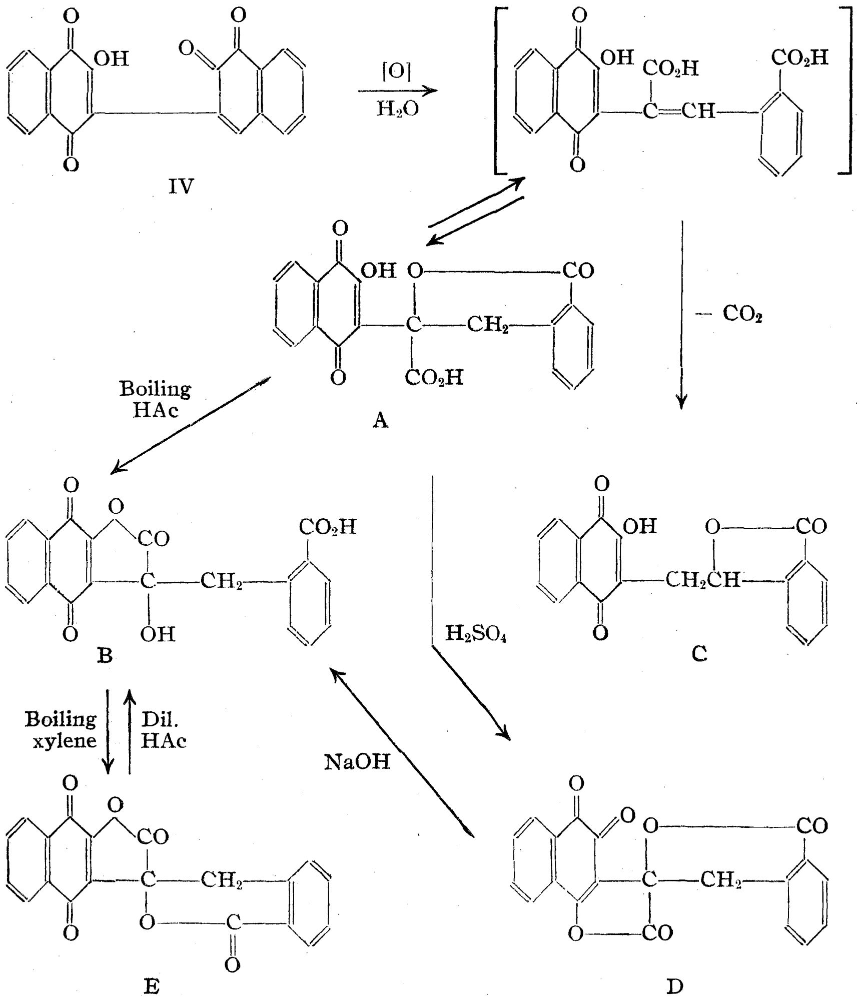
(4) Hooker, THIS JOURNAL, **58**, 1212 (1936).

(5) Witt and Dedichen, *Ber.*, **30**, 2663 (1897).

(6) Smith, *J. Chem. Soc.*, **32**, 560 (1877); **35**, 227 (1879).

posing an alkaline solution of A to the air the substance is converted in part into hydroxynaphthoquinone. The yellow color of compounds A, B and C also suggests the α-quinone structure. By the action of cold, concentrated sulfuric acid A, however, is converted into a red anhydro compound D which appears to be a quinone of the β-series, for it forms a bisulfite addition compound. Dilute alkali converts the substance into B. This interconversion of ortho and para quinone derivatives is likewise indicative of the structure of a hydroxynaphthoquinone.



The facts at present available concerning these and other transformation products suggest a provisional interpretation which is believed to be fundamentally sound if still uncertain in some details. The composition of the oxidation product A is such as to indicate that the reaction involves the rupture of the molecule between two singly linked carbon atoms with the acquisition of two hydroxyl groups. A normal α-diketone oxidation would yield a substance of the formula shown in brackets, but there is evidence that this cannot represent the structure of A. Such a substance probably would be orange or red, because of the unsaturated character of the side chain, and it would surely react with three moles of diazomethane; but A is yellow and yields a dimethyl derivative on treatment with this reagent. The presence in A of but one acidic group in addition to the original hydroxyl group of the quinone ring suggests that the dicarboxylic acid initially formed undergoes lactonization, and for reasons which will be given below compound A is regarded as a δ-lactone of the formula shown. That A is not the primary product is indeed clearly indicated by the color changes observed in carrying out the oxidation. On exposing the alkaline solution of IV to the air it acquires an intensely crimson color as the oxidation proceeds to completion, but the substance (A) which slowly separates after the solution has been acidified dissolves in alkali to an orange, and not a crimson, solution. A satisfactory explanation seems to be that the dibasic acid responsible for the crimson color isomerizes in the acidic solution to the less soluble lactone A. The change seems to be reversible, for on warming the orange alkaline solution of A it acquires a crimson color which persists on cooling.

It seems necessary to assume that A contains a δ- rather than a γ-lactone ring in order to account for the properties of the still more stable isomer B. Only one acidic group is present in B for the substance yields a monomethyl ester on reaction with diazomethane. The ester gives some methane on treatment with methylmagnesium iodide, but apparently other changes obscure the full reaction expected for an alcoholic hydroxyl group. This group seems to be in tertiary combination, for the ester is not acetylated in the presence of either acidic or basic catalysts. This is the chief reason for believing that in the formation of A the lactone ring does not close in the γ-position, for then B would contain a secondary alcoholic group amenable to acetylation. The properties of B, moreover, are suggestive of a δ- rather than a γ-hydroxy acid, for it is not very prone to form a dilactone. On boiling a xylene solution of the substance water is easily eliminated giving a yellow anhydro compound (E) which is regarded as a dilactone, but on simply crystallizing the compound from dilute acetic acid it reverts to B with the opening of the second lactone ring. The red compound D is regarded as a dilactone differing from E only in the character of the quinone group, and its ready formation directly from A is understandable in terms of the formulas suggested. According to the above interpretation the isomerization of A to B in acetic acid solution involves the opening of a δ-lactone ring and the closing of a more stable γ-lactone ring incorporating the acidic hydroxyl group of the quinone.

The ready formation of C in the decarboxylation reaction suggests that the carboxyl group is eliminated not directly from the lactone A but from the unsaturated acid with which A appears to be in equilibrium, particularly in pyridine solution. If an unsaturated hydroxyquinone acid is the immediate product of the decarboxylation it apparently lactonizes at once, for C is yellow, rather than orange-red, and has but one acidic group. The formula suggested for the compound is preferred to that of a dihydrofurano-α-naphthoquinone with a free carboxyl group because like other 2-hydroxy-3-alkyl-1,4-naphthoquinones, the compound can be methylated with diazomethane but not with methyl alcohol and a mineral acid. It seems likely that the substance is a γ-rather than a δ-lactone because it is quite stable and shows no tendency to revert to a hydroxy acid similar to B in aqueous solvents. In cold concentrated sulfuric acid solution C is slowly converted in part into a red anhydro compound F. This was obtained in only very small amounts and it has not been fully characterized, but it does not appear to be an ortho quinone. It is conceivable that the substance is the lactone (ϵ) of an unsaturated hydroxy-α-quinone acid, but there is as yet no evidence on this point.

With the possible exception of F the various compounds seem to be satisfactorily accounted for by the formulas suggested and on the basis of the structure IV for the substance resulting from the oxidation of β-naphthoquinone with ferric chloride. A rigid proof of the individual structures, however, is not available, and the above formulation may require some revision with respect to the exact character of the lactone rings.

Experimental Part

2 - Hydroxy - 3,3′ - dinaphthyl - 1,4,1′,2′ - diquinone (IV).—For the best results in the oxidation the conditions should be controlled more carefully than indicated by Wichelhaus.[3] β-Naphthoquinone of good quality (10 g.) was finely ground, made into a paste with a part of 400 cc. of water, rinsed into a flask, and treated with 40 g. of ferric chloride crystals dissolved in the rest of the water. The mixture is heated in a water-bath kept at 65–70° and the flask is constantly agitated. The quinone darkens and partly dissolves, and in about one hour the product suddenly becomes uniform brownish-yellow and settles, leaving a clear supernatant solution; the oxidation is then complete. Ordinarily the material is obtained in very satisfactory condition; yield 10.2 g. When the very pure, crystalline β-naphthoquinone described by Fieser and Fieser[7] is used the grinding of the sample is unnecessary and it is convenient simply to introduce the reagents and provide mechanical stirring. The yield is the same but the product is pure yellow.

For purification the amorphous brown or yellow material was crystallized from glacial acetic acid, using 45 cc. per gram. The first crop (7.7 g.) separated as deep orange-red needles of the best quality. The mother liquor from the crystallization of the brownish-yellow crude material was allowed to stand overnight and a compact orange-red deposit separated. This proved to be almost certainly the dinaphthyldiquinone (III) studied with Walsh,[8] identification being made by means of the color reactions with 1% sodium hydroxide solution.

The pure hydroxydiquinone when introduced to a bath at 230° darkens at about 240° and melts at 253–254° with decomposition. It imparts a bromine color to concentrated sulfuric acid and on absorption of moisture the solution deposits clusters of microcrystals. Water precipitates the unchanged compound as amorphous flocks changing to microcrystalline dots of very characteristic appearance. The compound dissolves easily in dilute alkali in the cold, as well as in sodium carbonate or bicarbonate solution. The solutions are orange-red and became darker when heated. On spontaneous evaporation of a drop of the alkaline solution there appears around it a very characteristic, almost black ring of microcrystals of the sodium salt.

In investigating the formation of the oxidation product the dinaphthyldiquinone III was boiled with strong ferric chloride solution, but it remained unchanged. At 65–70° hydroxynaphthoquinone was attacked to only a minor ex-

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[7] Fieser and Fieser, THIS JOURNAL, **57**, 491 (1935).

[8] Hooker and Walsh, *J. Chem. Soc.*, **65**, 321 (1894).

tent by aqueous ferric chloride. A mixture of equimolecular amounts of β-naphthoquinone and hydroxynaphthoquinone gave, after recrystallization, no more of the hydroxydiquinone than could be obtained from the β-naphthoquinone used.

The **acetyl derivative of IV** was prepared by slowly stirring 1 g. of the hydroxy compound into a solution of 0.2 cc. of concentrated sulfuric acid in 7 cc. of acetic anhydride at 30–40° for about one hour, a part of the acetate crystallizing during this period. The mixture was poured into water and after several hours the crystalline product (1.1 g.) was collected. The compound is readily soluble in benzene or glacial acetic acid, moderately soluble in alcohol. It crystallizes from methyl alcohol as orange-red prisms or tablets, m. p. 205–205.5°. It is slowly hydrolyzed by 1% sodium hydroxide to the starting material.

Anal. Calcd. for $C_{22}H_{12}O_6$: C, 70.96; H, 3.25. Found: C, 70.99, 70.97; H, 2.96, 3.39.

It may be noted that the analysis reported by Wichelhaus[3] for a compound, m. p. 164–165°, which he obtained by reductive acetylation and regarded as a tetraacetyl derivative agrees equally well with the percentages calculated for a pentaacetyl compound.

Conversion to β,β-Dinaphthyl.—A finely ground mixture of 2 g. of the hydroxy dinaphthyldiquinone (IV) and 80 g. of zinc dust was placed in a flask, covered with 60 g. of zinc dust, and heated to redness. The distillate, which amounted to about three drops, promptly solidified. The material from three runs was clarified and dried in ether solution, and after taking off most of the ether there was obtained a good yellow solid which was collected and washed with a little ether. After two crystallizations from alcohol it was obtained as thin, iridescent, faintly yellow-green plates, m. p. 180–181°; picrate, m. p. 182–183°.

The zinc dust distillation of di-α-naphthoquinone in the same way gave in similar yield a substance of identical appearance and properties and showing no depression in the melting point. A sample of β,β-dinaphthyl was also prepared by Dr. E. B. Hershberg from β-naphthylmagnesium bromide and β-bromonaphthalene and crystallized from benzene–ligroin. This material was almost colorless (but fluorescent) and melted 1.5–2° higher than the above samples but mixtures of the hydrocarbons and the picrates showed no depression. The synthetic hydrocarbon melted at 185–186°, corr.; picrate, orange-yellow needles from benzene, m. p. 186–187°, corr.

Synthesis of α,β-Dinaphthyl.[9]—A solution of 8.8 g. of α-tetralone in absolute ether was slowly added to a solution of the Grignard reagent prepared from 15 g. of β-bromonaphthalene and after refluxing the resulting clear solution for one hour the mixture was worked up in the usual way and the product distilled in vacuum. Vigorous elimination of water occurred at 170–200°, 1–2 g. of naphthalene came over in the fore-run, and the main fraction of unsaturated hydrocarbon distilled at 217–219° (3 mm.) as a yellowish oil; yield 11.3 g. (74%). This material (10.5 g.) was dehydrogenated by heating it with sulfur (1.35 g.) at 230–250° for forty-five minutes and the product was distilled at 2 mm. pressure. The resulting viscous oil slowly solidified and on crystallization there was obtained 9.1 g. of material, m. p. 72–73°. After two recrystallizations the hydrocarbon melted constantly at 74.5–75°, and a sample recovered from the purified picrate melted at the same temperature.

Anal.[10] Calcd. for $C_{20}H_{14}$: C, 94.44; H, 5.55. Found: C, 94.52; H, 5.72.

The hydrocarbon crystallizes from petroleum ether in small, ball-like clusters of microcrystals, and the molten material is very slow to solidify. In all of its properties the substance corresponds closely with the compound regarded by Watson Smith[6] as α,β-dinaphthyl (m. p. 76°), and the present results indicate that, contrary to the conclusions of Meyer and Hofmann,[11] Smith was completely successful in isolating the pure hydrocarbon from a mixture consisting chiefly of the two isomers.

The **dipicrate** was best prepared by using two equivalents of picric acid: 4.5 g. of the acid was dissolved in a hot solution of 2.54 g. of α,β-dinaphthyl in 40 cc. of absolute alcohol. The dipicrate which separated on cooling was dissolved with 2 g. of picric acid in 40 cc. of absolute alcohol, and on cooling there was obtained 5.4 g. of heavy, bright orange needles, m. p. 127–127.5°, corr. The melting point was not changed by further crystallization.

Anal.[10] Calcd. for $C_{20}H_{14}\cdot 2C_6H_3O_7N_3$: N, 11.80. Found: N, 11.57.

A monopicrate does not appear to be stable, for a solution of equivalent quantities of the components deposited almost exactly the theoretical quantity of the dipicrate and the pure hydrocarbon was recovered from the mother liquor. These observations clearly support the conclusion of Gump[12] that the compound which Wegscheider[13] had in hand was not α,β-dinaphthyl.

Compound A.—A solution of 18 g. of 2-hydroxy-3,3′-dinaphthyl-1,4,1′,2′-diquinone in 3600 cc. of 6% sodium hydroxide was distributed amongst six shallow trays of about 645 sq. cm. surface and allowed to evaporate spontaneously in a light room. The at first orange-red solution slowly changed to a permanent crimson. After two weeks the solutions had gone to dryness, and the residues were combined and dissolved in 13.2 liters of water. The intensely crimson alkaline solution was acidified with 480 cc. of concentrated hydrochloric acid made up to a volume of 1200 cc. with water, and the flocculent precipitate which separated immediately was filtered off without delay and discarded (as attempts to purify the material were not successful). The yellow acid filtrate, which should be refiltered quickly in case it is not perfectly clear, was allowed to stand at room temperature for five days, during which time the oxidation product (A) slowly separated as a dull brown-yellow microcrystalline deposit; yield 10.7 g. (54%).

In purifying the crude product care must be taken to avoid prolonged heating of the material in contact with solvents in which it is appreciably soluble (acetic acid or alcohol). One gram of the substance will dissolve in 74 cc. of glacial acetic acid if refluxing is continued for fifteen minutes, but by this time the compound is in part isomerized to B and only 0.22 g. of A separates on cooling. Very

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(9) This experiment was kindly carried out by Dr. E. B. Hershberg.

(10) Analysis by Mrs. G. M. Wellwood.

(11) Meyer and Hofmann, *Monatsh.*, **37**, 710 (1916).

(12) Gump, THIS JOURNAL, **53**, 380 (1931).

(13) Wegscheider, *Monatsh.*, **5**, 238 (1884); *Ber.*, **23**, 3199 (1890).

satisfactory material was obtained by refluxing for two minutes a suspension of 10 g. of the crude oxidation product with 100 cc. of glacial acetic acid, filtering the solution, and washing the undissolved substance with cold glacial acetic acid. The washed material was pure, bright yellow in color and weighed 8.6 g. The wash liquor deposited a crust of brown crystals which can be used for the preparation of B. In recrystallizing A it is not advisable to allow time for complete saturation of the solution. Thus 1 g. of the washed product was added to 75 cc. of boiling glacial acetic acid and after refluxing for three minutes the solution was filtered, leaving a residue of 0.56 g. of undissolved substance. The filtrate was reheated until clear (one minute) and on cooling it deposited 0.20 g. of bright yellow, diamond-shaped plates. Heated in a capillary tube the substance softens at about 201°, runs up the tube with gassing at 203–205°, and then gives a clear yellow liquid. It dissolves in dilute alkali or soda solution in the cold, giving orange solutions which become crimson on warming.

Anal. Calcd. for $C_{20}H_{12}O_7$: C, 65.93; H, 3.29. Found: C, 65.50, 65.71; H, 3.53, 3.50.

The **dimethyl derivative of A** was obtained by allowing the substance to stand in contact with an ethereal solution of diazomethane, taken in large excess, for several hours. The acid is sparingly soluble in the medium and it is converted only slowly into the ester, which appears as a less highly colored yellow solid. When nitrogen was no longer evolved the solvent was removed and the residue taken up in glacial acetic acid, in which it is moderately soluble. The solution was diluted at the boiling point with an equal volume of water and after standing at room temperature for several hours it deposited heavy, yellow, prismatic needles. The substance softens at about 220° and melts at 225–226°. It is insoluble in dilute alkali in the cold and hydrolysis occurs slowly at the boiling point, giving a red solution. In the Zerewitinoff test the compound liberated no gas from a Grignard reagent in diphenyl ether–xylene on being heated at 100° for ten minutes.

Anal.[10] Calcd. for $C_{20}H_{10}O_5(OCH_3)_2$: OCH_3, 15.82. Found: OCH_3, 15.74.

Oxidation of A.—While compound A can be recovered unchanged from its orange solution in cold 1% alkali if precipitated at once, the solution becomes much darker on standing, and on investigating the material recovered from such a solution after it had been exposed for two days it appeared to contain small amounts of A and B and a positive identification of hydroxynaphthoquinone was made by microscopic tests of the sodium and pyridine salts, the material precipitated from alkaline solution, and the color in sulfuric acid solution.

Compound B.—One gram of the substance A was refluxed with 100 cc. of glacial acetic for one and three-quarters hours and the resulting yellow solution was diluted with 100 cc. of hot water. On cooling the pure product slowly separated in the form of rather heavy, flat, yellow needles; yield 0.85 g. The behavior of the substance when heated in a capillary tube is quite characteristic. When introduced to a bath at 200° the material froths vigorously with the liberation of water and then subsides to a dry solid, but when heated gradually in a bath initially at room temperature no change can be detected in the appearance of the crystals as the material is more gently dehydrated. At about 247° minute droplets are formed at the surface of the glass, giving the appearance of orange lines across the tube, and at 264° the substance completely melts to a clear liquid showing some signs of decomposition.

Anal. Calcd. for $C_{20}H_{12}O_7$: C, 65.93; H, 3.29. Found: C, 65.85, 66.02; H, 3.48, 3.50.

The compound is stable to the prolonged action of hot glacial acetic acid with or without added hydrochloric acid. It dissolves in cold concentrated sulfuric acid to a light orange-yellow solution from which water precipitates the unchanged compound in an amorphous form rapidly crystallizing to branching curved needles. A drop of the solution exposed on a slide deposits characteristic frond-like clusters and circular groups of crystals. The sulfuric acid solution reddens on warming and then becomes dull brown-red. Compound B dissolves readily in cold 1% sodium hydroxide yielding a crimson solution. On attempting to acetylate B in pyridine solution the material was recovered, after crystallization, in an unchanged condition.

Compound B was also obtained by warming a suspension of 1 g. of the finely powdered hydroxy dinaphthyl-diquinone IV in 30 cc. of glacial acetic acid with 1.5 cc. of 30% hydrogen peroxide. After about thirty minutes the material had dissolved to an orange-yellow solution, and this became pure yellow at the end of one hour. The solution was treated with 20 cc. of hot water and on cooling it slowly deposited 0.4 g. of orange-yellow needles. This material was boiled with 15 cc. of glacial acetic acid for one hour, and after adding 7 cc. of water and cooling there was obtained 0.3 g. of yellow needles of B. The substance was identified by the usual tests and by conversion to the ester and the anhydride.

The **methyl ester of B**, prepared as above with diazomethane, crystallized very slowly from a solution in glacial acetic acid which had been diluted at the boiling point with an equal volume of water. It forms flat, pale yellow needles melting at 249–250°, with some previous softening.

Anal.[10] Calcd. for $C_{21}H_{14}O_7$: OCH_3, 8.20. Found: OCH_3, 8.38.

The ester is moderately soluble in glacial acetic acid, sparingly soluble in alcohol or benzene. It is not affected by boiling xylene and crystallizes from this solvent in one or two large, compact clusters of needles. The substance is insoluble in cold alkali but it is hydrolyzed rather readily at the boiling point. It was recovered unchanged after being heated at 100° with acetic anhydride in pyridine solution or in the presence of sulfuric acid. In the Zerewitinoff test 0.1 mole of methane was liberated in the cold and a total of 0.3 mole was evolved after heating at 100° for five minutes.

Compound E (α-Anhydride of B).—One-tenth gram of B was brought into solution in 15 cc. of xylene by gentle heating and shaking and the clear yellow solution was boiled for a minute or two on the hot-plate. A ring of moisture appeared and was allowed to escape, and soon the anhydride began to crystallize from the boiling solution as clusters of fine yellow needles. The material collected after cooling amounted to 0.08 g. and it was analyzed without further purification.

Anal.[10] Calcd. for $C_{20}H_{10}O_6$: C, 69.36; H, 2.91. Found: C, 69.62; H, 2.95.

Introduced in a capillary tube to a bath at 220° the substance shows no signs of frothing or other change, orange lines appear across the sample at about 249° and melting is complete at 264°. Except for any indication of loss of water, the behavior is identical with that of B, and it is inferred that the latter yields E on being heated without solvent. The anhydro compound is readily soluble in dioxane or tetrachloroethane but does not crystallize well even on the addition of benzene, in which it is sparingly soluble. It dissolves easily in glacial acetic acid and after dilution with hot water the solution deposits needles of B, easily distinguished from the anhydride by the frothing at 200° in a melting point capillary. Compound E dissolves easily in cold alkali or soda solution with a crimson color. On acidifying the cold alkaline solution this turns yellow and cloudy and a small amount of yellow material slowly separates. On boiling this at first dissolves to a clear solution which then deposits a yellow, granular product having the properties of E rather than B (no frothing at 200°). Compounds B and E behave exactly the same in this test and in the tests with sulfuric acid.

Compound D (β-Anhydride of B).—One gram of A was dissolved in 50 cc. of concentrated sulfuric acid at room temperature and after standing for one hour the red solution was poured into 1 liter of water. The flocculent orange-red precipitate was washed and dried (0.98 g.) and crystallized from 25 cc. of glacial acetic acid. The substance forms clusters of red, prismatic blades, m. p. 248–249.5°.

Anal. Calcd. for $C_{20}H_{10}O_6$: C, 69.36; H, 2.91. Found: C, 69.10; H, 3.09.

It dissolves slowly in cold sodium bisulfite solution and a colorless addition product separates. Addition of hydrochloric acid to a solution of the colorless material precipitates D. The compound dissolves rapidly in cold 1% sodium hydroxide solution and the yellow material which precipitates on acidification was identified, after crystallization, as B. Reaction occurred on treatment of D with diazomethane and the substance rapidly dissolved in the ether. A glass-like resin was left on evaporating the solvent and it could not be crystallized.

Compounds C.—One gram of A was refluxed with 50 cc. of alcohol for five and one-half hours and the resulting solution was allowed to cool and seeded with a crystal of B. After standing overnight 0.16 g. of needles of B deposited. The mother liquor was then evaporated to a volume of 25 cc. and on standing overnight a small additional quantity of B separated. After about ten days a mixture of B and C had crystallized and on warming the solvent in contact with this material the crystals of C dissolved and those of B were filtered off. On standing the mother liquor deposited 0.26 g. of plates of C in a nearly pure condition, m. p. 174–175°.

The substance was obtained in better yield as follows. A solution of 1 g. of A in 15 cc. of pyridine was heated with 0.05 g. of copper powder just at the boiling point for fifteen minutes, when carbon dioxide was no longer evolved, and the red solution was diluted with 100 cc. of water, filtered through a pad of Norite and treated with an excess of hydrochloric acid. The precipitate often carries down some of the pyridine salt, which gives it an orange color, but this can be decomposed by vigorous shaking, giving pure yellow material; yield 0.9 g. Recrystallized from alcohol or alcohol–water the substance formed lustrous yellow plates (0.7 g.) melting at 177.5–178° and giving no depression when mixed with the above sample. It is readily soluble in benzene, alcohol or ether.

Anal. Calcd. for $C_{19}H_{12}O_5$: C, 71.24; H, 3.77. Found: C, 71.12; H, 3.93.

The compound dissolves easily in cold dilute alkali (or soda) to a light cherry red solution which does not darken on warming, and the unchanged material is precipitated on acidification. It is not altered by prolonged heating at 100° with a mixture of equal parts of glacial acetic acid and concentrated hydrochloric acid, or by boiling the solution in xylene, or by refluxing for three hours a solution in methyl alcohol containing sulfuric acid.

Ester of C.—The reaction with diazomethane proceeds very rapidly and the material all passes into solution. The ester crystallizes very slowly from alcohol, in which it is readily soluble, forming bright yellow, elongated prisms, m. p. 165–166°. It is hydrolyzed slowly by hot 1% sodium hydroxide.

Anal.[10] Calcd. for $C_{20}H_{14}O_5$: C, 71.84; H, 4.22; OCH_3, 9.28. Found: C, 72.11; H, 4.41; OCH_3, 8.85.

Compound F (Anhydride of C).—The substance C (0.2 g.) gives a light orange-yellow solution in cold concentrated sulfuric acid (5 cc.) and if the fresh solution is poured into water the unchanged starting material is precipitated. The acid solution darkens on standing and after fifteen hours only a small amount of brown material is precipitated. At intermediate periods C is converted in part into F, as can be seen clearly by observing under the microscope the crystals deposited when a drop of the solution is exposed on a slide, the anhydride forming small rosets of orange-red needles. After three and one-half hours there seemed to be no further increase in the amount of this material and the orange product obtained on precipitation at this point consisted chiefly of unchanged C mixed with about 0.02 g. of the new substance. Being much less soluble in dilute alcohol than C, compound F was easily separated by dissolving the mixture in alcohol and adding water at the boiling point. The substance separated as bundles of hair-like, red needles. It decomposes at about 220–225° and does not dissolve appreciably in cold sodium bisulfite solution.

Anal.[10] Calcd. for $C_{19}H_{10}O_4$: C, 75.49; H, 3.34. Found: C, 75.45; H, 3.81.

Summary

It is shown that the substance obtained by Wichelhaus by the action of ferric chloride on β-naphthoquinone has the structure of 2-hydroxy-3,3′-dinaphthyl-1,4,1′,2′-diquinone. On exposure of the alkaline solution of the compound to the air for several days a smooth oxidation takes place with the cleavage of the *o*-quinone ring and the formation of an unsaturated hydroxynaphthoquinone dicarboxylic acid derivative which subsequently lactonizes. The resulting substance

has given rise to a number of interesting lactones and dilactones of both the α- and the β-naphthoquinone series and reminiscent of some of the compounds of the lapachol and lomatiol group. These compounds have been investigated and the changes have been for the most part satisfactorily explained.

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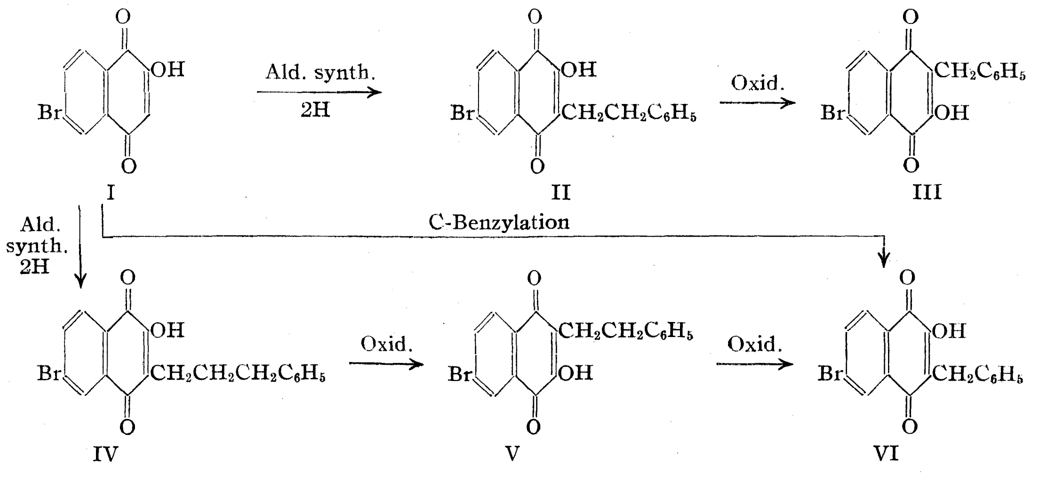
Concerning the Mechanism of the Hooker Oxidation

BY L. F. FIESER, J. L. HARTWELL[1] AND A. M. SELIGMAN[1]

In the course of his investigations of the oxidation of alkyl and alkenyl derivatives of hydroxynaphthoquinone,[2] the late Dr. Samuel C. Hooker came to the conclusion that the essential step in the remarkable reaction discovered by him consists in the opening of the quinone ring and its subsequent closing in a different manner, and consequently that the alkyl and hydroxyl groups exchange places as a result of the oxidation. In understanding with Dr. Hooker, and as already mentioned in one of his papers,[2b] we undertook to provide a rigid test of this part of the mechanism by studying the oxidation of naphthoquinones marked with a distinguishing substituent in the aromatic ring.



2-Hydroxy-6-bromo-1,4-naphthoquinone,[3] I, served as a convenient starting material for the preparation of compounds of the type desired, and it was converted into the derivatives II and IV by condensation with the appropriate aldehydes and hydrogenation of the unsaturated side chain of the condensation products, following the general synthetic method of Hooker.[4] Submitted to the Hooker oxidation with alkaline permanganate, the hydrocinnamyl derivative IV yielded a lower homolog isomeric with the synthetic β-phenylethyl compound II but not identical with this substance. The oxidation product therefore has the alternate structure V and the hydroxyl and alkyl groups have assumed new positions with respect to the bromine atom, in accordance with the theory of Hooker. A second oxidation should result in a reversion to the original positions, with the hydroxyl and bromine located at 2 and 6, respectively. That the second oxidation product indeed has the structure VI was established by the independent synthesis of this compound from the silver salt of I by the method of Fieser.[5] According to the theory an isomer of this benzyl derivative should result from the oxidation of the synthetic β-phenylethyl compound II, and this prediction also was verified.

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(1) The work on the bromonaphthoquinones and the experiments in the lapachol series were completed by J. L. Hartwell in 1933; the experiments with the alkylnaphthoquinones were carried out by A. M. Seligman in 1934.

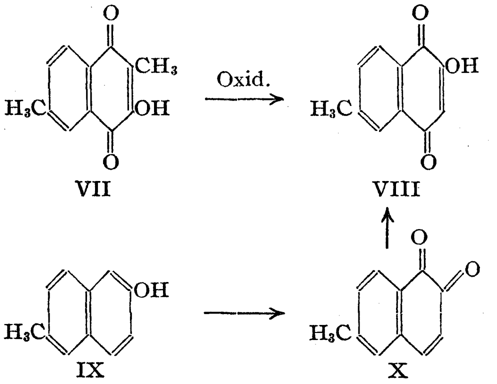
(2) Hooker, THIS JOURNAL, **58** (a) 1168; (b) 1174; Hooker and Steyermark, (c) 1179; (d) 1198 (1936).

(3) Fries and Schimmelschmidt, *Ann.*, **484**, 245 (1930).

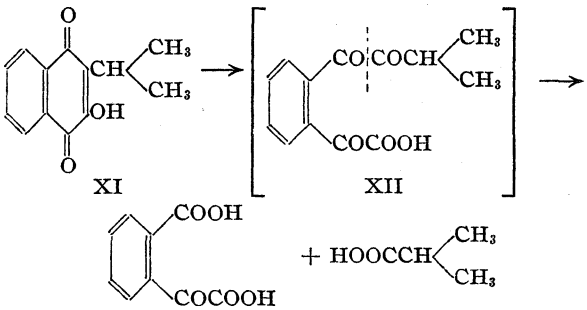
(4) Hooker, THIS JOURNAL, **58**, 1163 (1936).

(5) Fieser, *ibid.*, **48**, 3201 (1926).

While these experiments adequately establish the point at issue it seemed desirable to include in the study a case in which the structure of the product of a single oxidation, rather than of two successive oxidations, could be proved by direct synthesis. 2,6-Dimethyl-3-hydroxy-1,4-naphthoquinone[6] (VII) was investigated for the purpose and when oxidized by the Hooker method it was found to give in good yield a hydroxynaphthoquinone having one less methyl group. That it is the methyl group of the quinone ring which has been eliminated is shown very clearly by the observation that the oxidation product easily yields an ether on reaction with methyl alcohol in the presence of a trace of mineral acid, whereas under similar conditions the starting material (VII) is unchanged.[6] As in other cases[7] a substituent in the hydroxyquinone ring effectively blocks the addition reaction. That the hydroxyl group assumes a new position with respect to the remaining methyl group as a result of the oxidation was established by the synthesis of a compound of the structure VIII from 6-methyl-2-naphthol,[8] IX, as indicated. The compound proved to be identical with the oxidation product from VII. Regarding the structure of the starting material IX, obtained from β-methylnaphthalene by sulfonation and fusion, it was found that the substance forms a characteristic 1,8-phthaloyl derivative which can be rearranged with concentrated sulfuric acid to a methylhydroxybenzanthraquinone, showing that the 7(β)-position of the methylnaphthol is unoccupied. This provides an independent proof in confirmation of other, less direct, evidence[8,9] that the substituents are located in the 2- and 6-positions as in formula IX.



It may be concluded from these results that the hydroxyl group and the modified alkyl substituent exchange places as a result of the oxidation, exactly as predicted on the theory that the quinone ring opens in the course of the reaction. In the hope of securing still more direct evidence on this point we undertook to investigate the oxidation of a compound of such a structure that the quinone ring, once opened, could not subsequently be reestablished. A compound suitable for the purpose was obtained by submitting hydrolapachol[4] to two successive oxidations with alkaline permanganate, 2-isopropyl-3-hydroxy-1,4-naphthoquinone (XI) being easily obtained in this way in good yield. When this was treated with alkaline permanganate in the regular manner oxidation proceeded to the colorless stage as usual, but no pink or red color subsequently developed, even on long standing. According to the theory the oxidation should lead to the formation of the triketo acid XII which, lacking a methylene group in the proper position of the side chain, cannot undergo cyclization to a hydroxynaphthoquinone. On working up the acidified, colorless solution there was isolated in place of this substance phthalonic acid and isobutyric acid, which very probably arise from the oxidative cleavage of XII between the two adjacent carbonyl groups.



These observations lend considerable support to the view that the quinone ring opens in the first step of the Hooker oxidation, but our work casts no further light on the exact mechanism of the subsequent ring closure. There is perhaps a rough analogy in the conversion of 2-aceto-1-naphthylglyoxylic acid into 1,2-naphthindanedione,[10] but the reaction occurs in an acidic rather than an alkaline medium and the process definitely is one of oxidation, a point not yet clearly established in the case at hand.

In conclusion the senior author wishes to acknowledge his indebtedness to the late Dr. Hooker

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[6] Fieser and Seligman, THIS JOURNAL, **56**, 2690 (1934).

[7] Fieser, *ibid.*, **48**, 2922 (1926).

[8] Dziewoński, Schoenówna and Waldmann, *Ber.*, **58** 1212 (1925).

[9] Haworth, Letsky and Mavin, *J. Chem. Soc.*, 1784 (1932).

[10] Fieser, THIS JOURNAL, **51**, 940 (1929).

both for the permission to collaborate on this problem and for the useful and inspiring advice of his esteemed friend.

Experimental Part

Condensation of Aldehydes with 2-Hydroxy-6-bromo-1,4-naphthoquinone, Hydrogenation

The starting material, previously mentioned only incidentally in the literature,[3] was prepared conveniently from 6-bromo-1,2-naphthoquinone[3,11] as follows. On reaction with acetic anhydride–sulfuric acid by the usual procedure[12] this gave **1,2,4-triacetoxy-6-bromonaphthalene** in 62% yield, the purified material forming colorless needles, m. p. 162°, from alcohol.

Anal. Calcd. for $C_{16}H_{13}O_6Br$: C, 50.4; H, 3.44. Found: C, 50.6; H, 3.69.

On adding 145 g. of the powdered triacetate to a cold solution of 160 g. of potassium hydroxide in 730 cc. of 95% alcohol the temperature soon rose nearly to the boiling point and the solid dissolved to give a solution which rapidly turned dark brown. Oxidation to the quinone was completed by bubbling in air for one-half hour, after which the potassium salt of the product soon separated completely as small red crystals. Washed with alcohol, then with ether, the material was obtained in a very pure condition and in quantitative yield. As the potassium salt is sparingly soluble in water it was merely suspended in hot water and treated with dilute acid. The hydroxyquinone was obtained as a lemon-yellow, crystalline precipitate. It formed beautiful yellow needles, m. p. 204–205°, from alcohol containing a trace of acetic acid.

2 - Hydroxy - 3 - β - phenylvinyl - 6 - bromo - 1,4 - naphthoquinone was prepared by Hooker's method[4] but using more solvent. A solution of 10 g. of the hydroxybromoquinone in 225 cc. of glacial acetic acid was treated at 93° with 30 cc. of previously warmed concentrated hydrochloric acid, followed immediately by 22 cc. of phenylacetaldehyde. After digestion at 80° for one hour a large crop of red, crystalline material had separated and this was collected while the solution was still hot, as on cooling a brown substance separated. The collected material, after being washed with acetic acid, was obtained in a good condition; yield 56%. Crystallized from benzene it formed glistening, deep red needles, m. p. 243–244°, violet solution in alkali.

Anal. Calcd. for $C_{18}H_{11}O_3Br$: C, 60.9; H, 3.12. Found: C, 60.8; H, 3.32.

Reductive acetylation with zinc dust, acetic anhydride, and sodium acetate gave the **hydroquinone triacetate** in 86% yield, the compound forming colorless needles, m. p. 197–198°, from benzene–absolute alcohol.

Anal. Calcd. for $C_{24}H_{19}O_6Br$: C, 59.6; H, 3.96. Found: C, 59.8; H, 4.12.

Hydrogenation of the hydroxyquinone proceeded smoothly in alcoholic solution using Adams catalyst, giving **2-hydroxy-3-β-phenylethyl-6-bromo-1,4-naphthoquinone (II)**, which crystallizes from alcohol containing a little acetic acid as flat, golden-yellow needles, m. p. 180–181°; red color in alkali.

Anal. Calcd. for $C_{18}H_{13}O_3Br$: C, 60.5; H, 3.67. Found: C, 60.3; H, 3.81.

The hydroquinone triacetate of II formed fine, colorless needles from alcohol–benzene, m. p. 188–189°.

Anal. Calcd. for $C_{24}H_{21}O_6Br$: C, 59.4; H, 4.36. Found: C, 59.3; H, 4.49.

2 - Hydroxy - 3 - γ - phenyl - α - propenyl - 6 - bromo - 1,4-naphthoquinone was prepared as above, using hydrocinnamaldehyde, but the product did not separate from the hot reaction mixture. On pouring this into water there was obtained a brown precipitate mixed with black tar. After decanting the aqueous liquor the material was warmed with two portions of alcohol, for although this extracted some of the product it effectively removed the tar and left a fairly clean, crystalline yellowish residue (40% yield). For further purification the product was dissolved in 2% alcoholic potassium hydroxide and the violet solution was filtered from some dark residue and acidified. The precipitated material then crystallized well from benzene–petroleum ether to which a small amount of acetic acid was added, finally forming bright orange needles, m. p. 177–178°.

Anal. Calcd. for $C_{19}H_{13}O_3Br$: C, 61.8; H, 3.55. Found: C, 61.8; H, 3.85.

The hydroquinone triacetate formed colorless needles, m. p. 170–171°, from alcohol, benzene, or glacial acetic acid.

Anal. Calcd. for $C_{25}H_{21}O_6Br$: C, 60.4; H, 4.26. Found: C, 60.4; H, 4.31.

This triacetate slowly absorbed hydrogen in the presence of Adams catalyst giving the corresponding saturated compound, **1,2,4-triacetoxy-3-hydrocinnamyl-6-bromonaphthalene,** which formed needles, m. p. 170–172° (depresses the m. p. of the starting material).

Anal. Calcd. for $C_{25}H_{23}O_6Br$: C, 60.1; H, 4.64. Found: C, 60.1; H, 4.80.

The saturated triacetate was dissolved in hot acetone and hydrolyzed with alcoholic alkali, the solution being exposed to the air until quite red, diluted, and acidified. The yellow precipitate of **2-hydroxy-3-hydrocinnamyl-6-bromo-1,4-naphthoquinone,** IV, (92% yield) crystallized from alcohol–benzene containing a trace of acetic acid as golden-yellow scales melting at 170–171°.

Anal. Calcd. for $C_{19}H_{15}O_3Br$: C, 61.5; H, 4.08. Found: C, 61.4; H, 4.35.

Benzylation of 2-Hydroxy-6-bromo-1,4-naphthoquinone

A suspension of 6.2 g. of the silver salt of the hydroxyquinone with 3 g. of benzyl bromide in 70 cc. of absolute ether was allowed to stand in a stoppered flask overnight, when the red salt had been replaced by silver bromide. Three products were obtained, namely, **4-benzyloxy-6-bromo-1,2-naphthoquinone** (a), **2-hydroxy-3-benzyl-6-bromo-1,4-naphthoquinone** (b), and **2-benzyloxy-6-bromo-1,4-naphthoquinone** (c), and they were separated in this order as follows. The ethereal solution was filtered and set aside, while the residue was extracted with 100 cc. of hot benzene. On cooling the benzene solution the *o*-quinone ether (a) separated in a nearly pure condition; yield 0.6 g. (10%); crystallized from benzene it formed orange-yellow needles, m. p. 227–228°. The benzene mother

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(11) Fieser and Hartwell, THIS JOURNAL, **57**, 1479 (1935).

(12) Thiele and Winter, *Ann.*, **311**, 345 (1900).

liquor and the ethereal solution were combined and extracted with 2% alkali and the red alkaline solution on acidification gave 1.4 g. (24%) of the acidic isomer (b), which crystallized from absolute alcohol–benzene, with a trace of acetic acid, as golden-yellow plates, m. p. 192°. On drying and concentrating the benzene–ether mother liquor 0.6 g. (10%) of the *p*-quinone ether was obtained. It formed pale yellow needles from benzene, m. p. 201–202°.

Anal. Calcd. for $C_{17}H_{11}O_3Br$: C, 59.5; H, 3.23. Found: (a) C, 59.5; H, 3.59; (b) C, 59.5; H, 3.63; (c) C, 59.5; H, 3.49.

The structures of the non-acidic isomers (a) and (c) are inferred from the colors of the compounds, in analogy with known cases. It was noted that on the addition of a drop or two of sodium or potassium hydroxide to a solution of the *p*-quinone ether in acetone the solution became deep purplish-blue, the color changing after a few minutes to dull green with loss of strength. Both the alkali and the solvent acetone appear to be necessary for the production of the blue color, as other bases and other solvents were ineffective. The *o*-quinone ether gave only a faint pink coloration, and the test was negative with α-naphthoquinone and several of its simple derivatives. 2-Methoxy-1,4-naphthoquinone gave an exactly similar coloration.

Reductive acetylation of the acidic isomer gave **1,2,4-triacetoxy-3-benzyl-6-bromonaphthalene;** fine needles, m. p. 202–203°.

Anal. Calcd. for $C_{23}H_{19}O_6Br$: C, 58.6; H, 4.06. Found: C, 58.6; H, 4.29.

Oxidation of the Bromo Compounds

The Hydrocinnamyl Compound IV.—On account of the sparing solubility of the brominated quinones, the procedure was slightly modified as follows. A solution of 3 g. of IV in the required amount of hot benzene was stirred into 600 cc. of hot 1% sodium hydroxide solution and the red solution was cooled to 0° and treated with 189 cc. of 1% potassium permanganate solution, also at 0°. The color changes were as described by Hooker, the solution becoming practically colorless (spot test) and then reaching a maximum intensity of red in one to two hours. The yield of precipitated, nearly pure, material was 36%.[13] Crystallized from alcohol containing acetic acid the **3-hydroxy-2-β-phenylethyl-6-bromo-1,4-naphthoquinone** (V) formed golden-yellow needles, m. p. 173–175°. A mixture with the isomer II melted at 148–153°.

Anal. Calcd. for $C_{18}H_{13}O_3Br$: C, 60.5; H, 3.67. Found: C, 60.5; H, 3.93.

Further Oxidation of V.—From 0.9 g. of the above compound (V), oxidized in the same way, there was obtained in 54% yield a substance crystallizing as golden-yellow plates, m. p. 188–189°, and giving no depression with synthetic 2-hydroxy-3-benzyl-6-bromo-1,4-naphthoquinone, VI.

Oxidation of the Synthetic β-Phenylethyl Compound, II.—The oxidation product, obtained in 43% yield, crystallized from alcohol with a trace of acetic acid as golden-yellow needles, m. p. 158–159°. The melting point of the **3-hydroxy-2-benzyl-6-bromo-1,4-naphthoquinone** (III) was depressed about 10° by admixture with the isomeric 3-benzyl compound.

Anal. Calcd. for $C_{17}H_{11}O_3Br$: C, 59.5; H, 3.23. Found: C, 59.2; H, 3.43.

The **hydroquinone triacetate,** which formed colorless needles, m. p. 196–197°, also gave a depression with the isomeric 3-benzyl compound.

Anal. Calcd. for $C_{23}H_{19}O_6Br$: C, 58.6; H, 4.06. Found: C, 58.5; H, 4.34.

2-Isopropyl-3-hydroxy-1,4-naphthoquinone

Preparation.—Lapachol kindly supplied for the purpose by Dr. Hooker was converted into the hydro derivative[4] and this was oxidized[2a] to 2-isobutyl-3-hydroxy-1,4-naphthoquinone. The acetate of this substance formed pale yellow needles, m. p. 53.5–54° (Calcd.: C, 70.6; H, 5.93. Found: C, 70.6; H, 5.40). Oxidation of the hydroxy compound in 1% sodium hydroxide solution with 1% aqueous potassium permanganate gave **2-isopropyl-3-hydroxy-1,4-naphthoquinone** (XI) in 52% yield. The compound gave bright yellow needles, m. p. 92–93° from alcohol–acetic acid.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.2; H, 5.60. Found: C, 72.4; H, 5.76.

Oxidation.—When a solution of 1 g. of the quinone in 1% alkali was treated with an aqueous solution of 1.08 g. of potassium permanganate according to Hooker's procedure the oxidation was somewhat slower than usual and the supernatant liquor became colorless only after about two hours. Air was bubbled through the solution for two hours, but no reddening occurred. After removing the manganese dioxide and acidifying the colorless solution a strong odor of isobutyric acid was noted and the substance was expelled by distilling the solution to a small volume, adding water and repeating the process. The acid distillate neutralized 42 cc. of 0.1038 *N* alkali, corresponding to a yield of 61% of isobutyric acid. In another experiment 5 g. of the starting material gave an acid distillate containing isobutyric acid equivalent to a 65% yield, on the basis of titration. The neutral solution of the salt on evaporation left a residue (1.25 g.) which was treated with hydrogen chloride in the presence of ether. After filtering, and removing the solvent, the free acid (0.91 g.) was refluxed with *p*-toluidine (3.2 g.), and after extracting the unused reagent with dilute hydrochloric acid the residue was dried and crystallized from ligroin. Colorless plates, m. p. 104–105°, were obtained and a mixed melting point with a known sample of the *p*-toluide of isobutyric acid, m. p. 106–106.5°, established the identity of the substance.

The residue from the steam distillation in the first experiment (1 g. of starting material) was made faintly alkaline and treated with 0.4 g. of phenylhydrazine hydrochloride and a few drops of acetic acid. After heating the mixture for four hours on the steam-bath and cooling, a pale yellow solid separated mixed with resinous matter. The yellow substance was extracted with soda solution, leaving the resin undissolved, and on acidifying the filtrate a pale yellow crystalline precipitate separated (0.25 g.). The substance melted at 215° with gas evolution and it was identified as 3-phenyl-4-phthalazone-1-carboxylic acid by a mixed melting point determination with a sample of the

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[13] At the time of the experiment it was not recognized in Dr. Hooker's laboratory or in our own that the yield is generally improved by employing a higher concentration of alkali.

substance, m. p. 216–217°, dec., prepared from phthalonic acid and phenylhydrazine.[14]

Oxidation of 2,6-Dimethyl-3-hydroxy-1,4-naphthoquinone

Conversion to 2-Hydroxy-6-methyl-1,4-naphthoquinone.—In trial experiments it was found, in conformity with Hooker's observations,[2b] that the reaction proceeds best in a strongly alkaline medium, and the following method was adopted as the most satisfactory. A solution of 1.13 g. of the dimethylhydroxynaphthoquinone (VII) in 100 cc. of 6% sodium hydroxide was chilled in ice and treated all at once with a solution of 1.26 g. of potassium permanganate and 6 g. of sodium hydroxide in 126 cc. of water, also at 0°. After standing for two hours at room temperature, the manganese dioxide was removed and the filtered solution, which had become quite red, was acidified. Small yellow plates of the oxidation product separated in a good condition (0.78 g.) and a further amount (0.05 g.) was obtained by extracting the filtrate with ether; yield, 75%. The substance crystallized from benzene–ligroin as golden-yellow plates and from acetic acid as stout yellow needles; m. p. 199°, dec. It is sparingly soluble in water, moderately soluble in benzene, readily soluble in alcohol. The solutions in both alkali and sulfuric acid are red.

Anal. Calcd. for $C_{11}H_8O_3$: C, 70.19; H, 4.29. Found: C, 70.20; H, 4.30.

The methyl ether was obtained in good yield by refluxing for one and one-half hours a solution of 0.5 g. of the hydroxyquinone and 0.5 cc. of concentrated sulfuric acid in 25 cc. of methyl alcohol. The ether separated on cooling as fine, pale yellow needles, and after recrystallization it melted at 167–167.5°.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.25; H, 4.99. Found: C, 71.31; H, 5.01.

The hydroquinone triacetate formed small, colorless needles from benzene–ligroin, m. p. 157–158°.

Anal. Calcd. for $C_{17}H_{16}O_6$: C, 64.53; H, 5.10. Found: C, 64.34; H, 5.04.

Synthetic Preparation of 2-Hydroxy-6-methyl-1,4-naphthoquinone.—β-Methylnaphthalene (100 g.) was sulfonated according to Dziewoński, Schoenówna and Waldmann[8] but the filtered solution of the reaction product in water (1 liter) was neutralized with concentrated alkali. The sodium salt which separated was obtained in a pure condition after one recrystallization; yield, 80%; *p*-toluidine salt, flat needles from dilute alcohol, m. p. 250–251°. For conversion to 6-methyl-2-naphthol[8] 140 g. of the sodium salt was fused with a melt from 460 g. of potassium hydroxide and 7 cc. of water and the crude, precipitated material was coagulated by boiling, dried, and vacuum distilled, giving 50 g. (55%) of slightly pink material melting at 123° and suitable for further use. The methylnaphthol was coupled with diazotized sulfanilic acid and the dye was reduced with hydrosulfite essentially as described for the case of β-naphthol,[15] with allowance for a lower solubility in the present series, the yield of very nearly colorless 1-amino-6-methyl-2-naphthol hydrochloride being 50%. The oxidation to 6-methyl-1,2-naphthoquinone presented some difficulties and ferric chloride gave only what appeared to be a dimolecular product. The following details can be supplemented to the brief statement in the literature.[8] A suspension of 7 g. of the amine hydrochloride in 200 cc. of water was neutralized with 14 g. of sodium acetate crystals, 10 cc. of concentrated sulfuric acid was added and the mixture was poured into 3 liters of water. After adding an additional 30 cc. of the acid the solution on filtration was water-clear, and it was stirred well and treated all at once with a cold solution of 7 g. of potassium dichromate and 30 cc. of concentrated sulfuric acid in 150 cc. of water. The quinone separated as orange micro-crystals, m. p. 126°, in 60% yield.

Potassium 6-Methyl-1,2-naphthoquinone-4-sulfonate.—Attempts to introduce an hydroxyl group by the Thiele reaction were unsuccessful; a colorless product, m. p. 156–158°, slowly separated from the mixture but it did not have the properties of a hydroquinone triacetate. The addition of bisulfite, on the other hand, proceeded normally. The quinone (3.5 g.) was added very slowly with stirring to a solution at 25° of 3.6 g. of sodium bisulfite in 40 cc. of water and after one-half hour the resulting solution was filtered, treated with 0.4 cc. of concentrated sulfuric acid, boiled, cooled to 25°, and treated with 2.4 g. of potassium dichromate and 1.8 cc. of concentrated sulfuric acid in 7 cc. of water, followed by 40 cc. of saturated potassium chloride solution, added in portions as crystallization of the quinone sulfonate proceeded. On dissolving the compound in water containing a trace of bromine at 60°, clarifying the solution and adding potassium chloride,[16] the quinone sulfonate separated as fine orange needles of a monohydrate; yield 50%.

Anal. Calcd. for $C_{11}H_7O_5SK \cdot H_2O$: S, 10.40. Found: S, 10.48.

2-Methoxy-6-methyl-1,4-naphthoquinone was obtained by mixing 0.8 g. of the above sulfonate with a solution of 0.5 cc. of concentrated sulfuric acid in 5 cc. of methyl alcohol at 0°, gradually warming the mixture on the steam-bath, adding 5 cc. more methyl alcohol, and refluxing until the salt had disappeared. On cooling the methoxy compound separated as very fine, pale yellow needles (70% yield). On recrystallization the substance melted at 167–167.5° and gave no depression when mixed with the ether of the quinone obtained above as an oxidation product. The hydroxy compound was obtained on hydrolysis of the synthetic ether and both this substance and its hydroquinone triacetate were compared with the above samples and the identity fully established.

1,8-Phthaloyl-6-methyl-2-naphthol (1-Hydroxy-5-methylpleiadenedione).—On condensing 6-methyl-2-naphthol (10 g.) with phthalic anhydride in the presence of aluminum chloride at 200° by the previously described procedure,[17] the reaction product was obtained in a pure condition after one crystallization from glacial acetic acid; yield, 14.7 g. (81%). It forms bright yellow needles, m. p. 194–194.5°.

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.14; H, 4.20. Found: C, 79.47; H, 4.44.

2′-Hydroxy-4-methyl-1,2-benzanthraquinone.—As with the parent compound,[18] the rearrangement proceeded

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[14] Henriques, *Ber.*, **21**, 1610 (1888).

[15] Fieser and Fieser, THIS JOURNAL, **57**, 491 (1935).

[16] See Martin's method for the parent compound, ref. 15.

[17] Fieser, THIS JOURNAL, **55**, 4977 (1933).

[18] Fieser and Fieser, *ibid.*, **55**, 3342 (1933).

poorly and much material was lost through sulfonation. Three grams of the pleiadenedione was quickly stirred into a solution of 160 cc. of concentrated sulfuric acid and 80 cc. of water preheated to 170°. The initially yellow-red solution soon turned brown and after three minutes it was poured into boiling water, and after boiling the mixture to coagulate the red precipitated material this was collected and washed; yield 0.9 g. The material was purified through the acetate which crystallizes from glacial acetic in cottony clusters of canary-yellow needles, m. p. 218–219°. This was hydrolyzed with alcoholic alkali giving, after dilution, an intensely blue solution of the sparingly soluble sodium salt from which the hydroxyquinone separated on acidification as a fiery red precipitate of hair-like micro-needles. From alcohol the substance crystallized as orange-red plates, m. p. 256–258°, dec. Treated with sodium hydrosulfite, the blue alkaline solution gives a transient red color and then an orange-yellow vat.

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.14; H, 4.20. Found: C, 78.84; H, 4.66. Acetate, calcd. for $C_{21}H_{14}O_4$: C, 76.34; H, 4.27. Found: C, 76.42; H, 4.39.

Summary

By using 2-alkyl-3-hydroxy-1,4-naphthoquinones having reference groups in the aromatic ring it has been possible to prove that the substituents in the 2- and 3-positions exchange places in the course of the Hooker oxidation in exactly the manner predicted by the discoverer of the reaction. Hooker's view that the quinone ring is opened in the first step of the process has been substantiated by the isolation of products evidently arising from the type of intermediate postulated.

Converse Memorial Laboratory
Cambridge, Massachusetts Received April 16, 1936

[Contribution from the Chemical Laboratory of Harvard University]

The Electron Affinity of Free Radicals. X. A Potentiometric Method for Determining ΔF for the Addition of Sodium to an Organic Compound[1]

By H. E. Bent and N. B. Keevil

Most compounds containing sodium are very stable. A reaction leading to the formation of a compound involving the pure metal goes so nearly to completion that it is not possible to obtain an equilibrium constant from the concentration of unreacting material. Such reactions can be studied, however, with the aid of mercury.[2] Sodium forms compounds with mercury which are so stable that it is possible to remove sodium from other compounds by shaking them with mercury or a dilute amalgam. By choosing an amalgam of the proper concentration an equilibrium can be established favorable for analysis and the computation of an equilibrium constant. At equilibrium the reaction may be considered as a distribution experiment, the sodium in the mercury being in equilibrium with the sodium in the solution of the compound being studied. Since the thermodynamic properties of amalgams have been rather thoroughly studied, it is possible to calculate the free energy change which would have accompanied the reaction if solid sodium had been used.

The method is capable of quite general application but has certain disadvantages. In the first place the range of concentration of sodium amalgams which are liquid at room temperature is small. The increase in temperature necessary to extend the range of concentration appreciably would be so great as to decompose many organic compounds. The consequence of this rather narrow range of liquid amalgam is that only compounds which have a correspondingly narrow range of stability can be studied by this method. A second difficulty was encountered when studying reactions characterized by a large activation energy. Sometimes many months were required for the establishment of substantially equilibrium concentrations. The potentiometric method to be described seems likely to be free from these objections.

Both difficulties are inherently absent in a potentiometric method since a reaction does not need to proceed to the equilibrium point. The potential is a measure of the distance the system is from equilibrium and hence one might expect to be able to study with the aid of liquid amalgams reactions which would require solid amalgams by the analytical method. Furthermore, a reaction which proceeds very slowly might be expected to supply sufficient energy for a delicate electrical measurement while requiring years for substantial completion. Preliminary calculations indicated this to be the case.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 91st meeting of the American Chemical Society, Kansas City, Mo., April 13–17, 1936.

[2] Bent, This Journal, **52**, 1498 (1930).

The very delicacy of a potentiometric method, however, introduces new difficulties. The amounts of materials necessary to give a detectable e. m. f. are so small that traces of impurities are capable of producing side reactions which may be confused with the reaction being studied. Furthermore, the course of the reaction cannot be determined by an analysis of the products of the reaction. These difficulties may be overcome to a great extent by varying the concentrations of the substances involved in the reaction and noting the corresponding variation in the e. m. f. of the cell. As a further check on the reliability of the potentiometric method we have studied certain reactions by both methods. The compounds which have been studied in the greatest detail by the analytical method are organic free radicals. We have chosen three free radicals to study by the potentiometric method.

A cell is constructed in which the over-all reaction is the addition of sodium to an ethane to give two molecules of the sodium derivative of a free radical. These cells are constructed with one electrode of liquid sodium amalgam and the other of bright platinum. The electrolyte is an ether solution of the product of the reaction, that is, the sodium addition compound, NaR, R representing a free radical. The ethane is enclosed in a small glass capsule directly over the bright platinum electrode. When the cell has been brought to constant temperature in a thermostat and is ready for measurement the capsule is broken, thus saturating the electrolyte in the neighborhood of the platinum electrode with the ethane. A sintered Pyrex disk prevents the amalgam and solution in contact with the amalgam from coming in contact with the platinum. After some time the ethane diffuses through the ether to the amalgam but this is a process which is sufficiently slow to give no trouble. The over-all cell reaction may be considered as involving two primary reactions. At the amalgam electrode the reaction is $Na \longrightarrow Na^+ + \ominus$ while at the platinum electrode the reaction is $R_2 + 2\ominus \longrightarrow 2R^-$. These reactions are followed by the combination of the ions to form ion pairs.

An unexpected difficulty arose from certain fluctuating potentials which were observed before the capsule containing the free radical was broken. These potentials and the methods of eliminating them are discussed in the experimental section of the paper.

Materials

Details of the preparation of materials have been given in previous papers. The appropriate carbinol is first converted by hydrochloric acid into the chloride and this then converted either into the free radical or the sodium derivative of the free radical. All preparations were carried out in closed glass systems in the final stages. A slight improvement in technique has been developed. The sodium derivatives are prepared by shaking chloride with dilute sodium amalgam and then decanting the solution into a second tube and from there into small capsules, which are finally sealed off. In order to calculate the concentration of the resulting solution from the original amount of chloride introduced and the volume of ether it is necessary to avoid distillation during the final step of sealing off the capsules. In order to prevent decomposition of ether in contact with the hot glass it is also necessary to cool the capsules in liquid air or dry ice. This cooling may be accomplished quite readily without distillation by closing each tube leading to the capsule with a steel ball bearing which fits a seat previously ground in the glass by the same size ball bearing. These ball bearings may conveniently be moved around in the apparatus by means of a horseshoe magnet.

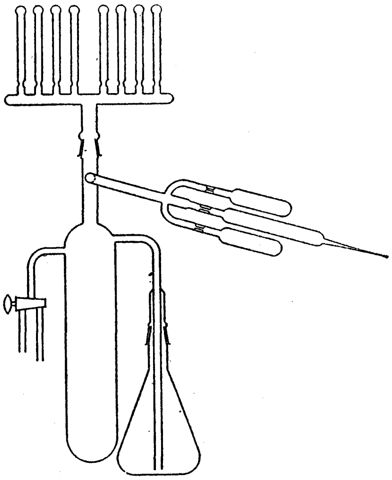

Fig. 1.

The apparatus shown in Fig. 1 was used in the preparation of the free radical. The operation of the apparatus is almost self-evident. The bulb containing the ring seal is used for the initial preparation of the free radical from the chloride and lead amalgam. By controlling the pressure, using nitrogen where necessary, the solution may be decanted over into the second tube without tipping or disturbing the precipitate of metallic chloride. This first tube may then be cleaned and refilled with suitable solvents for recrystallizing and washing, always flushing the tube with nitrogen. The capsules above the second tube are for three purposes. In two capsules solution saturated with free radical is removed for the purpose of determining the solubility and in another a sample is removed for determining the purity by oxygen absorption. After these samples have been removed the solvent is removed and the dry material loosened if necessary from the sides of the container by removing the ground joint and scraping with a steel wire, again using a counter stream of nitrogen. Finally the top of the apparatus is again attached and the solid free radical distributed between the small round-bottomed capsules. The ends of these capsules are sufficiently thin to allow crushing with a magnetic hammer in the final cell.

The apparatus for determining the purity of the free radical by oxygen absorption has been previously described.[3]

Experimental Procedure

The design of the cell was changed frequently in the course of the research. The last type to be used is illustrated in Fig. 2. A sintered glass disk[4] prevents rapid diffusion of the free radical from the platinum electrode to the amalgam where it would react. The disk also permits construction of a cell with relatively small resistance as the amalgam can flow against the disk without danger of passing through. It is important to have a notch filed in the top of the disk two or three millimeters in diameter in order to have a vapor connection between the two sides of the cell. If this is not done slight changes in temperature will cause surging of the liquid and consequent stirring.

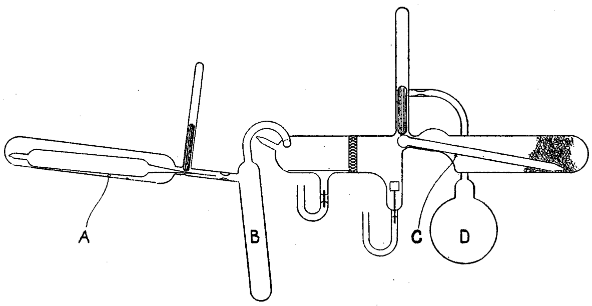

Fig. 2.

The sodium addition compound dissolved in ether, and free radical, are contained in capsules so arranged as to be broken by magnetic hammers. The cell is first baked and sparked as much as is possible without warming the organic materials. The amalgam is then introduced and then the electrolyte. The cell is placed in a thermostat and kept dark in order to avoid any possible effect of light on the free radical. Next tests are made for any potential which may be present before the capsule of the free radical is broken, and finally the free radical is introduced. A Wolf potentiometer reading directly to 10^{-5} v. was used with a L and N type HS galvanometer sensitive to 10^{-11} amp. The resistance of the cells was of the order of 10^6 ohms although in some of the earlier cells it was as high as 10^{12} ohms, thus making measurement difficult.

An unexpected difficulty was encountered in determining the potentials of the cells. The cells were found to possess a potential of the order of magnitude of 0.1 v. before the free radical had been introduced. This potential could not be eliminated and was difficult to explain. A great many experiments were performed to discover the cause of the potential but no theory was formulated which could account for all of the experiments. Assuming that the solution was not at equilibrium with the amalgam, cells were constructed which would allow further shaking of the solution and amalgam in the cell. This procedure altered the magnitude of the potential but did not eliminate it. A cell was constructed with gold, platinum and amalgam electrodes all in the same cell. No potential was obtained between two amalgam electrodes, and none between two platinum or between a gold and a platinum electrode. However, a very persistent potential was present between the gold or platinum and the amalgam electrode. This experiment seems to eliminate surface effects in the platinum as the sole cause of the potential as it would be improbable that the gold would behave in exactly the same manner. It seems very likely that the potential is due at least in part to the electrolyte as in some cells which had stood so long as to give very low potentials an addition of more electrolyte would give a larger voltage. This is rather hard to understand in the light of the fact that the reaction of amalgam with triphenylchloromethane is so rapid as to appear to be complete in ten or fifteen minutes. The cells had often been shaken for several days. The potential would persist for weeks in spite of all attempts to destroy it by short-circuiting the cell or even applying an external potential to the cell. After several weeks the value was usually reduced to a few millivolts. Under the circumstances the difficulty could be handled in two ways. In the first place it would be possible to wait until this initial e. m. f. had disappeared or become too small to be of importance. This would have involved a great delay in making measurements and introduced an additional uncertainty due to possible decomposition of the free radical. Furthermore it would seem entirely possible that the addition of the free radical might be a disturbing factor which would again give rise to the mysterious e. m. f. A better method seemed to be to assume that the mechanism giving rise to the initial e. m. f. involves such small amounts of material as to have but a very small capacity factor and that the addition of the large amount of free radical would mask completely any potential due to a side reaction. To test this assumption cells were constructed and measurements taken without delay when the initial e. m. f. was near its highest value. These cells seem to justify the assumption that the e. m. f. may be neglected.

Discussion of Results

The e. m. f. of a cell in which the over-all cell reaction is the addition of sodium to an ethane ($2Na + R_2 \longrightarrow 2NaR$) may be most conveniently considered in terms of the addition of sodium to the free radical ($Na + R \longrightarrow NaR$). The e. m. f. of the cell is then given by the equation

$$E = E_0 - \frac{RT}{nF} \ln \frac{(NaR)}{(Na)(R)} \qquad (1)$$

in which E_0 equals (RT/nF) ln K and "K" is the equilibrium constant for the reaction. The reason for treating the cell reaction in this fashion is that in earlier papers we have determined the free energy change accompanying the addition of sodium to various free radicals and from these

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(3) Bent, Gresham and Keevil, This Journal, **58**, 1307 (1936).

(4) Bruce and Bent, *ibid.*, **53**, 990 (1931).

TABLE I

EXPERIMENTAL CONCENTRATIONS AND VALUES OF E_0

Calculated from the equation $E = E_0 - \frac{RT}{nF} \ln \frac{(\text{NaR})}{(\text{Na})(\text{R})}$

Free radical	N of NaR in ether × 10^3	N of R in satd. soln. in ether × 10^3	N of Na in Hg × 10^2	E_0, calcd. from E	E_0 calcd. from previous analyt. data	Spurious e. m. f. Max.	Spurious e. m. f. Last values before run
Triphenylmethyl	1.11	0.519	0.903	0.999	1.01		
	1.11	.519	.903	.989			
	4.90	.519	.903	1.018		0.09	0.0078
	3.14	.519	.903	1.016		.065	.0070
	6.906	.519	5.04	1.015		.093	.0071
	5.71	.519	5.04	1.008		.064	.0011
	3.01	.519	5.04	1.011		.143	.01
	3.01	.519	5.04	1.001		.104	.079
Diphenyl-α-naphthyl	3.51	3.62	5.04	1.10	1.04	.070	− .014
	2.96	3.62	4.91	1.02		.085	− .012
Phenylbiphenyl-α-naphthyl	2.48	1.41	5.04	1.211	1.08	.195	.122
	1.04	1.41	5.04	1.038		.194	.145
		N of R_2 in satd. soln. in ether × 10^3		E, exptl.			
Dibiphenylene diphenylethane	2.58	0.106	5.13	0.599		0.565	0.515
	2.57	.106	5.04	.602		.639	.524

data can calculate the value of E_0. The values of E_0 so calculated have been found to be remarkably constant. We may summarize the results by saying that in twenty cases in which a group attached to the central carbon has been changed the average of the effects on the free energy change for the reaction is about one kilogram calorie and the maximum effect is three. These substitutions involve groups which are aliphatic, aromatic, polynuclear and heterocyclic. The small differences observed in passing from one free radical to another may be predicted roughly from the series to which the compound belongs and the number of benzene rings in the compound. The average value for E_0 is 1.08 v.

We have determined the value of E_0 of equation (1) for triphenylmethyl, diphenyl-α-naphthylmethyl and phenyl-diphenyl-α-naphthylmethyl by the potentiometric method. The purpose of these experiments was to test the method and in particular to discover whether or not we are justified in ignoring the initial potential which was observed before the introduction of the free radical. The results of these experiments are reported in Table I.

The concentration of NaR is determined at both the beginning and the end of the experiment. The activity of the sodium referred to pure metal as the standard state is calculated from the concentration of the amalgam with the aid of the equation of Bent and Hildebrand.[5] The first two runs reported on hexaphenylethane are not considered as good as the latter runs due to the unusually high resistance of the cell. Some of the cells could be measured to hundredths of a millivolt but it is doubtful if the results are significant to more than a few millivolts. The average of the last four cells on hexaphenylethane is in very good agreement with the average of the analytical measurements previously reported and recorded in the third from the last column of the table.

The results for the next two compounds are much less satisfactory. These compounds have not been studied as thoroughly by either the analytical or potentiometric method so that agreement as good as in the case of hexaphenylethane is hardly to be expected. We have no explanation, however, for such a large discrepancy as is shown by the next to the last value recorded in the table.

Table I leads to the conclusion that the potentiometric method measures the free energy of addition of sodium to the compound being studied. The evidence is particularly good in the case of hexaphenylethane. The variation in concentration of sodium in the amalgam and also of the product of the reaction in solution result in the expected effect on the potential of the cell. The results of the potentiometric method agree with

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(5) Bent and Hildebrand, THIS JOURNAL, **49**, 3011 (1927).

the analytical results at least as well as the results by the first method agree with each other.

We hoped to study by the method just described compounds which react too slowly to be measured by a direct analytical method. In particular we wished to study ethanes which dissociate into free radicals to such a slight extent that the reaction cannot be detected by ordinary means. If one knows E_0 in equation (1), the activity of the sodium in the amalgam used as an electrode and the concentration of the product of the reaction, then one has a method of calculating the concentration of free radical from the observed e. m. f. This concentration would then allow one to calculate the equilibrium constant for the dissociation of the ethane into the free radical and hence the strength of the C–C bond, providing certain assumptions are made regarding ΔS for the reaction.

The compound chosen was dibiphenylene-diphenylethane. This compound was prepared and studied in exactly the same kind of cell discussed above. The extent to which the ethane is dissociated is not definitely known but it has been estimated that ΔF for the process is greater than 7 kcal. This would mean that the observed e. m. f. should be small on account of the small concentration of free radical present. To our surprise we obtained a much larger value. This can only mean that our original assumption that E_0 is the same for all free radicals breaks down in the case of the first compound to which we attempt to apply it. If we reverse our procedure and attempt to calculate E_0 by assuming ΔF for the dissociation of the free radical to be at least 7 kcal. we obtain a value of at least 1.5 v. This result makes it seem very unlikely that the extension of the potentiometric method to the calculating of the strength of C–C bonds in this manner can be justified. It also indicates that one must be very cautious in drawing conclusions from experiments using sodium amalgam or sodium potassium alloy to cleave organic compounds. Since the stability of the sodium compound can vary by as much as 0.4 v. (9 kcal.) the reaction cannot be considered solely in the light of the breaking of a C–C bond.

It is interesting to discover that the large difference between the value of E_0 for triphenylmethyl and dibiphenylene-diphenylethane is quite in harmony with the relative strength of the corresponding hydrogen compounds as acids.[6] The following equations indicate the close connection between these two reactions.

$$\begin{aligned}
\mathrm{NaR} + \mathrm{HR'} &= \mathrm{NaR'} + \mathrm{HR} && (1)\\
\mathrm{Na^+} + \mathrm{R^-} &= \mathrm{NaR} && (2)\\
\mathrm{NaR'} &= \mathrm{Na^+} + \mathrm{R'^-} && (3)\\
\mathrm{H} + \mathrm{R'^*} &= \mathrm{HR'} && (4)\\
\mathrm{HR} &= \mathrm{H} + \mathrm{R^*} && (5)\\
\hline
\mathrm{R^-} + \mathrm{R'^*} &= \mathrm{R'^-} + \mathrm{R^*} && (6)\\
2\mathrm{Na} + \mathrm{R_2} &= 2\mathrm{NaR} && (7)
\end{aligned}$$

In these equations R and R′ are taken to represent triphenylmethyl and biphenylenephenylmethyl. Reaction (1) represents the action of a weak acid on the salt of a still weaker acid. The fact that the reaction takes place indicates that HR′ is a stronger acid than HR. In order to discover the fundamental property of the molecule which determines its acid strength we have written equations (2) to (5). According to Kraus and Fuoss the dissociation constant of a salt in a given solvent of low dielectric constant is determined primarily by the size of the ion. Since the two anions under consideration each contain just three benzene rings it seems very probable that the value of ΔF for reactions (2) and (3) will cancel as they are written. We next make the very plausible assumption that the strength of the hydrogen–carbon bond is the same in these two molecules. This is implied when we write reactions (4) and (5) and assume that ΔF for these two reactions will cancel. The asterisk on the free radical implies that only the hydrogen bond has been broken and that the free radical so formed is not stabilized by resonance energy. The free radical under discussion is therefore purely hypothetical and is introduced for convenience in discussing the significance of the resonance energy. The sum of reactions (1) to (5) is given in equation (6). This equation shows that two factors are involved in determining the strength of an acid. The first of these is the destruction of the charge on one ion and the creation of a charge on the other, that is, the transfer of an electron. The second is the destruction of the resonance energy present in one ion and the creation of resonance energy in the other anion. These two factors are also involved in the addition of sodium to an ethane as illustrated by equation (7). If we consider NaR to be an ion pair[7] then the addition of sodium to an ethane involves the creation of a negative ion with its accompanying resonance energy. We therefore come to the conclusion that the ease with which

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(6) Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

(7) Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

sodium will add to an ethane is determined not only by the strength of the carbon–carbon bond but also by those factors which determine the strength of the corresponding methane as an acid. According to McEwen[8] the difference in acid strength for these two methanes is about 16 kcal. The difference in the free energy of addition of sodium to the free radicals is found to be greater than 12 kcal. These results give a consistent explanation of the behavior of phenylfluorene as an acid and the stability of the sodium salt.

The results of the measurements on dibiphenylene-diphenylethane may be expressed in terms of the reaction $2Na + R_2 \longrightarrow 2NaR$ without any assumptions regarding the dissociation of the ethane into a free radical. ΔF so calculated is -61.9 kcal.

Summary

1. A potentiometric method is described for determining the free energy of addition of sodium to an organic compound.

2. An e. m. f. is reported which is not accounted for by accepted ideas of the nature of the compounds studied.

3. Dibiphenylene-diphenylethane is reported to have an abnormally large electron affinity which is directly related to the strength of phenylfluorene as an acid.

CAMBRIDGE, MASS.

RECEIVED APRIL 29, 1936

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[8] McEwen, THIS JOURNAL, 58, 1124 (1936).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Mesityl Phenyl Diketone

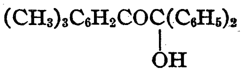
BY H. H. WEINSTOCK, JR., AND REYNOLD C. FUSON

Mesityl phenyl diketone (I) was selected for study because it appeared to afford an opportunity of determining the behavior of one of the carbonyl groups of an alpha diketone without interference from the other. It was supposed that the carbonyl group adjacent to the mesityl radical would be unaffected by most reagents, and that the diketone would, in fact, behave as a monoketone, in which, however, the carbonyl group would be unusually reactive. In general, this expectation has been supported by the experimental evidence; however, in certain reactions, both carbonyl groups seem to be directly involved.

The diketone behaves as a monoketone toward phenylmagnesium bromide, which converts it into the carbinol (II). Likewise the diketone gave a monoxime, a monosemicarbazone and a mono-2,4-dinitrophenylhydrazone. Also, it could not be induced to react with *o*-phenylenediamine. On the other hand, toward hydrogen peroxide the diketone behaves normally. Reduction with zinc and acetic acid gave a mixture of the two isomeric benzoins (III and IV).[1]

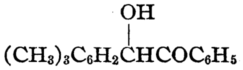
$(CH_3)_3C_6H_2COCOC_6H_5$

I



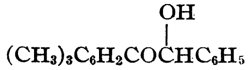
$(CH_3)_3C_6H_2CO\underset{\underset{\textstyle OH}{|}}{C}(C_6H_5)_2$

II



$(CH_3)_3C_6H_2\overset{\overset{\textstyle OH}{|}}{C}HCOC_6H_5$

III



$(CH_3)_3C_6H_2CO\overset{\overset{\textstyle OH}{|}}{C}HC_6H_5$

IV

Vigorous reduction of the diketone yields the desoxybenzoin, V.

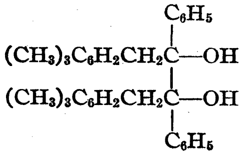
$(CH_3)_3C_6H_2CH_2COC_6H_5$

V

$(CH_3)_3C_6H_2COCH_2C_6H_5$

VI

This compound formed a phenylhydrazone and a dinitrophenylhydrazone, and with isopropylmagnesium bromide or ethylmagnesium bromide it was reduced to the pinacol (VII).



$$\begin{array}{r}C_6H_5\\ |\\ (CH_3)_3C_6H_2CH_2C{-}OH\\ |\\ (CH_3)_3C_6H_2CH_2C{-}OH\\ |\\ C_6H_5\end{array}$$

VII

The structure of V was proved by synthesizing it from mesitylacetyl chloride and benzene. The isomeric desoxy compound (VI) is known. Both of these desoxybenzoins yield the benzil (I) when oxidized with selenium dioxide. Here it would appear that reduction had taken place preferentially at the hindered carbonyl group. However, the explanation is evidently not so simple as this, because when either of the benzoins (III and IV) is reduced the product is invariably V, no trace of VI being produced. This is especially

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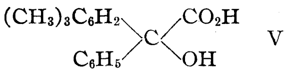
[1] Fuson, Weinstock and Ullyot, THIS JOURNAL, 57, 1803 (1935).

notable in the case of IV; here the yield of V is 78% of the theoretical amount.

The action of alkali brought about the benzilic acid rearrangement, yielding mesitylphenylglycolic acid (VIII).



$$\begin{array}{r}\mathrm{(CH_3)_3C_6H_2}\\ \mathrm{C_6H_5}\end{array}\!>\!\mathrm{C}\!<\!\begin{array}{l}\mathrm{CO_2H}\\ \mathrm{OH}\end{array}$$

VIII

The structure of this acid was proved by reducing it to mesitylphenylacetic acid.

Experimental

Mesityl Phenyl Diketone (I).—This compound was first obtained by the action of phenylmagnesium bromide on mesitylglyoxal,[2] but is more conveniently made by oxidation of benzyl mesityl ketone. The following procedure gave the diketone in yields of 83%.[3] A mixture of 80 g. of benzyl mesityl ketone,[4] 42 g. of selenium dioxide, 1200 cc. of dioxane, and 5 cc. of water was heated under reflux, with stirring, for three hours. The solution was decanted from the precipitated selenium and concentrated to a volume of 200 cc. When this solution was allowed to cool, the diketone separated in the form of yellow crystals, melting at 136–137°. A mixture with a specimen prepared by the method of Gray and Fuson showed no lowering of the melting point.

The monoxime of mesityl phenyl diketone was colorless, and melted at 155°.

Anal. Calcd. for $C_{17}H_{17}NO_2$: N, 5.24. Found: N, 5.43.

The monoxime was recovered unchanged when heated for forty-eight hours with an excess of hydroxylamine.

The mono 2,4-dinitrophenylhydrazone of mesityl phenyl diketone was orange in color, and melted at 232–232.5°.

Anal. Calcd. for $C_{23}H_{20}N_4O_5$: N, 12.96. Found: N, 12.72.

This compound was also obtained when 0.5 g. of IV was boiled for two minutes with 0.4 g. of 2,4-dinitrophenylhydrazine and 2 cc. of concentrated hydrochloric acid in a solution of 50 cc. of ethyl alcohol. The melting point was 230–231°. A mixed melting point with a sample of the mono-2,4-dinitrophenylhydrazone of mesityl phenyl diketone showed no depression.

Attempted Reaction with *o*-Phenylenediamine.—The starting material was quantitatively recovered in a high state of purity after treatment of I with the calculated amount of *o*-phenylenediamine in boiling solutions of absolute alcohol or glacial acetic acid.

Reaction with Hydrogen Peroxide.—Two grams of I, 25 cc. of 30% hydrogen peroxide, and 50 cc. of dioxane were boiled under reflux for two hours. There was obtained 1.85 g. of alkali-soluble material. Treatment with boiling water gave 0.95 g. of an insoluble substance; m. p. 152°. A mixed melting point with an authentic sample of 2,4,6-trimethylbenzoic acid was 152°. On cooling of the water solution, there was obtained a white product which melted at 121° after several recrystallizations from water. A mixed melting point determination proved the substance to be benzoic acid.[5]

Reaction with Phenylmagnesium Bromide.—To a solution of phenylmagnesium bromide prepared from 0.5 g. of magnesium, 4 g. of bromobenzene and 100 cc. of dry ether was added 1 g. of mesityl phenyl diketone. The mixture was stirred for three hours, and then decomposed with dilute hydrochloric acid. The *carbinol* (II) crystallized from alcohol in the form of colorless needles melting at 169.5–170°.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.63; H, 6.69. Found: C, 83.67; H, 6.85.

Reduction to the Benzoins.—A solution of 2 g. of mesityl phenyl diketone in 75 cc. of glacial acetic acid was heated to boiling and 10 g. of powdered zinc was added cautiously. The mixture was heated under reflux for five minutes, partially cooled and filtered. The filtrate was diluted with water until turbidity ensued. There resulted a precipitate of 0.65 g. of crystals melting at 94–98°. Recrystallization from alcohol gave the pure *2,4,6-trimethylbenzoin* (IV). The product alone or when mixed with an authentic specimen of the compound melted at 101–102°.

To 0.2 g. of the benzoin in 30 cc. of dry, high-boiling petroleum ether was added 1 cc. of phenyl isocyanate. The solution was heated under reflux for four hours and allowed to cool. The urethan formed colorless crystals melting at 160–161°. A mixed melting point with a sample of the *urethan of 2,4,6-trimethylbenzoin* was 160–161°.

When the filtrate from which the 2,4,6-trimethylbenzoin was obtained was further diluted, there was obtained the *2′,4′,6′-trimethylbenzoin* (III); after recrystallization from alcohol, it melted at 93.5–94°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.31; H, 7.14. Found: C, 80.15; H, 7.04.

The *urethan* melted at 141–142°.

Anal. Calcd. for $C_{24}H_{23}O_3N$: N, 3.76. Found: N, 3.89.

The *2,4-dinitrophenylhydrazone* melted at 211.5–212°.

Anal. Calcd. for $C_{23}H_{22}O_5N_4$: N, 12.90. Found: N, 12.72.

Oxidation converted 2′,4′,6′-trimethylbenzoin into mesityl phenyl diketone. The structure of this benzoin has been established by synthesizing it from mesitylene and phenylglyoxal.[6]

Phenyl 2,4,6-Trimethylbenzyl Ketone (V)

(a) From I by Reduction with Zinc and Acetic Acid.—A mixture of 7 g. of the diketone, 100 cc. of glacial acetic acid and 15 g. of zinc dust was boiled under reflux for ten hours, filtered, diluted with water and allowed to cool. The desoxybenzoin melted (from alcohol) at 163.5–164°; yield, 45%.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.56; mol. wt., 238. Found: C, 85.4; H, 7.63; mol. wt., 228.

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[2] Gray and Fuson, THIS JOURNAL, **56**, 739 (1934).

[3] Hatt, Pilgrim and Hurran [*J. Chem. Soc.*, 93 (1936)] have recently prepared the diketone by a similar method.

[4] This compound was made by the method of Klages and Lickroth [*Ber.*, **32**, 1564 (1899)] who described it as a solid melting below 30°. It has been found to melt (from alcohol) at 32–32.5°.

[5] A similar result has been reported by Hatt, Pilgrim and Hurran, ref. 3.

[6] Arnold and Fuson, THIS JOURNAL, **58**, 1295 (1936).

(b) From I by Reduction with Zinc and Alkali.—A mixture of 10 g. of I, 35 g. of zinc dust, 35 g. of potassium hydroxide (in 25 cc. of water) and 250 cc. of alcohol was boiled under reflux for four hours and allowed to stand overnight. The yield of V was 33% of the theoretical amount.

(c) From I by Reduction with Tin and Hydrochloric Acid.—A mixture of 3.0 g. of I, 5 g. of granulated tin, 20 cc. of concentrated hydrochloric acid and 100 cc. of ethyl alcohol was boiled under reflux for twelve hours. The yield of V was 76%.

(d) From the Benzoins.—The ketone (V) results when either III or IV is heated with zinc and acetic acid. A typical procedure is the following: a mixture of 1 g. of 2,4,6-trimethylbenzoin, 50 cc. of glacial acetic acid and 6 g. of zinc dust was boiled under reflux for twelve hours. A yield of 0.3 g. of V was obtained; m. p. 162–163°.

(e) From IV by Reduction with Tin and Hydrochloric Acid.—A mixture of 2.0 g. of IV, 5 g. of granulated tin, 20 cc. of concentrated hydrochloric acid and 100 cc. of ethyl alcohol was boiled under reflux for twenty hours. The yield of V was 78% of the theoretical amount. The melting point of the crude material was 161–164°.

(f) From Mesitylacetic Acid.—To 7.2 g. of mesitylacetic acid was added 25 cc. of thionyl chloride; the solution was allowed to stand for two hours, then it was heated for thirty minutes at 60°. The mixture was distilled under diminished pressure, the mesitylacetyl chloride being collected at 126–130° (10 mm.). The acid chloride was dissolved in 50 cc. of dry benzene and this solution was added dropwise to a mixture of 10 g. of aluminum chloride and 50 cc. of benzene. The mixture was allowed to stand at room temperature for five hours. There was obtained 2.5 g. of product melting at 145–152°. Recrystallization from alcohol gave the pure ketone (V), melting at 163.5–164°. Mixtures with samples prepared under (a) and (b) showed no depression of the melting point.

The *phenylhydrazone* of phenyl 2,4,6-trimethylbenzyl ketone had an orange color, and melted (from alcohol) at 104–105°.

Anal. Calcd. for $C_{23}H_{24}N_2$: N, 8.54. Found: N, 8.63.

The *2,4-dinitrophenylhydrazone* of phenyl 2,4,6-trimethylbenzyl ketone was orange in color and melted at 163°.

Anal. Calcd. for $C_{23}H_{22}O_4N_4$: N, 13.39. Found: N, 13.41.

A second compound was isolated from the mixture resulting from the action of 2,4-dinitrophenylhydrazine and the ketone. It had an orange color, melted at 190° and appeared to be a second 2,4-dinitrophenylhydrazone.

Anal. Calcd. for $C_{23}H_{22}O_4N_4$: N, 13.39. Found: N, 13.21.

The pinacol (*VII*) was produced when phenyl 2,4,6-trimethylbenzyl ketone was treated with an excess of ethylmagnesium bromide or isopropylmagnesium bromide. The pinacol is very insoluble in alcohol, but can be recrystallized from glacial acetic acid. It melts at 241–242°.

Anal. Calcd. for $C_{34}H_{38}O_2$: C, 85.35; H, 7.95; mol. wt., 478. Found: C, 85.40; H, 7.96; mol. wt. (Rast), 437.

Oxidation of 1 g. of V with 0.5 g. of selenium dioxide in 25 cc. of dioxane and 0.5 cc. of water gave 0.6 g. of the diketone (I). The reaction was carried out by heating the mixture for ten hours at 80°.

The *p*-Chlorobenzal Derivative of Benzyl Mesityl Ketone.—A mixture of 1 g. of *p*-chlorobenzaldehyde, 10 cc. of 10% sodium hydroxide solution, 0.66 g. of benzyl mesityl ketone and 50 cc. of alcohol was allowed to stand overnight. A precipitate formed. The solution was diluted with an equal volume of water, and the product removed on a filter. There resulted 0.89 g. of product melting at 135–137°. Recrystallization from alcohol raised the melting point to 141°.

Anal. Calcd. for $C_{24}H_{21}OCl$: C, 79.85; H, 5.83. Found: C, 79.96; H, 6.08.

It was found that the foregoing procedure could be used for the detection of small amounts of benzyl mesityl ketone.

Mesitylacetic acid was prepared by reduction of mesitylglycolic acid with iodine and phosphorus, as reported by Claus.[7] A mixture of 3.0 g. of red phosphorus, 1.0 g. of iodine and 100 cc. of glacial acetic acid was allowed to stand at room temperature for fifteen minutes. There was added 5 cc. of water and 8.8 g. of mesitylglycolic acid. The mixture was boiled under reflux for four hours, and filtered while hot into 100 cc. of a saturated solution of sodium bisulfite. The yield of the acid (m. p. 166°) was 90%.

Mesitylphenylglycolic acid was not obtained as the free acid. It crystallized with one molecule of alcohol of solvation.

A mixture of 5.0 g. of mesityl phenyl diketone, 10 g. of potassium hydroxide in 20 cc. of water, and 250 cc. of methyl alcohol was boiled under reflux for ten hours. The solvent was removed at 60°, water was added and the alkali-insoluble material removed by filtration. The aqueous solution was poured into a mixture of ice and concentrated hydrochloric acid. The gum which separated was recrystallized from methyl alcohol. The yield of the colorless compound, melting at 87–89°, was 62%.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.52; H, 7.28; neut. equiv., 302. Found: C, 71.55; H, 7.24; neut. equiv., 300.

The *methyl ester* was obtained in good yields when the acid was treated with methyl sulfate in alkaline solution. It separated from alcohol solutions as colorless crystals, melting at 111–111.5°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.06; H, 7.05. Found: C, 76.38; H, 7.04.

A second acid was obtained when the above acid was recrystallized several times from ethyl alcohol. It appeared to have one molecule of ethyl alcohol of solvation; it melted at 84–85°.

Anal. Calcd. for $C_{19}H_{24}O_4$: C, 72.15; H, 7.59; neut. equiv., 316. Found: C, 72.03, 72.36; H, 7.74, 7.80; neut. equiv., 313.

This compound was also isolated from the acidified mother liquor when I was treated with zinc and potassium hydroxide in ethyl alcohol solution in the preparation of V.

Mesitylphenylacetic acid was prepared from mesitylphenylglycolic acid by reduction with iodine and phosphorus by the procedure analogous to that utilized for the preparation of diphenylacetic acid.[8] The melting point

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[7] Claus, *J. prakt. Chem.*, **41**, 508 (1890).

[8] "Organic Syntheses," John Wiley and Sons, Inc., New York N. Y., Coll. Vol. I, p. 82.

of the colorless compound was 173–173.5°, which agrees with that given by Maxwell and Adams.[9]

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.31; H, 7.09; neut. equiv., 254. Found: C, 80.29; H, 7.39; neut. equiv., 256.

Mesitylphenylacetic acid was also synthesized by boiling a mixture of 1 g. of mesitylphenylglycolic acid, 30 cc. of glacial acetic acid and 6 g. of zinc under reflux for eighteen hours. There was obtained 0.5 g. of product which, on recrystallization, melted at 173°. A mixed melting point with the product obtained in the iodine and phosphorus reduction of mesitylphenylglycolic acid showed no depression.

Summary

Mesityl phenyl diketone reacts as a monoketone toward the Grignard reagent, semicarbazide, 2,4-dinitrophenylhydrazine and hydroxylamine. Toward hydrogen peroxide, as well as in the benzilic acid rearrangement, the diketone behaves normally.

Reducing agents convert the diketone to a mixture of the two isomeric benzoins. Drastic reduction *affects only the hindered carbonyl group* and gives phenyl 2,4,6-trimethylbenzyl ketone.

Urbana, Illinois Received April 13, 1936

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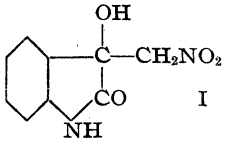
[9] Maxwell and Adams, This Journal, **52**, 2959 (1930).

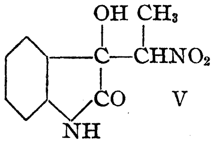
[Contribution from Nichols Laboratory of New York University]

Oxindole Amines from Isatin[1]

By William R. Conn[2] and H. G. Lindwall

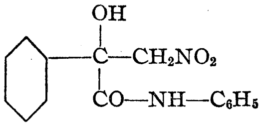
It has been reported previously[3] that nitromethane will condense with beta-naphthisatin to yield 3-hydroxy-3-(nitromethyl)-β-naphthoxindole. It has now been found that a similar reaction with nitromethane occurs in the case of isatin, and of certain substituted isatins in the presence of diethylamine, with the formation of the corresponding aldol-like condensation products. Isatin and nitromethane yield 3-hydroxy-3-(nitromethyl)-oxindole (I); substituted derivatives of I (II, III and IV) result from the condensations employing, respectively, N-ethylisatin, 5-bromo-N-ethylisatin and N-methylisatin. Nitroethane and isatin yield an analogous product (V).


I


V

At room temperature or for short periods of heating, these five nitro compounds exhibit unexpected resistance toward dehydrating agents such as acetic anhydride, acetyl chloride or hydrochloric acid. When heated with neutral solvents gradual decomposition takes place with the formation of the original isatin and the nitroalkane. The extent of this decomposition can be greatly decreased by the presence of a small amount of glacial acetic acid in the solvent. Heated alone, these nitro compounds again decompose through reversal of the aldol condensation; examination of the melts shows the presence of the isatin and the nitro-alkane. Heating in water containing even small amounts of organic or inorganic base causes speedy reversal of the condensation.

For purposes of generalization, a straight-chain alpha-keto-amide, benzoylformanilide, was condensed with nitromethane. The product, VI, has properties similar to those described above for compounds I–V.


VI

Reduction of 3-hydroxy-3-(nitromethyl)-oxindole (I) catalytically with Adams platinic oxide catalyst[4] or by treatment with concentrated hydrochloric acid and mossy tin, gave the hydrochloride of 3-hydroxy-3-(aminomethyl)-oxindole (VII). Similar treatment of II and III with tin and hydrochloric acid yielded in the same manner the hydrochlorides of the aminomethyloxindoles, respectively, IX and X.

In one of several runs of the reduction of I to form VII by the tin–hydrochloric acid method, VII was obtained contaminated with a compound which was found to be the intermediate reduction

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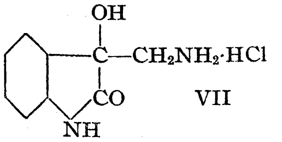
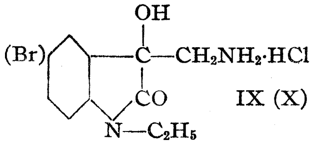
[1] From the dissertation presented by William R. Conn to the Faculty of the Graduate School of New York University in candidacy for the degree of Doctor of Philosophy.

[2] University Fellow in Chemistry.

[3] Zrike and Lindwall, This Journal, **57**, 207–8 (1935).

[4] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., 1932, p. 452.

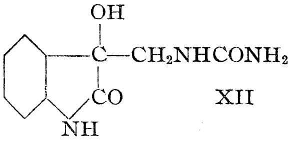

VII

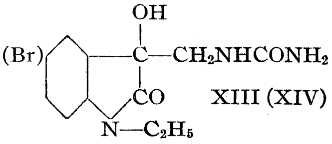

IX (X)

product (VIII) 3-hydroxy-3-(hydroxylaminomethyl)-oxindole hydrochloride. Compound VIII was not encountered in the other runs of this reaction.

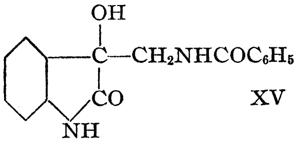
Reduction of VI (the product of condensation of nitromethane with benzoylformanilide) with tin and hydrochloric acid did not follow the normal course; the reduction product was not investigated.

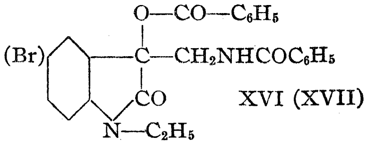
Compounds VII, IX and X were found to exhibit several of the properties common to primary amines. With potassium cyanate the corresponding substituted ureas, the uramidomethyloxindoles, XII, XIII and XIV, respectively, are formed.


XII

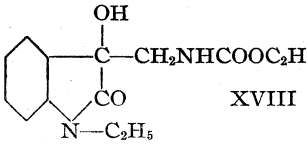

XIII (XIV)

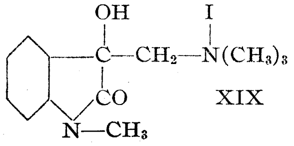
Treatment of VII with benzoyl chloride brings about benzoylation of the amino group and yields 3 - hydroxy - 3 - (benzoylaminomethyl) - oxindole (XV). For compounds IX and X the hydroxy group, as well as the primary amino group, is benzoylated, yielding XVI and XVII, respectively.


XV


XVI (XVII)

Furthermore, treatment of IX with ethyl chloroformate causes the formation of the urethan (XVIII). Methylation of VII with methyl iodide gives the quaternary ammonium salt (XIX).


XVIII


XIX

It is planned to continue this work on the synthesis of oxindole-amine derivatives. Certain of these products will be studied physiologically.

Experimental Part

3-Hydroxy-3-(nitromethyl)-oxindole (I).—Isatin (44.1 g.) was suspended in a solution of nitromethane (36.6 g.) and 40 cc. of absolute ethyl alcohol. After cooling in ice, 3 cc. of diethylamine was added. In one day at ice-box temperature 71% of crude product separated. Crystallization from glacial acetic acid yielded hexagonal colorless crystals, m. p. 135–140°, dec., soluble in alcohol, acetone, benzene. Compounds II, III and IV were prepared by the same general method, and have solubilities similar to those of I.

Anal. Calcd. for $C_9H_8O_4N_2$: C, 51.90; H, 3.88; N, 13.46. Found: C, 52.24; H, 3.82; N, 13.24.

3 - Hydroxy - 3 - (nitromethyl) - 1 - ethyloxindole (II) from N-ethylisatin and nitromethane; yield, crude, 60% after two days; colorless prisms from carbon tetrachloride; m. p. 84–85°, dec.

Anal. Calcd. for $C_{11}H_{12}O_4N_2$: N, 11.86. Found: N, 11.91.

3 - Hydroxy - 3 - (nitromethyl) - 5 - bromo - 1 - ethyloxindole (III) from 5-bromo-N-ethylisatin and nitromethane; yield, crude, 93% after overnight; small colorless plates from ethyl alcohol containing a trace of glacial acetic acid; m. p. 123–125°, dec.

Anal. Calcd. for $C_{11}H_{11}O_4N_2Br$: N, 8.89. Found: N, 8.65.

3 - Hydroxy - 3 - (nitromethyl) - 1 - methyloxindole (IV) from N-methylisatin and nitromethane; yield, crude, 70% after two days; large needles from hot benzene containing a trace of glacial acetic acid; m. p. 98–99°, dec.

Anal. Calcd. for $C_{10}H_{10}O_4N_2$: C, 54.03; H, 4.54; N, 12.61. Found: C, 54.42; H, 4.70; N, 12.55, 12.42.

3-Hydroxy-3-(α-nitroethyl)oxindole (V) from isatin and nitroethane; yield, crude, 80% after two days; hexagonal crystals from glacial acetic acid; m. p. 145–150° with reddening at 140°.

Anal. Calcd. for $C_{10}H_{10}O_4N_2$: N, 12.61. Found: N, 12.20, 12.40.

Properties of I, II, III, IV, V. (A) Dehydrating Agents.—Compound I, boiled in acetic anhydride for one minute, was unchanged; prolonged refluxing caused decomposition with evolution of red fumes. Short boiling of I with acetyl chloride, or long standing at room temperature with that reagent, had no effect. Four hours in acetic anhydride at 100° caused no change in IV. Three minutes of boiling in concentrated hydrochloric acid had no effect upon II and IV. Compound IV was unchanged after standing for one week at room temperature in absolute alcohol saturated with dry hydrogen chloride.

(B) **Alkali.**—All five of these nitro compounds were decomposed, through reversal of the condensation reaction, to form the original reactants when heated in water or organic solvents containing traces of organic or inorganic bases. Isatin, or the respective isatin derivative, was identified in each case. Compound IV, dissolved in potassium hydroxide solution, imparted a yellow color to the solution; acidification with hydrochloric, acetic or carbonic acids yielded a red gum which became colorless and crystalline upon standing for a few minutes; the product was the original IV.

(C) **Heat.**—All five nitro compounds decomposed into the original reactants when melted; this was shown by examination of the melts. Slow decomposition, quantitative in a few hours, takes place when these compounds are heated in neutral organic solvents or in water; this decomposition is effectively avoided when a small amount of acetic acid is present in the solvent.

2 - Phenyl - 2 - hydroxy - 3 - nitropropaneanilide (VI).—Diethylamine (10 drops) was added to the cooled mixture of benzoylformanilide (13.5 g.), nitromethane (4.1 g.), and 10 cc. of absolute alcohol. Crystals began to form after five minutes; after overnight a 96% yield of crude product resulted; colorless needles after crystallization from glacial acetic acid; m. p. 143–144°, dec.; soluble in alcohol, acetone. Boiling in concentrated hydrochloric acid, or in acetic anhydride, for two hours produced no change; two minutes of boiling in water containing a small amount of diethylamine caused decomposition as shown by the identification of benzoylformanilide.

Anal. Calcd. for $C_{15}H_{14}O_4N_2$: N, 9.79. Found: N, 9.67.

3 - Hydroxy - 3 - (aminomethyl) - oxindole Hydrochloride (VII). (A) Catalytic Reduction of I.—Compound I (20.8 g.) was dissolved in 240 cc. of absolute alcohol containing 11 cc. of glacial acetic acid. To the clear solution was added 0.2 g. of Adams platinic oxide catalyst[4] and the mixture was subjected to the action of hydrogen under 3 atm. pressure at room temperature with mechanical agitation. In two hours the pressure dropped the calculated amount for absorption of three moles of hydrogen; the time varied somewhat with different runs. The catalyst was removed, 12 cc. of concentrated hydrochloric acid was added, and the solution was evaporated to half its original volume at room temperature under diminished pressure. Crystals separated as needles, the yield being augmented to 62% upon further concentration. Acetic acid was necessary in the reduction; without it a non-crystalline substance, not identified, separated before the calculated amount of hydrogen had been used. Compound VII is soluble in alcohol, glacial acetic acid; crystallized from the latter, it is obtained as colorless leaflets, m. p. 195–197°, dec.

Anal. Calcd. for $C_9H_{11}O_2N_2Cl$: N, 13.05; Cl, 16.52; active hydrogen atoms, 5. Found: N, 12.92, 12.86; Cl, 16.41, 16.34; active hydrogen atoms,[5] 5.

Picrate of VII.—Soluble in alcohol, acetic acid, acetone, benzene; long needles from 50% alcohol, which become powdered upon desiccation; m. p. 165–166°, dec.

Anal. Calcd. for $C_{15}H_{13}O_9N_5$: N, 17.20. Found: N, 16.40.

(B) Reduction of I by Tin and Hydrochloric Acid. (VII).—A sample of I was warmed at 45° with twice the theoretical amount of mossy tin and concentrated hydrochloric acid until most of the tin had been used. The mixture was then diluted and tin removed as the sulfide. Concentration of the solution at room temperature yielded VII. (In one run of several, VIII, described below, was obtained.) The yield of VII after repeated crystallizations from glacial acetic acid was 10%.

3 - Hydroxy - 3 - (hydroxylaminomethyl) - oxindole (VIII) was obtained in one run of Method B (VII, above); insoluble in the more common organic solvents; crystallized from dilute hydrochloric acid as colorless needles, m. p. 194°.

Anal. Calcd. for $C_9H_{11}O_3N_2Cl$: Cl, 15.39. Found: Cl, 15.40.

Picrate of VIII.—Fine needles from acetic acid; m. p. 174°.

3 - Hydroxy - 3 - (aminomethyl) - 1 - ethyloxindole Hydrochloride (IX) from II.—Compound II (23.6 g.) was suspended in 87 cc. of concentrated hydrochloric acid and heated on a steam-bath while 47.6 g. of mossy tin was added gradually. The mixture was then held at its boiling point for three hours with the gradual addition of more tin (23.8 g.) and more hydrochloric acid (45 cc.). The tin was finally removed as the sulfide, and the solution was evaporated to dryness at room temperature; leaflets from isoamyl alcohol; m. p. 180–182°, dec.; yield, 50%; soluble in alcohol, glacial acetic acid.

Anal. Calcd. for $C_{11}H_{15}O_2N_2Cl$: C, 54.41; H, 6.23; N, 11.54; Cl, 14.63; active hydrogen atoms, 4. Found: C, 54.17; H, 6.55; N, 11.54; Cl, 14.46, 14.57; active hydrogen atoms, 4.

Picrate of IX. Yellow flakes from ethyl alcohol; m. p. 168–169°.

Anal. Calcd. for $C_{17}H_{17}O_9N_5$: N, 16.10. Found: N, 16.42.

3 - Hydroxy - 3 - (aminomethyl) - 5 - bromo - 1 - ethyloxindole Hydrochloride (X) from III.—This was prepared by the same method as that used above for the preparation of IX; small needles from isoamyl alcohol; m. p. 192–194°, dec.; yield 27%.

Anal. Calcd. for $C_{11}H_{14}O_2N_2ClBr$: Cl, 11.03. Found: Cl, 11.02, 11.16.

Picrate of X.—Small yellow leaflets from ethyl alcohol; m. p. 182–183°.

Anal. Calcd. for $C_{17}H_{16}O_9N_5Br$: N, 13.62. Found: N, 13.39.

Compound XI by the Reduction of VI.—Reduction of VI, by means of tin and concentrated hydrochloric acid, yielded XI which crystallizes as colorless prisms from glacial acetic

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[5] Zerewitinoff, *Ber.*, **40**, 2028 (1907); **41**, 2239 (1908).

acid; yield 8 g. from 14 g. of VI; m. p. 208–210°. Analyses for C, H, N did not agree with the formula for the simple primary amine; the compound has not been investigated further.

3 - Hydroxy - 3 - (uramidomethyl) - oxindole (XII) from VII; 3-Hydroxy-3-(uramidomethyl) - 1 - ethyloxindole (XIII) from IX; 3-Hydroxy-3-(uramidomethyl)-5-bromo-1-ethyloxindole (XIV) from X.—Compounds XII, XIII and XIV were prepared by treatment of the respective amine hydrochlorides in water solution with potassium cyanate. In each case the product was recrystallized from hot water; yields, 90% approx.

Compound XII.—M. p. 208–209°, dec.

Anal. Calcd. for $C_{10}H_{11}O_3N_3$: N, 19.00. Found: N, 18.65.

Compound XIII.—M. p. 216–217°, dec.

Anal. Calcd. for $C_{12}H_{15}O_3N_3$: C, 57.81; H, 6.07; N, 16.86. Found: C, 57.81; H, 6.35, 6.13; N, 16.21.

Compound XIV.—M. p. 218–220°, dec.

Anal. Calcd. for $C_{12}H_{14}O_3N_3Br$: N, 12.82. Found: N, 12.84.

3-Hydroxy-3-(benzoylaminomethyl)-oxindole (XV) from VII.—One gram of VII was dissolved in 10 cc. of water containing 3 g. of sodium carbonate; benzoyl chloride (slightly more than two moles) was added with shaking. The product separated over a period of several hours. It was washed with sodium carbonate solution; flat colorless rods from acetone; m. p. 177°; soluble in alcohol, acetic acid; yield 75%.

Anal. Calcd. for $C_{16}H_{14}O_3N_2$: C, 68.07; H, 5.01; N, 10.08. Found: C, 68.45; H, 5.65; N, 10.07.

3 - (Benzoylhydroxy - 3 - (benzoylaminomethyl) - 1 - ethyloxindole (XVI) from IX; 3 - (Benzoylhydroxy) - 3 - (benzoylaminomethyl) - 5 - bromo - 1 - ethyloxindole (XVII) from X.—Compound IX, or X, was dissolved in 10% sodium hydroxide solution, or in sodium carbonate solution, and an excess of benzoyl chloride was added with shaking. Compounds XVI and XVII, respectively, resulted; each was recrystallized from ethyl alcohol. Yields, 90% approx.

Compound XVI.—Hexagonal crystals; m. p. 191°, with dec.

Anal. Calcd. for $C_{25}H_{22}O_4N_2$: C, 72.43; H, 5.35; N, 6.76. Found: C, 72.02; H, 5.31; N, 6.80.

Compound XVII.—Prisms; m. p. 204°.

Anal. Calcd. for $C_{25}H_{21}O_4N_2Br$: C, 60.85; H, 4.30; N, 5.68. Found: C, 60.68; H, 4.70; N, 5.71.

3 - Hydroxy - 3 - (ethylcarbamidomethyl) - 1 - ethyloxindole (XVIII) from IX.—Compound IX (1.2 g.) was dissolved in 6 cc. of water containing 2.1 g. of potassium carbonate. The solution was cooled, and an excess of ethyl chloroformate was added. A quantitative yield of product separated; colorless prisms from ethyl alcohol; m. p. 166°.

Anal. Calcd. for $C_{14}H_{18}O_4N_2$: C, 60.41; H, 6.52; N, 10.07. Found: C, 60.12; H, 6.59; N, 10.32.

(3 - Hydroxy - 1 - methyloxindolyl - 3) - methyltrimethylammonium Iodide (XIX) from VII.—Compound VII (1.1 g.) dissolved in 28 cc. of absolute alcohol was treated with 2.5 g. of barium hydroxide hydrate and 2.6 g. of methyl iodide. After standing at room temperature for two days, the mixture was heated at 40° for two days, and finally was heated on the steam-bath for three hours, with addition of 0.5 g. more of methyl iodide. After cooling, 1 cc. of concentrated hydrochloric acid was added, and the solution was dried. To isolate the product, ether was added dropwise; yield 43%; feather-like clusters from ethyl alcohol; m. p. 227°, dec.

Anal. Calcd. for $C_{13}H_{19}O_2N_2I$: C, 43.08; H, 5.29; N, 7.73. Found: C, 42.64; H, 5.41; N, 7.50.

Summary

Isatin, N-ethylisatin, 5-bromo-N-ethylisatin and N-methylisatin react with nitromethane to yield aldol-like nitro condensation products. Isatin and nitroethane react similarly, as does benzoylformanilide with nitromethane.

The products derived thus from isatin, N-ethylisatin, and 5-bromo-N-ethylisatin were reduced to the corresponding primary amine hydrochlorides. These amines yield urea derivatives and benzoylated products. Certain urethan and quaternary ammonium salt formations are described.

New York, N. Y. Received April 6, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY AND THE RESEARCH LABORATORY OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Preparation of Dibenzyl Ketone and Phenylacetone

BY CHARLES D. HURD AND CHARLES L. THOMAS

Recently there was described[1] the preparation of dibenzyl ketone by heating a mixture of acetic anhydride and phenylacetic acid. Additional experience with this synthesis has shown that the method as originally published is not given in sufficient detail to ensure infallible results. These details are supplied in the present paper. It has been found also that potassium acetate is a helpful ingredient in the reaction mixture. With it, the product seems to be more easily purified than otherwise.

In addition to dibenzyl ketone it has been found that phenylacetone is also a product of the reaction. These steps account for the changes which occur

$$C_6H_5CH_2COOH + (CH_3CO)_2O \longrightarrow C_6H_5CH_2COOCOCH_3 + CH_3COOH \quad (1)$$

$$C_6H_5CH_2COOCOCH_3 \longrightarrow C_6H_5CH_2COCH_3 + CO_2 \quad (2)$$

$$C_6H_5CH_2COOCOCH_3 \longrightarrow (C_6H_5CH_2CO)_2O + (CH_3CO)_2O \quad (3)$$

$$(C_6H_5CH_2CO)_2O \longrightarrow C_6H_5CH_2COCH_2C_6H_5 + CO_2 \quad (4)$$

Phenylacetone and dibenzyl ketone evidently are pyrolytic products of phenylacetic acetic anhydride and phenylacetic anhydride, respectively. That dibenzyl ketone is formed in greater yields than phenylacetone is evidence that reaction 3 has a greater reaction rate than reaction 2. Or, if reaction 3 is an equilibrium reaction the evidence would indicate that phenylacetic acetic anhydride disappears more rapidly through reactions 3 and 4 than through reaction 2. Indirectly this may indicate that reaction 4 is faster, under the conditions obtaining in the experiment, than reaction 2.

Experimental Part

Fifty grams of phenylacetic acid was weighed into a 250-cc. three-necked flask. Then 50 g. of redistilled acetic anhydride and 2.5 g. of fused, anhydrous potassium acetate were added. A thermometer was placed in the liquid and the mixture refluxed for two hours, during which time the thermometer in the liquid registered 149–150°. A good fractionating column was inserted in place of the reflux condenser and the mixture distilled. The distillation was carried out very slowly so that the distillate was mainly acetic acid. The following table gives a typical distillation.

Time, min.	Temp., °C. Vapor	Temp., °C. Liquid
0	119	150
45	121	154
57	122	160
70	122.5	165
74	120	171
78	118	182
80	115	193
81	114	199
83	113	204

After forty-five minutes carbon dioxide was evolved slowly. The rate increased to a maximum at about seventy-five minutes, but carbon dioxide was still being evolved slowly when the distillation was stopped. A total of 4 liters of gas was collected which was pure carbon dioxide (over 99.3% CO_2). Heating the liquid above 200–205° produced resinification with a decreased yield of ketones.

The residue was placed in a 50-cc. Claisen flask. Acetic anhydride (5 cc.) was used as a rinse. The mixture was distilled at 3 mm.: 30–75°, chiefly acetic anhydride; 75–160°, a 26-g. fraction; residue, 16 g. Redistillation (755 mm.) of the 26-g. fraction gave 8 g. (16% yield) of phenylacetone, b. p. 215–220°, and 16 g. (41% yield) of dibenzyl ketone, b. p. 317–320° (m. p. 30°). The phenylacetone was identified as the phenylhydrazone,[2] m. p. 84.5–85°.

Dibenzyl ketone may be prepared in almost the theoretical yields from phenylacetic acid by passing it over a special thoria catalyst[3] at 345°. The present method, however, possesses the advantage of simplicity and convenience which might in many instances more than make up for the lower yield.

Summary

A detailed technique is given for producing dibenzyl ketone from phenylacetic acid and acetic anhydride. Phenylacetone is formed concurrently.

EVANSTON, ILLINOIS
RIVERSIDE, ILLINOIS

RECEIVED MAY 8, 1936

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[1] Hurd, Christ and Thomas, THIS JOURNAL, **55**, 2589 (1933).

[2] Beckh [*Ber.*, **31**, 3163 (1898)] lists the m. p. as 85°.

[3] Kistler, Swann and Appel, *Ind. Eng. Chem.*, **26**, 388 (1934).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY]

The Dielectric Constant of Dioxane–Water Mixtures between 0 and 80°

BY GÖSTA ÅKERLÖF AND OLIVER A. SHORT

Dioxane is in many respects a remarkable substance. In accordance with its symmetrical structure dioxane has a very small dipole moment, which possibly even may be equal to zero. Yet dioxane is completely miscible in all proportions with such a highly polar compound as water and quite large quantities of strong electrolytes are needed to salt it out. However, this particular property, combined with a very low dielectric constant, makes dioxane–water mixtures highly suitable as solvents for the study of the behavior of electrolytes in media of continuously and rapidly varying dielectric constant. This has been pointed out and made use of already by Kraus and Fuoss,[1] who studied the conductance of certain strong electrolytes in dioxane–water mixtures. The values they used for the dielectric constants of these mixtures were obtained by G. S. Hooper and our results to be presented below are in good agreement with his, but since the measurements were carried out only at a single temperature and principally confined to mixtures containing small quantities of water, a more complete study was deemed desirable.

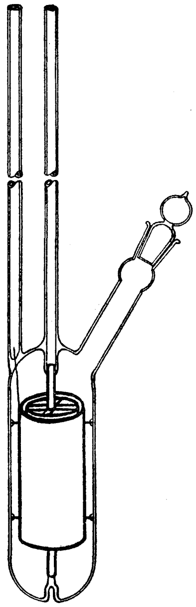

Fig. 1.—Cell.

Apparatus and Materials.—The experimental method employed was practically identical with the procedure previously given[2] and therefore a repetition is unnecessary. The wave length used was, also as before, 150 meters. Due to the relatively great length of the leads to the test cell in the present case they were twisted together and the readings of the resonance circuit were calibrated at a large number of points against a continuously variable precision condenser calibrated by the Naval Research Laboratory and kindly loaned to us by Professor Norman I. Adams of the Sloane Physics Laboratory. The design of the test cells is given by Fig. 1. The electrodes were made of platinum and firmly held in place, the outer grounded one by a number of short wires, one end of which was welded to the electrode and the other end fused into the wall of the glass vessel. The inner electrode was held by an upper and a lower cross welded to a center tube, also of platinum. Two cells were employed, one with a capacity of about 13.70 and the other of 55.0 $\mu\mu$F. For the calibration of the smaller cell water was used employing the value obtained by Wyman[3] for its dielectric constant at 20°. The large cell was calibrated by readings at several temperatures with a 70 wt. % dioxane–water mixture, the dielectric constant of which previously had been measured at the same temperatures with the small cell. The use of platinum electrodes was resorted to after a futile attempt

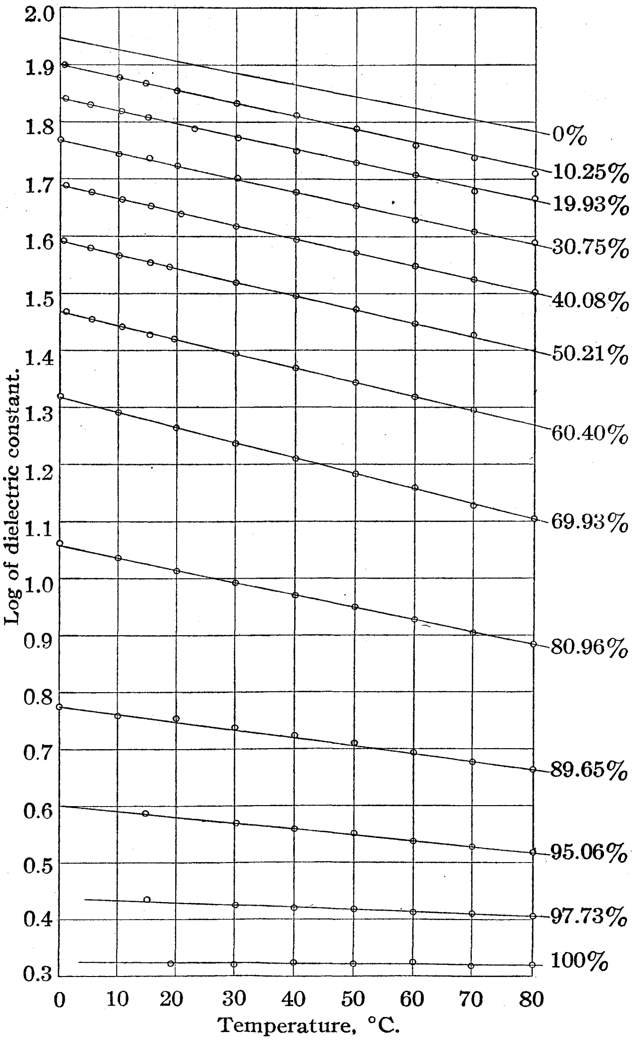

Fig. 2.—Curves for the logarithm of the dielectric constant of dioxane–water mixtures of constant composition and varying temperature.

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(1) Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933).

(2) G. Åkerlöf, *ibid.*, **54**, 4125 (1932).

(3) Wyman, *Phys. Rev.*, **35**, 623 (1930); *cf.* Drake, Pierce and Dow, *ibid.*, **35**, 613 (1930).

TABLE I

INTERPOLATED VALUES FOR THE DIELECTRIC CONSTANT OF A SERIES OF DIOXANE–WATER MIXTURES AT VARIOUS ROUND TEMPERATURES

Dioxane, wt. %	Temperature, °C. 0	10	20	30	40	50	60	70	80	90	95	98	100
0	88.31	78.86	69.16	59.34	49.37	39.50	29.84	20.37	12.19	6.16	3.91	2.73	2.109
10	84.25	75.06	65.68	56.24	46.71	37.31	28.17	19.25	11.58	5.93	3.82	2.70	2.104
20	80.37	71.43	62.38	53.30	44.19	35.25	26.60	18.20	10.99	5.71	3.74	2.68	2.102
30	76.73	67.98	59.24	50.52	41.80	33.30	25.12	17.20	10.44	5.50	3.65	2.65	2.100
40	73.12	64.70	56.26	47.88	39.54	31.46	23.72	16.26	9.91	5.30	3.57	2.62	2.098
50	69.85	61.57	53.43	45.38	37.41	29.72	22.40	15.37	9.41	5.10	3.49	2.60	2.096
60	66.62	68.60	50.75	43.01	35.39	28.08	21.15	14.52	8.93	4.91	3.41	2.57	2.094
70	63.50	55.77	48.20	40.76	33.48	26.52	19.97	13.73	8.48	4.73	3.33	2.55	2.092
80	60.58	53.07	45.77	38.63	31.67	25.05	18.86	12.97	8.05	4.56	3.25	2.52	2.090

to use cells with silver films for the same purpose.[4] The results obtained with the silver films were erroneous but the closest approach to the true values for the dielectric constant was found in the case of mixtures containing a high percentage of dioxane.

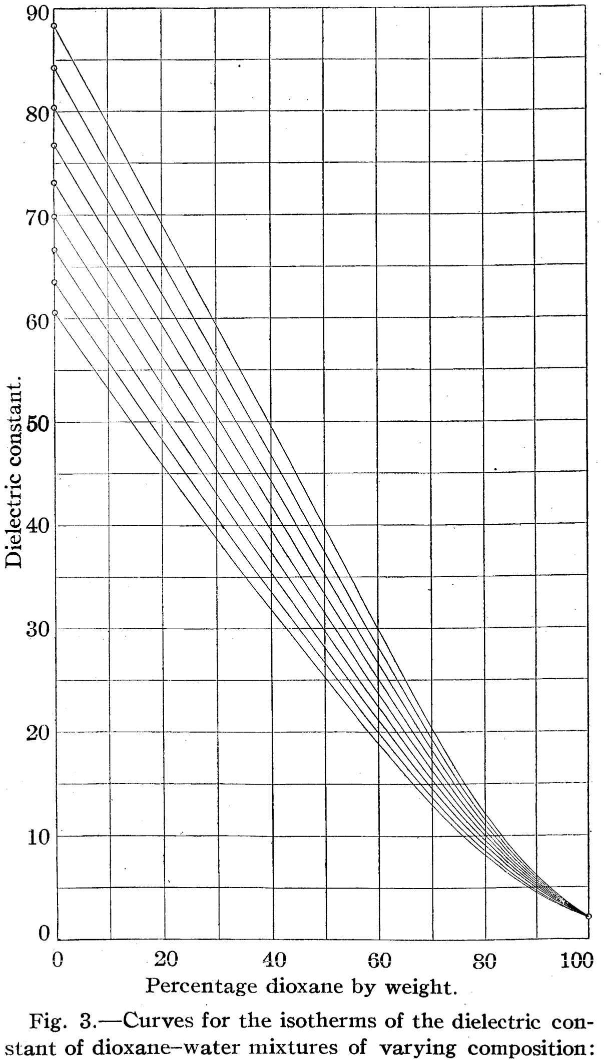

Fig. 3.—Curves for the isotherms of the dielectric constant of dioxane–water mixtures of varying composition: top curve 0° isotherm, then follow in order those for 10, 20, 30, 40, 50, 60, 70 and 80°.

The raw material for the dioxane employed was a commercial varnish remover from the Carbide and Carbon Chemicals Corporation and it consisted apparently of practically pure dioxane. The raw dioxane was first refluxed in an all-glass apparatus with sodium metal for several hours. The distilled product was then subjected to a fractional crystallization in an apparatus with a mercury-sealed stirrer. After four recrystallizations the freezing point had gone up to 11.78°, which value did not show any further visible changes upon repeating the freezing process. Water was obtained from a Barnstead still for conductivity water.

Experimental Results.—The dielectric constant data obtained have been plotted in Fig. 2 using the equation employed by Åkerlöf

$$\log D = \log a - bt \qquad (1)$$

where D is the observed dielectric constant of the solvent mixture, a and b are empirical constants and t is the temperature. As previously had been found in numerous other cases this equation was also in the case of dioxane–water mixtures able to express the experimental data well within their estimated accuracy. Using equation (1) the original measurements have been interpolated to round temperatures and weight per cent. of dioxane and a summary of the result is given in Table I. For interpolation to odd temperatures the following table may be used:

Dioxane, wt. %	Log a	b
0	1.9461	0.00205
10	1.8969	.00215
20	1.8398	.00224
30	1.7734	.00233
40	1.6935	.00241
50	1.5965	.00247
60	1.4747	.00249
70	1.3090	.00245
80	1.0860	.00225
90	0.7896	.00164
95	.5923	.00100
100	.3234	.00004

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[4] The design of the cells was practically identical with that of the cells used by Sugden, *J. Chem. Soc.*, 768 (1933); *cf.* Sayce and Briscoe, *ibid.*, 315 (1925); Ball, *ibid.*, 570 (1930).

A graphical representation of the isotherms for the variation of the dielectric constant of the dioxane–water mixtures with changing composition is shown in Fig. 3.

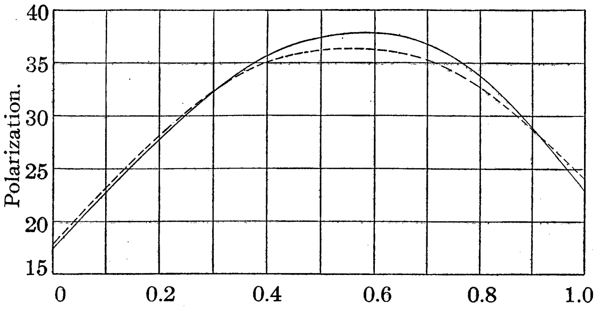

Fig. 4.—Curves for the dielectric polarization of dioxane–water mixtures at 20 and 70°; dotted curve 70° isotherm.

The curve for the molar dielectric polarization of dioxane–water mixtures is considerably different from that of a number of other organic solvent–water mixtures. In the case of methyl and ethyl alcohol–, ethylene glycol– and glycerol–water mixtures, a practically linear variation of the polarization over the entire mixture range is obtained when it is plotted against the mole fraction of one of the components. The polarization of a mixture P_{12} is given by the equation

$$P_{12} = f_1P_1 + f_2P_2 = \frac{D-1}{D+2}\,\frac{f_1M_1 + f_2M_2}{d} \qquad (2)$$

where f_1 and f_2 denote mole fractions, M_1 and M_2 molecular weights and d is the density of the mixture. In Table II is given the calculated values for 20 and 70° and the corresponding curves are shown in Fig. 4. Data used for the density of dioxane–water mixtures were those of Herz and Lorenz.[5]

TABLE II

THE DIELECTRIC POLARIZATION OF DIOXANE–WATER MIXTURES AT 20 AND 70°

Dioxane, wt. %	Dioxane mole fr.	P_{12} at 20°	P_{12} at 70°
0	0	17.39	17.59
10	0.0222	18.66	18.82
20	.0487	20.10	20.31
30	.0806	21.83	22.11
40	.1200	23.94	24.26
50	.1699	26.54	26.84
60	.2349	29.69	29.83
70	.3232	33.21	33.00
80	.4501	36.65	35.78
90	.6481	37.47	35.78
95	.7954	34.06	32.92
98	.9093	28.35	28.40
100	1.0000	22.90	24.06

According to present theory, if a substance is non-polar its polarization is constant and independent of the concentration. Thus since dioxane as already mentioned probably is non-polar we might calculate the variations of the polarization of water in dioxane–water mixtures. The calculated values vary approximately linearly when plotted against the dioxane mole fraction as shown in Fig. 5 for the 20° isotherm, but the theoretical significance of this result is difficult to understand. The polarization of water in pure dioxane at 20° extrapolates to 88.0, while the corresponding value in pure water is only 17.4.

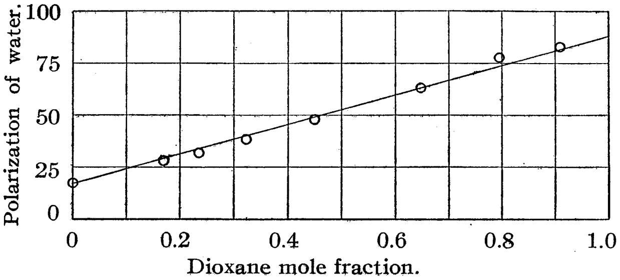

Fig. 5.—Curve for the dielectric polarization of water in dioxane–water mixtures at 20°.

The authors wish to express their appreciation of the help given them by Professor Norman I. Adams.

Summary

The dielectric constant of a series of dioxane–water mixtures has been measured over the temperature range 0 to 80° for a wave length of 150 meters and using a resonance method.

NEW HAVEN, CONN. RECEIVED MAY 8, 1936

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[5] Herz and Lorenz, *Z. physik. Chem.*, **A140**, 406 (1929).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

The Catalytic Decomposition of Hydrogen Peroxide in a Bromine–Bromide Solution. Effect of Light on the Steady-state Rate

BY ROBERT LIVINGSTON AND E. A. SCHOELD

That exposure to diffuse daylight produces a pronounced decrease in the steady-state concentration of bromine in a hydrogen peroxide–bromine–bromide mixture was remarked in 1923 by Bray and Livingston.[1] On the basis of the mechanism which they adopted for the catalytic decomposition of hydrogen peroxide occurring in these solutions, they predicted that the irradiation of the reaction mixtures with light of constant intensity would not affect the steady-state rate of the decomposition. However, this prediction was not tested experimentally.

More recently[2] it has been suggested that the decomposition of hydrogen peroxide may be a chain reaction in acid as well as in basic solutions. In so far as the halogen–halide catalyzed reactions are concerned, this suggestion appears to be based entirely upon analogy, and is in contradiction to several experimental observations of these reactions.[3]

The measurements presented here substantially check the predictions of Bray and Livingston,[1] and afford definite evidence that the bromine sensitized photochemical decomposition of hydrogen peroxide is not a chain reaction.

Experimental Methods.—The analytical methods for the determination of hydrogen peroxide and bromine in the reacting mixtures were similar to those of Bray and Livingston.[1] The "dark reaction" mixture was kept in a black-coated flask, which was immersed in a large water thermostat, maintained at 35°.[4] The "light-reaction" vessel was a short Pyrex cylinder, with sealed on plane ends. It was provided with a water-sealed glass stirrer, to prevent the development of concentration gradients due to the photochemical action. The oxygen, evolved during the reaction, escaped through the water seal of the stirrer. This reaction vessel and a similar vessel, which was kept filled with distilled water, were sealed into a flat metal box, which was provided with openings into which the ends of the cylinders fitted. Water from the large thermostat was circulated through this box. Although the ends of the reaction vessel were not jacketed, tests showed that the temperature of the reaction mixture was not more than 0.1° below that of the large thermostat.

In beginning an experiment, a volume of reaction mixture was prepared from stock solutions of hydrogen peroxide and hydrogen bromide, sufficient to fill both the "dark" and "light-reaction" vessels. Both vessels were filled, and the cylindrical cell was irradiated with light of constant intensity. After sufficient time (about three hours) was allowed for steady-state conditions to be attained, samples were removed from each of the reaction mixtures and were analyzed for hydrogen peroxide. After a measured lapse of time, of from one to four hours, samples were again removed from each of the vessels and were analyzed both for peroxide and for bromine.

These measurements made possible the computation of the first order rate constant k of equation 1

$$-d(H_2O_2)/dt = k(H_2O_2) \tag{1}$$

and the termolecular catalytic rate constant, K of equation 2

$$-d(H_2O_2)/dt = K(H_2O_2)(H^+)(Br^-) \tag{2}$$

In the computation of K, correction was made for tribromide formation[1] (p. 1262). However, no correction was made for the kinetic salt effect,[5] since in these experiments we were interested primarily in the comparison of the "light" and "dark" rates of initially identical solutions.

The light source used in these experiments was a 500-watt "stereopticon" tungsten-filament lamp provided with a system of condensing lenses and a Corning heat-absorbing neutral-green filter. The light intensity was measured with a galvanometer–surface thermopile system, which was

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[1] Bray and Livingston, THIS JOURNAL, **45**, 1264 (1923).

[2] See for example, Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford Univ. Press, New York, 1933, p. 211.

[3] If these processes were chain reactions it should be expected that they would be sensitive to the presence of inhibitors, including those substances which are commonly used as hydrogen peroxide preservatives. That this is not the case for the iodine–iodide catalysis was shown by Bohnson, *J. Phys. Chem.*, **25**, 19 (1925); for the bromine–bromide catalysis by Bray and Livingston, reference 1, p. 1260; and for the chlorine–chloride catalysis by Livingston and Bray, THIS JOURNAL, **47**, 2069 (1925).

[4] A lower temperature would have been preferable, but would have required somewhat more elaborate equipment, since these experiments were performed during the summer months, when the average temperature of both air and cooling water was above 25° and the relative humidity was high.

[5] See Livingston, THIS JOURNAL, **48**, 53 (1926).

TABLE I

SUMMARY OF MEASUREMENTS AND COMPUTATIONS

		Dark reaction					Light reaction							Comparison of dark and light reactions		
Expt.	Initial concn. $(HBr)_0$	$(H_2O_2)_0$	$\Sigma(Br_2)$	$k_d \times 10^3$	$K_d \times 10^2$	R_d	$(H_2O_2)_0$	$\Sigma(Br_2)$	$k_l \times 10^3$	$K_l \times 10^2$	R_l	$I_{abs.}$	M/Q	k_l/k_d	K_l/K_d	$\frac{(Br_2)_d}{(Br_2)_l}$
1	0.330	0.1517	0.0174	5.71	6.90	0.42	0.1675	0.0172	5.68	6.83	0.41	0	..	0.99	0.99	1.01
2	.165	.1206	.0008	1.90	7.15	.03	.1272	.0005	1.95	7.26	.02	8.7	0.68	1.02	1.01	1.60
3	.322	.0601	.0165	5.59	7.02	.44	.0537	.0154	5.61	6.91	.42	15.1	.08	1.00	0.98	1.07
4	.248	.0829	.0063	3.62	6.70	.42	.0921	.0051	3.69	6.66	.28	17.7	.34	1.02	.99	1.24
5	.320	.1020	.0167	6.02	7.70	.47	.1244	.0158	6.12	7.71	.43	25.3	.50	1.02	1.00	1.06
6	.320	.1112	.0157	5.49	6.90	.43	.1216	.0136	5.77	7.00	.34	25.9	.91	1.05	1.01	1.15
7	.248	.1000	.0061	3.62	6.68	.37	.0981	.0046	3.77	6.74	.30	27.0	.48	1.04	1.01	1.32
8	.320	.1287	.0163	6.16	7.83	.45	.1459	.0151	6.23	7.75	.43	30.0	.34	1.01	0.99	1.08
9	.322	.0265	.0176	5.04	6.45	.49	.0243	.0155	5.17	6.35	.45	32.4	.08	1.03	.98	1.14
10	.248	.0832	.0066	3.92	7.29	.46	.0881	.0044	4.03	7.18	.29	32.9	.26	1.03	.99	1.50
11	.330	.0734	.0167	5.72	6.82	.43	.0781	.0147	5.88	6.78	.33	35.0	.33	1.03	.99	1.14
12	.280	.0869	.0115	4.92	7.70	.52	.0988	.0096	4.90	7.45	.41	38.6	.04	1.00	.97	1.20
13	.330	.1582	.0187	6.05	7.46	.48	.1714	.0157	6.25	7.33	.36	39.2	.70	1.03	.98	1.19
14	.332	.1210	.0160	5.79	7.22	.40	.1314	.0135	6.39	7.63	.33	74.7	1.28	1.10	1.05	1.18
15	.332	.1019	.0171	5.72	6.94	.45	.0910	.0154	6.19	7.63	.44	114.2	0.40	1.10	1.09	1.11
16	.322	.1005	.0158	5.78	7.18	.43	.1110	.0137	6.20	7.43	.33	129.7	.34	1.07	1.04	1.15

calibrated against a U. S. Bureau of Standards standard lamp, in the usual manner. The water jacket, which surrounded both the "light reaction" cell and the similar vessel filled with water, was so arranged that it could be slid along a track to place either cell in the path of the beam of light. The intensity of the light absorbed by the reaction mixture was obtained by comparing the energy transmitted through the two cells, taking into account the difference in transmission of the cells when they were both filled with water, and the effect of the second window of the reaction cell.

Measurements and Computations.—The results of the experiments are summarized in Table I. All concentrations are expressed as moles per liter. In computing the rate constants, k and K, natural logarithms were used and time was expressed in minutes. The symbol $\Sigma(Br_2)$ represents the molar concentration of the total titratable bromine, expressed as Br_2. R is the steady-state function[1], and is defined by the equation $R = (Br_2)/(H^+)^2(Br^-)^2$. $I_{abs.}$ is the intensity of the light absorbed expressed in deflection of the galvanometer in centimeters.

The last three columns compare the results of corresponding measurements in the dark and in the light. Experiment 1 was a "blank," in that the light reaction cell was not illuminated.

In thirteen of the fifteen experiments performed the first order reaction constant, k, was greater for the "light reaction" than for the "dark;" in no case was it less. However, it is noteworthy that this increase in k is about six-fold less than the corresponding change (which is in the opposite direction) in the steady-state concentration of the bromine. The values of the third order rate constant, K, do not exhibit any consistent effect of light. The average value of K_l/K_d is 1.005 ± 0.008, where the error is the average error of the averaged value.[6] These results may be taken as evidence that the only effect of visible light on this system is to increase the specific reaction rate of the reduction of bromine by hydrogen peroxide. To a first approximation equation 2 represents the rate of the light reaction as well as the dark reaction, the increase in the absolute rate being completely accounted for by the increase in the steady-state concentration of the hydrobromic acid.

The quantum yield, M/Q, was computed with the aid of the following assumptions. The average wave length of the absorbed light was assumed to be 5300 Å. This value was chosen upon the basis of a qualitative consideration of the energy distribution of the light from a tungsten filament and of the absorption curve for bromine. Although the average wave length of the absorbed light is undoubtedly a function of the concentration of bromine, it is quite probable that the present assumption does not introduce an error of more than 20%. The rate of the purely photochemical reaction was assumed to be equal to $(k_l - k_d)(H_2O_2)$. The quantum yield was computed by means of the expression

$$(k_l - k_d)(H_2O_2)VNh\nu/S \cdot I_{abs.}$$

Where (H_2O_2) is the average concentration of hy-

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[6] The corresponding average of k_l/k_d is 1.037 ± 0.006. This value is given only for purposes of comparison, since the ratio k_l/k_d is undoubtedly a function of the intensity of the absorbed light.

drogen peroxide during an experiment, V is the volume of the "light reaction" vessel, N is Avogadro's number, $I_{\text{abs.}}$ is the average intensity of the absorbed light expressed as galvanometer deflection in centimeters, $h\nu$ is the energy of a photon of λ 5300 Å., and S is the sensitivity of the galvanometer thermopile system in ergs per minute per cm. deflection. This expression will give the true value of the quantum yield only if it is directly proportional to the concentration of the hydrogen peroxide.[7] However, if the quantum yield were independent of the concentration of hydrogen peroxide, the error introduced by the use of this approximate relation would be less than the average error of the experimental determination of the quantum yield. The average value of the quantum yield (so computed) is 0.4.[8] It is noteworthy that this value is less than unity, and is therefore not in agreement with any chain mechanism of the reaction. More exact measurements of the effect of light on the steady-state rate and function (preferably at a lower temperature and at lower concentrations of peroxide) must be available before a detailed discussion of the mechanism of the photochemical process will be justifiable.

Summary

1. The steady-rate of the decomposition of hydrogen peroxide in bromine–bromide solutions has been measured in the dark and in the light, under otherwise comparable conditions. Although light increases the absolute rate of the reaction, within the limits of experimental error the rate for either the dark or light reaction may be represented by the equation $V = K(H_2O_2)(H^+)(Br^-)$. The increase in the absolute rate is satisfactorily accounted for by the increase in the steady-state concentration of hydrobromic acid.

2. The quantum yield for the bromo sensitized decomposition of hydrogen peroxide has been computed (with the aid of certain simplifying assumptions), and has been shown to have an average value less than unity.

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[7] Even for this case the method is an approximate one, since $k_d(H_2O_2)$ does not properly represent the rate of the thermal reaction which is taking place in the illuminated solution. Although this quantity may be readily corrected for the differences in the steady-state concentrations of H^+, Br^- and Br_2 in the "light" and "dark" reacting mixtures, the corrected values of the quantum yield do not differ greatly from the approximate values given in Table I. Therefore, for the sake of simplicity and brevity only the approximate method is presented here.

[8] The value of M/Q for experiment 14 appears to be out of the range of the random distribution of errors and has been excluded from the average.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

The Action of Magnesium on Homonuclear Dibromodiphenyls

BY FRANCIS H. CASE

The study of the action of magnesium on homonuclear dibromo aromatic hydrocarbons has thus far been confined to the compounds *m*- and *p*-dibromobenzene,[1] 3,4-dibromotoluene, *sym*-tribromotoluene, 1,3-dimethyl-4,6-dibromobenzene,[2] and 1,2 and 1,4-dibromonaphthalenes.[3] In the case of *p*-dibromobenzene, which has been rather extensively investigated, it was first believed that in the presence of two atoms of magnesium[4] only one atom of bromine is capable of reacting. Later investigations, however, showed that in an inert atmosphere a part of the second atom[5] of magnesium will react to form a di-Grignard, but this reaction never reaches completion. Thus it has been found that with both *p*- and *m*-dibromobenzene, 87% of the original two atoms of magnesium enters the reaction; 3,4-dibromotoluene, 83%; 1,3-dimethyl-4,6-dibromobenzene, 49.6% of the total bromine; *sym*-tribromotoluene, no reaction; 1,4-dibromonaphthalene, 72% magnesium; 1,2-dibromonaphthalene, 75.5% magnesium. It is worthy of note that in the few cases where unsymmetrical dibromides have been investigated, in only one instance (1,2-dibromonaphthalene) have results been obtained that would indicate which of the bromine atoms is more readily attacked by the magnesium.

The object of the present investigation has been to determine the extent to which certain homonuclear dibromodiphenyls react with two atoms of magnesium, and in the case of unsymmetrical de-

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[1] Salkind and Rogovina, *J. Russ. Phys.-Chem. Soc.*, **59**, 1013 (1927).

[2] Salkind, *J. Gen. Chem.* (U. S. S. R.), **1**, 193 (1931).

[3] Salkind, *Ber.*, **67**, 1031 (1934).

[4] Pink, *J. Chem. Soc.*, **123**, 3418 (1923).

[5] (a) Quelet, *Bull. soc. chim.*, **41**, 933 (1927); (b) Gilman, Beaber and Jones, *Rec. trav. chim.*, **48**, 597 (1929).

rivatives, which bromine atom is preferentially attacked. The compounds chosen for this study were 2,5, 3,5, 2,4 and 3,4-dibromodiphenyls. The preparation of the first three of these dibromides was according to the directions of Scarborough.[6] It should be noted however that 2,4-dibromodiphenyl, which was not obtained in a state of purity by this author, has now been isolated. The preparation of the 3,4-isomer is described in another paper from this Laboratory.[7]

In the experiments to be described, the amount of di-Grignard formation in each case was estimated by weighing the amount of diphenyl solidifying in the receiver after fractional distillation of the hydrolytic products. This method cannot be regarded as strictly accurate as the diphenyl obtained in this way is not entirely pure, yet it gives a better idea of the amount of di-Grignard formation than if the diphenyl obtained were recrystallized, since losses involved in crystallization are large. The nature of the mono-Grignard reagent simultaneously formed was established by oxidizing the monobromodiphenyl resulting from hydrolysis and identifying the corresponding bromobenzoic acid. The unused magnesium was determined by measuring the hydrogen evolved on treatment of the mixture after completion of the reaction with dilute sulfuric acid. The bromine going into water solution was determined gravimetrically.

The results of the experiments in which each of the four isomeric dibromodiphenyls mentioned above was treated with two atoms of magnesium show that the isomers, arranged in the order of decreasing extent of reaction with magnesium, are 2,4, 2,5, 3,5, 3,4. In fact the last-mentioned compound could not be made to react when treated with the activated copper–magnesium alloy of Gilman.[8] From the hydrolytic products of the reactions involving the 2,4- and 2,5-isomers, liquids were obtained which both yielded on oxidation with chromic anhydride, *o*-bromobenzoic acid, thus indicating that in each case the bromine in 2-position was the one less readily attacked. A similar process yielded in the case of 3,5-dibromodiphenyl, *m*-bromobenzoic acid. The close check between the amount of magnesium consumed and the amount of bromine in water solution (indicating a ratio of one atom of each) and the small amount of high boiling residue obtained indicate the absence of any considerable amount of coupling.

The activated copper–magnesium alloy was also used with each of the isomeric dibromodiphenyls, increasing the yield of di-Grignard in the cases of those which reacted with ordinary magnesium.

By treating the 2,5 and 3,5-isomers, respectively, with one atom of magnesium, followed by carbon dioxide, the acids 2-bromodiphenyl-5-carboxylic acid, prepared by Cook and Cook[9] by the oxidation of 2-bromo-5-methyldiphenyl, and 3-bromodiphenyl-5-carboxylic acid, heretofore unknown, were obtained.

In only one case (the 2,5-isomer) was the dicarboxylic acid resulting from the action of carbon dioxide on the di-Grignard formed by the action of 2 atoms of copper–magnesium alloy on the corresponding dibromide, isolated in a state of purity. The 3,5-isomer yielded an acid which could not be freed entirely from bromine even by repeated crystallization. This recalls the difficulties experienced by Gilman[5b] in attempts to obtain pure terephthalic acid from *p*-dibromobenzene. In the case of the 2,4-dibromide, no dicarboxylic acid was found. In the cases of the 2,5, 3,5, and 2,4-isomers, relatively large amounts of monobromocarboxylic acid were isolated. One must therefore conclude that although, as shown by previous experiments, the di-Grignard is formed to a large extent, yet on treatment with carbon dioxide it is partly unaffected as shown by the presence of a certain amount of diphenyl after hydrolysis, and is subject to side reactions leading to the formation of acidic resins obtained as by-products.

Experimental

Preparation of Dibromodiphenyls.—These compounds were tested for absence of nitrogen, and gave a correct bromine analysis.

Preparation of 2,4-Dibromodiphenyl.—By the hydrolysis of 78.5 g. of 4,6-dibromo-3-acetaminodiphenyl with alcoholic hydrobromic acid was obtained 69.2 g. of crude base. The base, dissolved in alcohol, and treated with excess of 1–1 sulfuric acid, was deaminized by means of sodium nitrite. In order to remove from the final product all traces of nitrogenous matter, it was dissolved in absolute ether and filtered from a white precipitate which formed, then washed successively with aqueous hydrobromic acid, and sodium bicarbonate solution. On redistillation, 28 g. was obtained, b. p. 174–176° (7 mm.).

Anal. Calcd. for $C_{12}H_8Br_2$: Br, 51.25. Found: Br, 51.11.

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(6) Scarborough, *J. Chem. Soc.*, 557 (1926); **89**, 3000 (1927).

(7) Case, THIS JOURNAL, **58**, 1249 (1936).

(8) Gilman, Peterson and Schulze, *Rec. trav. chim.*, **47**, 19 (1928).

(9) Cook and Cook, THIS JOURNAL, **55**, 1217 (1933).

Action of Dibromodiphenyls on Two Atoms of Magnesium.—Fifteen and six-tenths grams (0.05 mol) of dibromodiphenyl dissolved in absolute ether was refluxed not less than fifteen hours with 2.4 g. of magnesium in the presence of a trace of iodine. With the 3,5 and 2,5 isomers and plain magnesium, an atmosphere of nitrogen was maintained, but in all other experiments hydrogen was the inert gas used. On completion of the reactions, hydrolysis was effected by dilute sulfuric acid, the evolved hydrogen being collected over water. Ether vapors were removed by absorption in concentrated sulfuric acid. The ether layer was carefully separated from the water layer, the latter being analyzed for bromine, after removal of the iodine by means of sodium nitrite. The ether layer was evaporated, and the residue fractionated in a vacuum, the amount of solid collecting in the receiver being weighed as diphenyl. The higher boiling liquid was oxidized by means of chromic anhydride in glacial acetic acid, and the resulting bromobenzoic acid identified by a mixed melting point with an authentic specimen. The results are shown in Table I.

TABLE I

ACTION OF DIBROMODIPHENYLS ON TWO ATOMS OF MAGNESIUM

Isomer (0.05 mole)		3,5	2,5	2,4
Mg unused, g.		0.83	0.83	0.73
Bromine in solution	g.	4.86	5.29	5.59
	%	61	66	70
Diphenyl	g.	2.0	3.0	4.3
	%	26	39	56
Mono-Br-diphenyl, g.		7	4.5	3.9
Benzoic acid from oxidation of mono-Br-diphenyl		*m*-Br-	*o*-Br-	*o*-Br-

Action of the Dibromodiphenyls on Two Atoms of Copper-Magnesium Alloy.—Fifteen and six-tenths grams of dibromodiphenyl, dissolved in absolute ether, was refluxed for not less than fifteen hours with approximately 3 g. of activated copper–magnesium alloy prepared according to the directions of Gilman, Peterson and Schulze.[8] The results are shown in Table II.

TABLE II

ACTION OF DIBROMODIPHENYLS ON TWO ATOMS OF Cu-Mg ALLOY

Isomer (0.05 mole)		3,5	2,5	2,4	3,4
Bromine reacting	g.	5.57	6.44	6.56	No reaction
	%	69.6	80.5	82.0	
Yield of diphenyl, g.		2.7	5.3	6.0	....
Diphenyl, %		35.1	68.8	77.9	....

The 3,4-dibromodiphenyl would not react even though a small amount of the activated magnesium of Gilman and Kirby was added to the reaction mixture.[10]

Action of 3,5-Dibromodiphenyl on 1 Atom of Mg + CO_2.—One-twentieth mole of 3,5-dibromodiphenyl was treated with 1.2 g. of magnesium as before. After complete solution of the magnesium, carbon dioxide was passed into the mixture, cooled by ice and salt, for two hours. Decomposition was then effected by dilute hydrochloric acid. The ether solution was washed with alkali, the acid reprecipitated with concd. hydrochloric acid and extracted with ether. After removal of the ether the acid was crystallized from benzene and petroleum ether; yield 3.5 g.; m. p. 177–178°.

Anal. Calcd. for $C_{13}H_9O_2Br$: Br, 28.85. Found: Br, 29.21.

Action of 2,5-Dibromodiphenyl on 1 Atom of Mg + CO_2.—The procedure was the same as with the 3,5-isomer. Two grams of a monobromodiphenyl carboxylic acid was obtained, m. p. 247–248°. The 2-bromodiphenyl-5-carboxylic acid of Cook and Cook melted at 242–243°. The identity of the acid obtained above was further confirmed by the fact that the mono-Grignard reagent on hydrolysis yields only *o*-bromodiphenyl.

Anal. Calcd. for $C_{13}H_9O_2Br$: Br, 28.85. Found: Br, 28.72.

Action of the Dibromodiphenyls on 2 Atoms of Cu–Mg alloy + CO_2.—The quantities used were the same as when the Grignard was directly hydrolyzed. The results are shown in Table III.

TABLE III

ACTION OF CARBON DIOXIDE ON DIPHENYL DI-GRIGNARD REAGENTS

Dibromodiphenyl (15.6 g. used)		3,5	2,5	2,4
Yield of bromocarboxylic acid	g.	5.7	1.9	2.0
	%	41	14	15
Yield of dicarboxylic acid	g.	1.3	2.2	0
	%	11	18	0
Diphenyl isolated, g.		0.2	1.0	0.6

Action of 3,5-Dibromodiphenyl.—After the decomposition of the carbon dioxide–Grignard complex with hydrochloric acid, the precipitated acids were extracted with ether, and removed from the ether by extraction with potassium hydroxide. After reprecipitation with concd. hydrochloric acid, 10 g. of crude acid was obtained. This was separated by means of hot benzene into a soluble fraction which on recrystallization from a methyl alcohol–water mixture yielded 5.7 g. of crude 3-bromodiphenyl-5-carboxylic acid, m. p. 168–170°. The benzene-insoluble portion, weighing 1.9 g. was recrystallized four times from glacial acetic acid, yielding 0.6 g. of an acid melting at 330–334° but still containing 1.19% bromine. Equivalent weight: calcd. for $C_{14}H_{10}O_4$: 121. Found: 126.

Action of 2,5-Dibromodiphenyl.—The mixed acids (12.5 g.) obtained by adding hydrochloric acid to the alkaline extract of the original ether solution, and again extracting with ether, were extracted with hot benzene, yielding 4.5 g. of benzene insoluble material, which after repeated crystallization from a benzene–ether mixture yielded 0.5 g. of pure diphenyl-2,5-dicarboxylic acid, m. p. 274–275°.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.40; H, 4.16. Found: C, 69.62; H, 4.35.

The benzene soluble portion of the above extraction, after several crystallizations from a benzene–petroleum ether mixture, yielded 1.9 g. of 2-bromodiphenyl-5-carboxylic acid, m. p. 247–248°, previously described. The original ether solution, after extraction with sodium hydroxide solution, yielded after evaporation 1 g. of diphenyl.

Action of 2,4-Dibromodiphenyl.—The original ether solution, after extraction with sodium hydroxide solution, acidification of the alkaline solution with hydrochloric

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(10) Gilman and Kirby, *Rec. trav. chim.*, **54**, 577 (1935).

acid, and extraction with ether yielded 10 g. of crude acid, which dissolved in hot benzene. After several crystallizations from methyl alcohol, 2 g. of an acid was obtained, melting at 213–214°, yielding finally an acid of m. p. 218–219°, which melted unchanged with 2-bromodiphenyl-4-carboxylic acid, prepared from 4-methyl-2-bromoaniline by the method of Gomberg and Pernert.[11]

The original ether solution, after extraction with sodium hydroxide, yielded 0.6 g. of diphenyl.

The author acknowledges the assistance of Mr. Henry Sloviter in connection with a portion of the analytical work in this paper.

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[11] Gomberg and Pernert, THIS JOURNAL, **48**, 1372 (1926).

Summary

1. A study has been made of the extent of the reaction of 3,5, 2,5, 2,4 and 3,4-dibromodiphenyls, respectively, with (a) one and two atoms of magnesium; (b) two atomic proportions of activated copper–magnesium alloy.

2. The nature of the resulting products has been determined when the Grignard reagent is (a) directly hydrolyzed; (b) first treated with carbon dioxide and then hydrolyzed.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

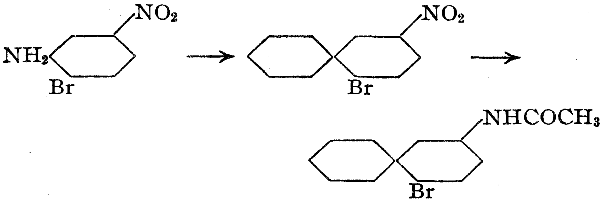
The Preparation of 3,4-Dibromodiphenyl

BY FRANCIS H. CASE

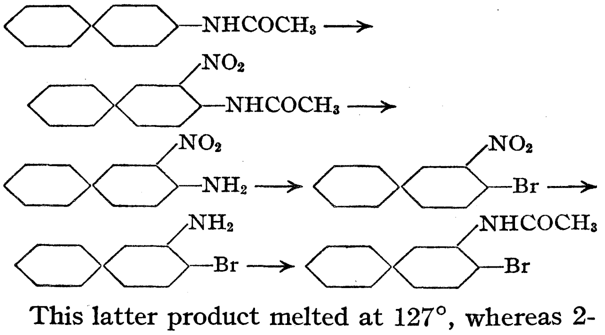
The preparation of 3,4-dibromodiphenyl has previously been reported by Scarborough,[1] who stated that it could be obtained by the replacement by bromine of the amino group in the bromo amine resulting from the hydrolysis of what he believed to be 4-bromo-3-acetaminodiphenyl. Scarborough's evidence for the structure of the dibromodiphenyl is based on its oxidation by chromic anhydride to 3,4-dibromobenzoic acid. Reasoning back he therefore concluded that on monobromination 3-acetaminodiphenyl is substituted in the 4-position rather than in the more to be expected 6-position.

In a study of the action of magnesium on various homonuclear dibromodiphenyls,[2] the so-called 3,4-dibromodiphenyl of Scarborough was subjected to the action of two atoms of magnesium–copper alloy, followed by carbon dioxide. The two acids resulting were identified as 2-bromodiphenyl-5-carboxylic acid, and diphenyl-2,5-dicarboxylic acid. This suggested the possibility that Scarborough's dibromodiphenyl was derived from 2-bromo-5-acetaminodiphenyl, the normal bromination product. On repeating the oxidation of the dibromodiphenyl, however, a small amount of 3,4-dibromobenzoic acid was obtained, in addition to the expected 2,5-dibromobenzoic acid (also in small quantity). The amounts of the two dibromo acids isolated after oxidation do not, however, give a satisfactory idea of the amounts of dibromides present in the original mixture, as experiments with the pure dibromides indicate that the 2,5-isomer is much more easily destroyed by oxidation than the 3,4.

2-Bromo-5-acetaminodiphenyl was next synthesized by the reaction of Gomberg and Pernert,[3] as follows:



4-Bromo-3-acetaminodiphenyl was prepared by the following series of reactions



This latter product melted at 127°, whereas 2-bromo-5-acetaminodiphenyl prepared by Gomberg's method melts at 162–163°, and Scarborough's bromo-3-acetaminodiphenyl at 163–164°. The latter two products when mixed showed no change in melting point. Since the dibromodiphenyl obtained from Scarborough's

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[1] Scarborough, *J. Chem. Soc.*, 3000 (1927).

[2] Case, THIS JOURNAL, **58**, 1246 (1936).

[3] Gomberg and Pernert, *ibid.*, **48**, 1372 (1926).

product by hydrolysis and use of the Gattermann reaction yields on oxidation both 3,4- and 2,5-dibromobenzoic acid, and gives with magnesium the mono and dicarboxylic acids related to 2,5-dibromodiphenyl, it seems evident that Scarborough's bromoacetaminodiphenyl is a mixture of two isomers, having a constant melting point. This type of mixture is not unfamiliar in the diphenyl series, as a similar one is obtained by brominating *p*-acetaminodiphenyl.[4]

3,4-Dibromodiphenyl was prepared in this Laboratory by hydrolyzing 4-bromo-3-acetaminodiphenyl to the free base and applying the Gattermann reaction. This product, on oxidation, yielded exclusively 3,4-dibromobenzoic acid.

In the process of identification of the acids resulting from the action of magnesium on Scarborough's dibromodiphenyl, two hitherto undescribed bromo acids were prepared: namely, 3-bromodiphenyl-4-carboxylic acid and 4-bromodiphenyl-3-carboxylic acid.

Experimental Part

3-Nitro-4-bromodiphenyl.—This was prepared in quantity by combining the reaction mixtures from unit batches of 50 g. of 3-nitro-4-aminodiphenyl and working them up together. For a unit batch 50 g. of finely powdered nitro amine was warmed on the steam-bath with 300 cc. of 40% hydrobromic acid. When the mixture had turned to a light brown color, it was cooled to 10°, and diazotized by slowly adding 23 g. of powdered sodium nitrite and shaking the stoppered flask. After standing for a half-hour the mixture was treated with 7 g. of copper powder and heated with a low flame for about half an hour after all apparent reaction had ceased. At this point all the batches were combined, the 3-nitro-4-bromodiphenyl extracted with ether, and twice distilled; yield from 294 g. of 3-nitro-4-aminodiphenyl, 249 g. of 3-nitro-4-bromodiphenyl, b. p. 210–220° (5 mm.). The pure product boils at 210–215° (6 mm.).

Anal. Calcd. for $C_{12}H_8NO_2Br$: Br, 28.75. Found: 28.86.

3-Amino-4-bromodiphenyl.—To 307 g. of $SnCl_2{\cdot}2H_2O$ dissolved in 900 cc. of absolute alcohol was added 126 g. of 3-nitro-4-bromodiphenyl, the reaction mixture being cooled at first with ice, and then refluxed overnight. After removal of the alcohol the residue was treated with concentrated sodium hydroxide to dissolve the tin salts, and the base was then extracted with ether. On removal of the ether, the 3-amino-4-bromodiphenyl was crystallized from a mixture of benzene and petroleum ether. It was found that the bromine atom was removed either by catalytic reduction or by reduction with tin and hydrochloric acid; yield 74 g.; m. p. 97–98°.

Anal. Calcd. for $C_{12}H_{10}NBr$: Br, 32.22. Found: Br, 32.44.

3-Acetamino-4-bromodiphenyl.—This was prepared by the action of acetic anhydride on the base. It crystallizes from methyl alcohol, m. p. 127°.

Anal. Calcd. for $C_{14}H_{12}NOBr$: Br, 27.56. Found: Br, 27.50.

3,4-Dibromodiphenyl.—A mixture of 37.2 g. of 3-amino-4-bromodiphenyl and 192 cc. of 40% hydrobromic acid cooled to 10° was diazotized by the slow addition of 13 g. of sodium nitrite, the flask being repeatedly stoppered and shaken. After standing a half-hour, the mixture was heated with copper powder, the heating being continued for a half hour after the reaction subsided. The dibromodiphenyl was extracted with ether and distilled *in vacuo.* The crude liquid was washed with aqueous hydrobromic acid to remove unchanged base, then dried, dissolved in absolute ether and saturated with dry hydrogen bromide. The precipitated hydrobromide was filtered off, the ether solution washed with sodium bicarbonate, dried and the process repeated. The yield of nitrogen-free base was 33 g., b. p. 192–195° (5 mm.).

Anal. Calcd. for $C_{12}H_8Br_2$: Br, 51.25. Found: Br, 51.23.

2-Bromo-5-nitroaniline.—This was prepared by the bromination of *m*-nitroaniline according to the directions of Wheeler.[5] That it was this isomer was proven by the isolation of *p*-nitrobromobenzene from the deaminized product.

2-Bromo-5-nitrodiphenyl.—The cooled paste made by heating 90 g. of 2-bromo-5-nitroaniline with 100 cc. of concd. hydrochloric acid and 40 cc. of water was diazotized with a saturated solution of 36 g. of sodium nitrite. To the diazonium salt solution was added 300 cc. of benzene and then 128 cc. of 5 *N* sodium hydroxide, keeping the temperature below 5°. After standing overnight, the benzene was removed, yielding 36 g. of a product boiling at 190–215° (10 mm.), and solid at room temperature. On recrystallization from benzene–petroleum ether it melted at 80–81°.

Anal. Calcd. for $C_{12}H_8NO_2Br$: Br, 28.75. Found: 28.36.

2-Bromo-5-acetaminodiphenyl.—The 2-bromo-5-nitrodiphenyl was reduced by the theoretical quantity of stannous chloride in absolute alcohol to the amine, and this was acetylated by means of acetic anhydride. The 2-bromo-5-acetaminodiphenyl thus obtained was recrystallized from methyl alcohol, melting at 162–163°, and unchanged when mixed with the product resulting from the bromination of 3-acetaminodiphenyl.

Anal. Calcd. for $C_{14}H_{12}NOBr$: Br, 27.56. Found: Br, 27.51.

The 2-bromo-5-acetaminodiphenyl was converted to the corresponding dibromodiphenyl which yielded on oxidation 2,5-dibromobenzoic acid, m. p. 153–154°.

Action of Magnesium on Scarborough's Dibromodiphenyl.—The complex prepared by passing carbon dioxide into the Grignard reagent from 15.6 g. of the above dibromodiphenyl was decomposed with hydrochloric acid,[2] the acid solution extracted with ether and the organic acids removed by extraction of the ether solution with sodium hydroxide solution. After reprecipitation with hydro-

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(4) Kenyon and Robinson, *J. Chem. Soc.*, 3050 (1926); Scarborough, *ibid.*, 560 (1926).

(5) Wheeler, *Am. Chem. J.*, **17**, 699 (1895).

chloric acid, reëxtraction with ether, and removal of the ether, a gummy solid was obtained weighing 9 g. This was extracted with benzene. The benzene insoluble part, after several crystallizations from a benzene–methyl alcohol mixture, melted at 276–277°, and unchanged when mixed with a sample of diphenyl-2,5-dicarboxylic acid.[2] The benzene-soluble part after several crystallizations from benzene–petroleum ether, melted at 248–249°, and unchanged when mixed with a sample of 2-bromodiphenyl-5-carboxylic acid.[2] From the ether solution extracted by alkali, 1.1 g. of diphenyl was isolated.

4-Bromodiphenyl-3-carboxylic Acid.—Seventy-one grams of 4-bromo-3-methylaniline, obtained by brominating 3-acettoluide, was treated with 110 cc. of water and 76 cc. of concd. hydrochloric acid. The suspension was then diazotized with 27.5 g. of sodium nitrite in saturated solution, treated with 300 cc. of benzene and gradually with 110 cc. of 5 *N* sodium hydroxide keeping the temperature below 5°. After standing overnight the benzene was removed, yielding 18 g. of a liquid boiling at 165–170° (3 mm.). On oxidation with aqueous permanganate and crystallization from benzene, 4-bromodiphenyl-3-carboxylic acid was obtained, m. p. 194–195°.

Anal. Calcd. for $C_{13}H_9O_2Br$: Br, 28.85. Found: Br, 28.70.

3-Bromodiphenyl-4-carboxylic Acid.—4-Nitro-2-aminotoluene was prepared by the nitration[6] of *o*-toluidine. It was converted to 4-nitro-2-bromotoluene by the Gattermann reaction. From this, by reduction with stannous chloride in hydrochloric acid, was prepared 2-bromo-4-aminotoluene (acetyl derivative, m. p. 111–112°. Beilstein gives 113°). Sixty-five grams of 2-bromo-4-aminotoluene was treated with 70 cc. of concd. hydrochloric acid and 60 cc. of water, and diazotized with 26 g. of sodium nitrite in 50 cc. of water. The resulting solution was treated with 300 cc. of benzene and gradually with 100 cc. of 5 *N* sodium hydroxide solution. After standing overnight, the benzene solution was separated and the benzene removed by distillation, yielding 19.5 g. of an oil boiling at 165–170° (7 mm.). On oxidation with aqueous potassium permanganate solution and crystallization from methyl alcohol–petroleum ether, 3-bromodiphenyl-4-carboxylic acid, m. p. 179–180° was obtained.

Anal. Calcd. for $C_{13}H_9O_2Br$: Br, 28.85. Found: Br, 29.05.

The author acknowledges the assistance of Mr. Max Gabis in the preparation of certain intermediates involved in this work.

Summary

1. The "3,4-dibromodiphenyl" of Scarborough has been shown to be a mixture containing largely the 2,5-isomer, and some of the 3,4.

2. 3,4-Dibromodiphenyl has been synthesized.

3. The bromination product of 3-acetaminodiphenyl is believed to be a constant melting mixture of 4-bromo-3-acetamino- and 2-bromo-5-acetaminodiphenyls.

4. Both of these pure products have been synthesized.

5. The syntheses of 4-bromodiphenyl-3-carboxylic acid and of 3-bromo-diphenyl-4-carboxylic acid are described.

Philadelphia, Penna. Received May 18, 1936

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(6) Schiff and Vanni, *Ann.*, **268**, 322 (1892).

[Contribution from the Department of Chemistry of Stanford University]

Saponins and Sapogenins. IV. The Isolation of Amolonin and Determination of the Products of Hydrolysis

By P. C. Jurs and C. R. Noller

The hydrolysis of crude methyl alcoholic extracts of the bulbs of *Chlorogalum pomeridianum*, Kunth, commonly known as California soap plant or amole, has been shown to yield two crystalline sapogenins.[1] One of these was assigned the formula $C_{26}H_{40}O_2(OH)_2$ and the name *chlorogenin*, it being isomeric with but different than gitogenin, while the other was found to be identical with tigogenin, then believed to have the formula $C_{26}H_{41}O_2(OH)$. Recent work[2] indicates that gitogenin and tigogenin have the formulas $C_{27}H_{42}O_2(OH)_2$ and $C_{27}H_{43}O_2(OH)$, respectively, and chlorogenin is now known to have the formula $C_{27}H_{42}O_2(OH)_2$.[3]

The isolation of two sapogenins indicated that at least two saponins were present and early attempts by Liang to isolate the saponins proved this to be the case.[4] On cooling hot aqueous solutions of the mixed saponins or hot methyl alcoholic extracts of the roots, a product deposited that on hydrolysis yielded pure tigogenin, while hydrolysis of the more soluble fractions in the filtrates yielded largely chlorogenin. It appeared

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(1) Liang and Noller, This Journal, **57**, 525 (1935).

(2) Simpson and Jacobs, *J. Biol. Chem.*, **109**, 573 (1935); Tschesche and Hagedorn, *Ber.*, **68**, 1412 (1935).

(3) Private communication from Dr. L. F. Fieser. The results of extremely accurate combustions on chlorogenin at the Chemical Laboratory of Harvard University gave C, 74.956, 74.982; H, 10.249, 10.253. Calcd. for $C_{27}H_{44}O_4$: C, 74.955; H, 10.251.

(4) Liang, Thesis, Stanford University, 1934.

that it should be possible to isolate the less soluble saponin in a pure state and the present paper deals with the isolation of a pure crystalline saponin and with the quantitative determination of the products formed on hydrolysis.

At first an attempt was made to purify the less soluble saponin fraction by a triangular fractional crystallization from methyl and ethyl alcohol. This was partially successful and resulted in the isolation of two saponins, one of which was crystalline and the other amorphous, and which differed in specific rotation and solubility in methyl and ethyl alcohols. Both of these saponins yielded tigogenin on hydrolysis, a fact that increases the minimum number of saponins present in the plant.

Fractional crystallization was tedious but it was found that these two saponins possessed a marked difference in solubility in *t*-butyl alcohol and this gave a rapid method for obtaining the less soluble fraction in a pure form and in quantity. The mixed saponins were repeatedly extracted with hot *t*-butyl alcohol to remove most of the amorphous saponin, and the insoluble portion repeatedly crystallized from ethyl and methyl alcohol until the product was crystalline (Fig. 1) and had a constant rotation. These crystals apparently contain alcohol of crystallization since on drying they fall to an amorphous powder. Although this saponin is only slightly soluble in cold water, its aqueous solutions show all the typical properties of a saponin such as the formation of a stable foam on shaking, toxicity to fish and hemolysis of red blood corpuscles.

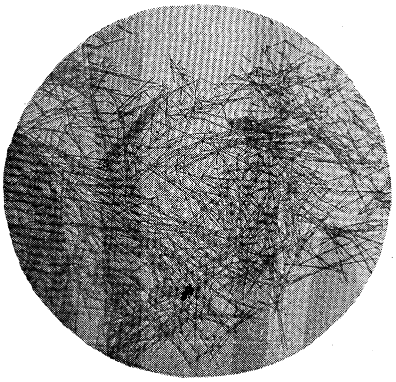

Fig. 1.—Photomicrograph of crystalline amolonin.

The pure crystalline saponin, which has been named "*amolonin*," was hydrolyzed and the sugars identified by the usual procedures. Positive tests were obtained for *d*-glucose, *d*-galactose, *l*-rhamnose and ketoses. Tests for pentoses, mannose and uronic acids were negative. Quantitative estimations showed that the hydrolysis could be represented by the equation

$$\underset{\text{amolonin}}{C_{63}H_{87}O_{14}(OH)_{17}} + 6H_2O \longrightarrow$$
$$\underset{\text{tigogenin}}{C_{27}H_{43}O_2(OH)} + \underset{d\text{-glucose}}{3C_6H_{12}O_6} + \underset{d\text{-galactose}}{C_6H_{12}O_6} + \underset{l\text{-rhamnose}}{2C_6H_{12}O_5}$$

The ketoses are present only in small amounts in the hydrolytic products and probably arise from the aldohexoses by a Lobry de Bruyn–van Ekenstein[5] interconversion.

The formula $C_{63}H_{87}O_{14}(OH)_{17}$ was confirmed by the preparation of a septadeca-acetyl derivative.

Experimental

Isolation of Saponins by Fractional Crystallization.—The bulbs were collected in March, the hairy covering and leaves discarded and the remainder ground in a food chopper. The liquid portion of the ground pulp was removed by a cider press and the press cake washed twice with cold water and twice with methyl alcohol, pressing each time to remove the liquid. The damp press cake was repeatedly extracted with boiling methyl alcohol until the extract no longer gave a precipitate on cooling. The gelatinous brown precipitates were filtered and evaporated to dryness under a vacuum. Further crops were obtained by concentrating the alcoholic filtrates.

When the crude saponin obtained in this way was subjected to a fractional crystallization with sufficient treatments with Norite to remove the color completely, two main fractions were obtained. The less soluble fraction consisted of definitely crystalline needles, $[\alpha]_{546}$ −74.2°, in pyridine. One gram on hydrolysis in 50% aqueous methyl alcohol containing 5% hydrogen chloride gave 0.304 g. of tigogenin, m. p. 197–201° (corr.); after crystallization from isopropyl alcohol and then from benzene it melted at 200–207°. This saponin fraction had a solubility in methyl alcohol of 0.36 g. and in ethyl alcohol of 0.24 g. per 100 g. of solvent at 25° and was practically insoluble in hot *t*-butyl alcohol. The more soluble fraction was usually amorphous although sometimes hair-like crystals were observed under the microscope. The specific rotation in pyridine varied from −68.7 to −63.8° and apparently became less as purification proceeded. One gram on hydrolysis gave 0.411 g. of sapogenin, m. p. 189–204° (corr.) which after crystallization from isopropyl alcohol and from benzene melted at 197–202°. A mixed melting point determination with the sapogenin from the needles showed no depression. The amorphous saponin had a solubility in methyl alcohol of 1.62 g. and in ethyl alcohol of 2.45 g. per 100 g. of solvent at 25° and was quite soluble in hot *t*-butyl alcohol. Both saponins had a low solubility in benzene, acetone, carbon tetrachloride and ether and a high solubility in pyridine, dioxane and glacial acetic acid.

Isolation of Amolonin by Extraction.—The crude dried saponin obtained as above was ground to a powder and

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[5] Lobry de Bruyn and van Ekenstein, *Rec. trav. chim.*, **14**, 156, 204 (1895); Spoehr and Wilbur, *J. Biol. Chem.*, **69**, 421 (1926).

extracted with ten times its weight of boiling *t*-butyl alcohol. The drying, grinding and extraction of the insoluble portion was repeated three or four times until the loss in weight on an extraction was less than 2%. The light brown dried powder was recrystallized from ethyl alcohol and then repeatedly from methyl alcohol until the product was colorless, completely crystalline under the microscope and had a constant rotation. The recrystallizations from methyl alcohol were best performed by dissolving in a minimum of boiling solvent and then concentrating to from one-half to one-fifth of the original volume and cooling rapidly. The product was deposited as amorphous spheres which on standing for some time changed into microscopic needles (Fig. 1). During the first crystallization the crystals appeared to be mixed with small, spherical, gelatinous globules when examined under the microscope but these disappeared as the purification proceeded.

The crystals obtained in this way fell to an amorphous powder on drying. This product gave no perceptible ash on ignition; $[\alpha]^{23}_{546}$ −75.5° in pyridine, −67.5° in dioxane.

Qualitative Detection of Hydrolytic Products.—Pure amolonin was hydrolyzed completely by heating with twenty times its weight of 50% aqueous methyl alcohol containing 5% sulfuric acid. The mixture was heated in a pressure bottle at 100–110° with shaking for two days. The tigogenin was filtered and the filtrate analyzed qualitatively by a procedure essentially as recommended by van der Haar[6] unless otherwise noted.

The usual naphthoresorcinol color reaction for uronic acids, when applied to both the original saponin and to the barium uronate fraction[7] of the sugars, gave doubtful positive tests. Spectrographic examination of benzene extracts compared with controls, especially after the extracts had stood for several hours, showed definitely the absence of uronic acids.

Both types of reactions recommended by van der Haar[6] for the detection of ketoses gave positive tests. Later quantitative work, however, showed that the ketoses were present in such small amount that their presence may be explained by a Lobry de Bruyn–van Ekenstein interconversion[5] during the preparation of the sugar solution. It is possible that fructose does not occur in other saponins where it has been reported as a hydrolytic product.[8]

Nitric acid oxidation of the mixed sugars gave mucic acid, identified by its melting point (209–210°) and mixed melting point, crystal form and the crystal form of its insoluble thallous salt, and saccharic acid identified by the crystal form of its acid potassium salt and by the preparation and analysis of the silver salt. This indicates the presence of galactose and of glucose in the saponin molecule. That these sugars are the *d*-forms is shown by the fact that they are fermented by the yeasts, *Torula lactosa* and *Torula alactosa*, which do not ferment the *l*-forms. The non-formation of a phenyl-hydrazone was taken to indicate the absence of mannose.

For the detection of pentoses and methyl pentoses the tests depending on their conversion to furfural and methylfurfural and on the color reactions for these compounds were used. Both visual and spectroscopic examination of the color reactions showed the absence of pentoses and the presence of methyl pentoses. To identify the methylpentose, the glucose was removed by fermentation with baker's yeast and the solution of galactose and methyl pentose treated with α-methylphenylhydrazine. The formation and identification of the methylphenylhydrazone of galactose, m. p. 187.8° (corr.) further proved the presence of this sugar. After the removal of galactose as the hydrazone, the methylpentose was regenerated and the solution freed of methylphenylhydrazine by treatment with formaldehyde as recommended by van der Haar.[6] On subsequent reaction with *p*-bromophenylhydrazine an osazone formed which appeared to be identical with *p*-bromophenylrhamnosazone as determined by melting point (213–214° corr.) and mixed melting point with an authentic specimen. This identification was not considered entirely satisfactory because the product could not be recrystallized, and the melting points were really decomposition points. Examination under the polarizing microscope did not yield further information since *p*-bromophenylrhamnosazone needles show parallel extinction. The β-naphthylhydrazone was a much more satisfactory derivative and proved to be identical (m. p. 190–191°, $[\alpha]_{546}$ −12.6° in pyridine) with the β-naphthylhydrazone of *l*-rhamnose. The extinction angle of the crystals is 42.3°.

No other products of hydrolysis were detected and the following quantitative work shows that no other components can be present in the saponin molecule.

Estimation of Tigogenin.—Samples of pure amolonin weighing from 0.3 to 3.0 g. were hydrolyzed under different conditions and the amount of tigogenin formed was determined by filtering, washing and drying to constant weight at 100°. Hydrolyses in 50% aqueous methyl alcohol containing 5% hydrogen chloride at the boiling point for seventy hours gave 30.4 and 29.4% tigogenin. Using 5% sulfuric acid and shaking in a sealed tube at 90° for sixty-five hours gave 28.4 and 28.0% tigogenin. Using water containing 4% sulfuric acid and shaking in a sealed tube at 90° for five days gave 30.4%. The average of these five determinations is 29.3%.

Preparation of Sugar Solutions for Analysis.—The filtrates after removal of tigogenin were treated with freshly prepared pure barium carbonate, made from barium hydroxide and carbon dioxide, care being taken to avoid an excess of barium carbonate and to maintain the *p*H at 6.0 ± 0.5. In this way appreciable conversion of the aldohexoses to ketoses is avoided. The solutions were evaporated in a vacuum desiccator at 40–50° until a thick sirup was obtained. Any precipitate that formed during the evaporation was filtered and the *p*H of the filtrate adjusted before further evaporation. Solutions of this sirup failed to ferment and it was thought at first that this might be due to the traces of barium salts that always remained. Solutions neutralized with sodium bicarbonate, however, behaved in the same way. It was found that non-fermentation was due to the presence of barium or of sodium methyl sulfate, an appreciable amount of methyl hydrogen sulfate having been formed during the hydrolysis in 50%

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(6) Van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydsaüren," Gebrüder Borntraeger, Berlin, 1920.

(7) Link and Dickson, *J. Biol. Chem.*, **86**, 491 (1930); Link and Nedden, *ibid.*, **94**, 307 (1932); Hopkins, Peterson and Fred, THIS JOURNAL, **53**, 306 (1931).

(8) Kofler, "Die Saponine," Julius Springer, Vienna, 1927, p. 96.

methyl alcohol. These salts were removed either by repeated extraction of the sugars with absolute alcohol and evaporation to dryness, or by boiling the sirup with dilute sulfuric acid for several hours and precipitating the sulfuric acid with barium carbonate. The sugar sirups prepared in this way were diluted to a known volume and aliquot portions analyzed according to procedures recommended by van der Haar.[6]

Rhamnose.—In order to avoid undue decomposition of the rhamnose the determinations were made on sugar solutions from which barium methyl sulfate had not been removed completely. The sugars from 1.8835 g. of amolonin were diluted to 10 cc. and 3.67 cc. of this solution yielded 0.1204 g. of methylfurfural phloroglucide. From Ellet's tables as given by van der Haar this corresponds to 0.1826 g. (0.00100 mole) of rhamnose hydrate. The corresponding amount of amolonin would have yielded 0.00048 mole of tigogenin so that the molecular ratio is 2 to 1.

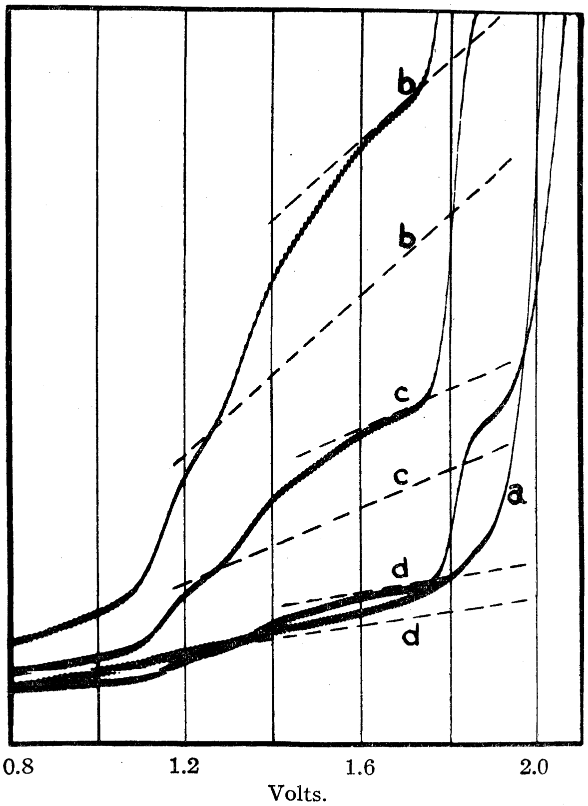

Fig. 2.—Polarigram of sugar solution from the hydrolysis of amolonin.

Ketoses.—The simplest procedure for the estimation of ketoses in the presence of aldoses is by means of the polarigraph since ketoses are reduced at the dropping mercury cathode whereas aldoses are not.[9] If a polarigram is made of a solution of a ketose, the potential at which the wave develops depends on the sugar, the temperature and somewhat on the concentration, while the height of the wave, that is, the vertical distance between two lines tangential to the curve at the points of inflection, is directly proportional to the concentration. The test solution was made by diluting the sugars from 2.9081 g. of amolonin to 25 cc. Figure 2 shows four curves: (a) 5 cc. of 0.2 *M* calcium chloride in the cell, hydrogen bubbled through for twenty minutes and the curve taken at $s = 0.1$ (s = sensitivity of the galvanometer); (b) 0.1 cc. of test solution added to the cell, hydrogen passed through for ten minutes and the curve taken at $s = 0.1$; (c) repeat of (b) at $s = 0.05$; (d) repeat of (b) at $s = 0.02$. Figure 3 gives curves for a solution of fructose of known concentration which gave curves similar to the unknown when run under the same conditions. The correct concentration to accomplish this was arrived at by trial and was 0.0111 mg. of fructose per cc. in approximately 0.2 *M* calcium chloride solution. The letters have the same significance as in Fig. 2. It is seen that the fructose wave occurs at approximately the same voltage as the unknown. Height bb in Fig. 3 is 3.16 cm. while height cc at half the sensitivity is 1.51 cm., which checks the reproducibility of separate runs. Taking the height of 1.51 cm. as corresponding to a concentration of 0.0111 mg. of fructose per cc., the height cc in Fig. 2 of 1.01 cm. corresponds to 0.00743 mg. per cc. of calcium chloride solution or 0.379 mg. (0.0000021 mole) per cc. of original sugar solution. The corresponding amount of amolonin would have yielded 0.000081 mole of tigogenin, or one mole of fructose for 38 moles of tigogenin, an impossible ratio.

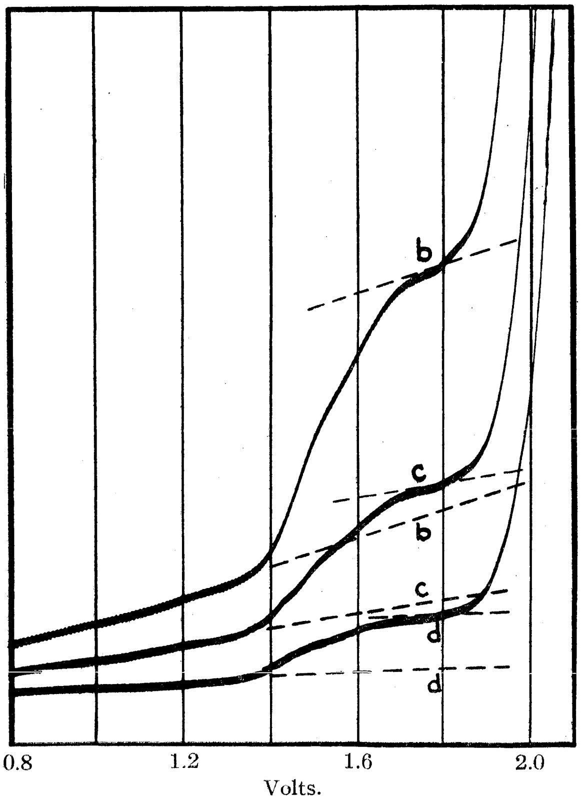

Fig. 3.—Polarigram of standard fructose solution.

It should be noted that two minor waves occur in Fig. 2 beginning at approximately 1.1 and 1.8 volts that do not

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[9] Heyrovský and Smoleř, *Coll. Czechoslov. Chem. Comm.*, **4**, 521 (1932); *C. A.*, **27**, 1828 (1933). We are indebted to Dr. O. H. Mueller of the Physiology Department for the use of his polarigraph and for his assistance in this investigation.

occur in Fig. 3. The wave at 1.8 v. is due to traces of barium ion but the impurity causing that at 1.1 v. is unknown.

Glucose and Galactose.—These sugars were determined by fermentation in van Iterson–Kluyver tubes according to the general procedure given by van der Haar. Special yeasts, different from those recommended by van der Haar, were obtained in pure culture through the courtesy of Professor T. Skogsberg of the Hopkins Marine Station. These yeasts were *Torula lactosa* and *Torula alactosa*, both of which ferment *d*-glucose and *d*-galactose, and *Torula datilla* and *Torula monosa*, which ferment glucose but not galactose. None of these yeasts ferments *l*-rhamnose.[10] Controls were run on 1, 2 and 4% solutions of glucose and galactose with each yeast in order to determine the carbon dioxide evolved and the amount of carbon dioxide remaining in solution. The latter volume depended on the type of yeast and the sugar, and for the mixture of sugars a weighted average was used and added to the volume read. Table I gives the average values for the data obtained on the controls. The gas volumes are for 0° and 760 mm.

TABLE I

CONTROL FERMENTATIONS OF GLUCOSE AND GALACTOSE

	Vol. of CO_2 dissolved per cc. of solution		Mg. of hexose per cc. of CO_2 formed	
Sugar	Glucose	Galactose	Glucose	Galactose
T. datilla	0.51	...	4.65	..
T. monosa	.42	...	4.75	..
T. alactosa	.51	0.48	4.70	4.61
T. lactosa	.65	.14	4.37	5.10

In a typical run the purified sugars from 2.9081 g. of amolonin were diluted to 25 cc. and 3 cc. of this solution mixed with 6 cc. of nutrient broth. The solution was passed through a Chamberland filter and 1 cc. placed in each of four fermentation tubes and inoculated under sterile conditions with the four yeasts. The volumes of carbon dioxide evolved after three days at 32° were corrected to 0° and 760 mm. and the estimated amount of dissolved carbon dioxide added. This gave for *T. datilla*, 3.28 cc., *T. monosa*, 3.24 cc.; *T. alactosa*, 4.22 cc., *T. lactosa*, 4.12 cc. The first two volumes can be converted to glucose directly and correspond to 15.3 and 15.4 mg. per cc. The volumes of carbon dioxide from galactose can be obtained by subtracting each of the volumes from *T. datilla* and *T. monosa* from each of the volumes from *T. alactosa* and *T. lactosa*, giving, respectively, 0.94, 0.98, 0.84, and 0.88 cc. When the first two volumes are multiplied by 4.61 and the last two by 5.1, one obtains 4.3, 4.5, 4.3 and 4.5 mg. of galactose per cc. Multiplying by the aliquot factor, 75, one obtains 1.1512 g. (0.00639 mole) of glucose and 0.330 g. (0.00183 mole) of galactose from 2.9081 g. of amolonin which yields 0.00203 mole of tigogenin. The ratio of tigogenin to glucose to galactose is therefore 1 to 3 to 1.

The results of the determinations of rhamnose, glucose and galactose were checked by comparison with total aldoses by iodine oxidation.[11] Thus a solution of the mixed sugars gave rhamnose 12.6 mg. per cc. and total hexoses by fermentation 29.5 mg. per cc. or a total of 42.0 mg. per cc. The average aldose content found by iodine oxidation on the assumption of 2 moles of methylpentose to 4 moles of hexose was 40.1 mg. per cc.

Septadeca-acetylamolonin.—Amolonin was fully acetylated by dissolving 0.970 g. in 5.4 cc. of pyridine and 4.9 cc. of acetic anhydride. After standing for one day at room temperature, the solution was poured into water and filtered. The precipitate was crystallized from dilute methyl alcohol and dried in vacuum at 100°; $[\alpha]^{20}_{546}$ −33.65° in pyridine; recrystallized and dried, $[\alpha]^{20}_{546}$ −33.53°. Analysis for acetyl:[12] Calcd. for $C_{63}H_{87}O_{14}(OCOCH_3)_{17}$: % acetyl, 35.32. Found: 35.67, 35.14.

Combustion Analyses.—Amolonin Calcd. for $C_{63}H_{104}O_{31}$: C, 55.71; H, 7.74. Found: C, 55.39, 55.38, 55.56, 55.32; H, 7.99, 7.98, 8.02, 7.94. Amolonin Septadeca-acetate. Calcd. for $C_{97}H_{138}H_{48}$: C, 56.23; H, 6.71. Found: C, 55.85 55.78; H, 6.90, 6.82.

Summary

Amolonin, a crystalline saponin obtained from *Chlorogalum pomeridianum* has the formula $C_{63}H_{87}O_{14}(OH)_{17}$. On hydrolysis it yields for each mole of tigogenin, one mole of *d*-galactose, two moles of *l*-rhamnose and three moles of *d*-glucose. The septadeca-acetyl derivative of amolonin has been prepared.

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[10] Harrison, *Trans. Roy. Soc. Can.*, **21**, Sec. 5, 341 (1927); **22**, Sec. 5, 187 (1928).

[11] Cajori, *J. Biol. Chem.*, **54**, 617 (1922); Macleod and Robison, *Biochem. J.*, **23**, 517 (1929).

[12] Gattermann–Wieland, "Laboratory Methods of Organic Chemistry," Macmillan Co., New York, 1932, p. 70.

[CONTRIBUTION FROM THE DEPARTMENTS OF AGRICULTURAL BACTERIOLOGY AND AGRICULTURAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

Mechanism of Symbiotic Nitrogen Fixation. I. The Influence of pN_2[1]

BY P. W. WILSON

Research on fixation of elemental nitrogen through association of leguminous plant and bacteria (*Rhizobia sp.*) has been conducted for almost a century, but the chemical mechanism of the process has remained practically unattacked. The scanty nature of our knowledge of this aspect of the problem arises mainly from lack of suitable techniques to carry on the research; the isolation of intermediates, which has been so successful in elucidating the mechanism of a fermentation reaction, is not readily applied because of difficulties in separating from the plant cells products which may be definitely ascribed to the fixation process.

Application of physical chemistry techniques to the problem hitherto has not been attempted.[2] Even without definite knowledge of the exact nature of the key-reactions, many of their properties may be ascertained by determining the effect of controlled changes in the physical and chemical environment, *e. g.*, temperature, *p*H, oxidation–reduction potentials, and pressure of gases (nitrogen, oxygen, carbon dioxide). In this paper are discussed the effects of changes in the pN_2 of the atmosphere supplied inoculated clover plants on the fixation reaction.

Experimental and Results

Technique.—Red clover (*Trifolium pratense*) was used as the host plant and inoculated with an efficient strain of the proper organism, *Rhizobium trifolii*. Twenty plants were grown in a 10-liter Pyrex pressure bottle on a nitrogen-poor sand substrate to which was added the required plant nutrients. An atmosphere of any desired composition was maintained in these bottles by evacuation followed by addition of the required gases. Cylinder gases, passed through a purifying chain of sodium hydroxide, sulfuric acid, alkaline potassium permanganate, distilled water, and finally a sterile cotton filter were used in all the experiments. The atmospheres were renewed twice a week; the pCO_2 was maintained inside the bottles at 0.1 to 0.5% by the method described by Smyth.[3] In a few experiments 64-oz. (2-liter) flint glass bottles were used as the plant container, but these were not so satisfactory because of difficulty in maintaining uniform pCO_2 and of the restriction on the growth of the plant. The experiments were conducted in a greenhouse equipped with artificial lighting and other means for controlling light and temperature.[4] At the start of each experiment the plants were supplied with air containing 0.1% carbon dioxide until fixation was well under way and the period of nitrogen hunger was passed. They were then transferred to the various atmospheres and allowed to grow for fifteen to fifty-five days before harvest. No combined forms of nitrogen were furnished the inoculated plants, but a sufficient quantity of all other plant nutrients was available; hence the limiting factor for growth was primarily rate of fixation of free nitrogen. Plants given combined nitrogen were supplied with 3 to 5 mg. of NH_4NO_3–N per bottle at the start which enabled them to be at the same stage of development as the inoculated plants at the time atmospheres were first changed. Five to 10 mg. of NH_4NO_3–N was then added weekly to all cultures of the combined nitrogen series depending on the rate of growth maintained by the plants; this addition of NH_4NO_3–N was uniform to all plants in the combined nitrogen series in a given experiment, *i. e.*, each culture received the same quantity at each time of addition.

In the first experiments it was found that replicates of the same treatment might vary 10 to 20% in total nitrogen per 10 plants at time of harvest. In an effort to reduce the variation, plant cultures *in a given experiment* were selected for uniformity at time they were placed under the different atmospheres and various technical devices employed, *e. g.*, rotation of cultures on the benches in the green house, in an effort to eliminate the non-uniformity of environmental factors. In spite of these precautions variations of 5 to 10% frequently were observed in duplicates. Since plant growth tends to be logarithmic in the early stages of development, initial small differences may be increased considerably unless the experiments are extremely short-time in nature. The best solution of this technical difficulty appears to be to draw conclusions only after numerous replications of the experiments have been made under conditions which will vary the *rate* and *extent of growth* together with a statistical analysis of the data. In this report data are considered from a total of 20 experiments covering a time period of two years. The experiments were made during all seasons with consequent differences in (1) rate of growth (average daily gain per 10 inoculated plants has varied from 0.2 to 1.0 mg.); (2) extent of growth (from 5 to 35 mg. total nitrogen per 10 plants); (3) length of experiment (from 15 to 57 days); and (4) initial size of plant (initial nitrogen content from 1.05 to 3.50 mg.).

Preliminary experiments were made as follows: one series of clover plants was grown under a vacuum of 0.5 atm., a second at atmospheric pres-

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(1) Herman Frasch Foundation in Agricultural Chemistry, Paper No. 119.

(2) Burk and collaborators have been very successful in studying the mechanism of fixation by *Azotobacter* through the physical chemical approach; [*Ergebnisse Enzymforsch*, **3**, 23 (1934)]. The Warburg technique used by Burk would not be applicable to the symbiotic process so long as fixation must be accomplished with the association of bacteria and plants.

(3) Smyth, *Science*, **80**, 294 (1934).

(4) Wilson and Georgi, *Bot. Gaz.*, **94**, 346 (1932).

sure and a third at a pressure of 1.8 atm. maintained by added nitrogen gas. In this manner plants developed under pN_2 of 0.39, 0.78 and 1.56 atmospheres; under these conditions it was found that the fixation of nitrogen is independent of the pN_2 used as is indicated by the data in Table I, experiments I and II.

TABLE I

EFFECT OF pN_2 ON NITROGEN FIXATION OF RED CLOVER IN ABSENCE OF INERT GAS

pN_2, atm.	Total pressure, atm.	Dry weight, mg.	Total N, mg.	% N
		Expt. I		
0.39	0.50	760	21.42	2.82
.78	1.00	877	24.10	2.75
1.56	1.76	805	21.50	2.67
		Expt. II		
0.39	0.50	1045	26.75	2.56
.78	1.00	1032	26.40	2.56
1.56	1.76	1174	29.50	2.51
		Expt. III		
0.75	1.00	366	7.65	2.09
.20	0.45	323	6.55	2.03
.11	.36	359	7.25	2.02
.06	.31	274	4.83	1.76
		Expt. IV		
0.80	1.00	1600	28.0	1.75
.20	0.40	1555	26.9	1.73
.11	.31	1635	29.0	1.77
.06	.26	1083	17.0	1.57
		Expt. V		
0.25	0.45	1265	30.7	2.43
.12	.32	1190	25.7	2.16
.06	.26	546	9.55	1.75
		Expt. VI		
0.25	0.45	1590	35.7	2.25
.12	.32	1620	34.0	2.10
.06	.26	682	10.3	1.51

Expt.	Dates	Days at pN_2 shown in	N at start, mg.
I	6/16/33–8/6/33	30	2.06
II	8/14/33–10/14/33	51	2.38
III	2/1/35–3/7/35	15	1.50
IV	3/11/35–5/27/35	43	2.20
V	9/23/35–12/2/35	32	2.45
VI	10/16/35–12/28/35	40	2.50

TABLE II

COMPARISON OF pN_2 ON ASSIMILATION OF FREE AND COMBINED NITROGEN BY RED CLOVER

pN_2, atm.	Total pressure, atm.	Dry weight, mg.	Total N, mg.	% N
		Expt. VII, Inoculated		
0.90	1.00	732	19.4	2.65
		816	22.7	2.79
.40	0.50	958	25.1	2.62
		1002	27.1	2.71
.20	.30	578	15.2	2.64
		774	20.4	2.64
07	.17	394	8.9	2.26
		NH_4NO_3		
0.40	0.50	1025	29.0	2.83
.20	.30	889	26.6	2.99
.07	.17	906	32.0	3.53
		Expt. VIII, Inoculated		
0.90	1.00	1110	24.3	2.19
		930	20.8	2.24
.40	0.50	700	14.7	2.10
		760	16.4	2.16
.20	.30	860	18.3	2.13
		770	17.0	2.20
.07	.17	490	9.3	1.90
		NH_4NO_3		
0.90	1.00	850	26.6	3.13
.40	0.50	1220	30.0	2.46
		1130	30.6	2.71
.20	.30	1020	32.3	3.16
		690	23.0	3.33
.07	.17	820	27.0	3.29
		1020	31.7	3.11
		Expt. IX, Inoculated		
0.80	1.00	860	18.3	2.13
.70	1.00	880	20.3	2.31
.20	0.50	930	21.7	2.33
.08	.38	610	10.8	1.77
.04	.34	620	7.2	1.16
		NH_4NO_3		
0.70	1.00	720	29.7	4.12
.20	0.50	830	31.5	3.80
.08	.38	895	33.6	3.75
.04	.34	860	34.6	4.02
		Expt. X, Inoculated		
0.80	1.00	572	15.1	2.64
.15	0.35	550	13.75	2.50
.10	.30	581	16.50	2.74
.07	.27	497	10.35	2.08
.04	.24	289	5.00	1.73
		NH_4NO_3		
0.80	1.00	810	24.0	2.96
.15	0.35	920	23.6	2.57
.10	.30	820	24.1	2.95
.07	.27	840	25.0	2.99
.04	.24	830	24.2	2.91

Expt.	Dates	Days at pN_2 shown	N at start, mg.
VII	7/5/34–9/3/34	38	1.55
VIII	9/12/34–11/2/34	25	3.50
IX	11/9/34–1/2/35	27	2.50
X	12/9/35–2/4/36	29	2.05

These observations were confirmed and extended by experiments in which the pN_2 was varied from 0.06 to 0.80 atm., the pO_2 being kept constant in a given experiment, and no inert gas being added, *i. e.*, the plants were grown under different total pressures. The results of experiments III and IV show (Table I) that the nitrogen fixation by red clover is independent of the pN_2 above 0.11 atm. but if the pN_2 is decreased to 0.06 atm. a definite inhibition of fixation occurs. This decrease of fixation with pN_2 at pressures below 0.11 atm. was further confirmed in experiments V and VI in which only the lower pressures were included. As shown by the data at the bottom of the table the response is independent of the length of time of experiment (time varied three-fold) or the development of plant at time placed under different pN_2 (initial nitrogen content varied two-fold).

In order to demonstrate that the response to pN_2 is concerned with the nitrogen fixation process in the plant and not with the general development, it is necessary to demonstrate that growth of uninoculated plants receiving combined nitrogen is completely independent of the pN_2. This was done in a series of experiments whose results are summarized in Table II.

Duplicate determinations are given for experiments VII and VIII in order to illustrate the variation found. Because of the limited number of bottles available not all the cultures were made in duplicate in these first experiments, but in later work this was always done, and by improvements in the technique already described, the variation was somewhat reduced. The values given in tables for experiments III to VI and IX to XV are averages of duplicates whose total nitrogen content differed by 10% or less. The data presented in Table II indicate that fixation of nitrogen by clover is essentially independent of the pN_2 of the atmosphere until the latter is decreased to a pressure below 0.10 atm. The effect of the pN_2 in this lower range is clearly on the fixation process and not on the general development of the plant since the nitrogen content of plants supplied combined nitrogen is independent of the pN_2 over the entire range studied.

That the characteristics of the pN_2 function do not arise because of growing the plants under reduced pressures was demonstrated in further experiments in which the nitrogen removed was replaced by the inert gases, helium and argon. Since the argon used contained 16% nitrogen, it was not feasible to use partial pressures of nitrogen below 0.16 atm. when this gas was added. Experiments XI, XII and XV were made in 64-oz. bottles, the others in 10-liter bottles. The data in Table III indicate that fixation of elemental nitrogen by inoculated clover plants grown in the presence of helium, argon, or no added inert gas is independent of the pN_2 as this is varied from about 0.10 to 0.80 atm. Below a pN_2 of 0.10 atm. fixation decreases rapidly with the nitrogen content of the atmosphere. As observed in the other experiments this effect of the pN_2 is on the fixation process since plants supplied combined forms of nitrogen assimilate these independent of the pN_2 in the atmosphere.

From the data of Table III certain generalizations concerning the symbiotic nitrogen-fixing enzyme system in red clover may be formulated, but before this is done, it is necessary that the essential characteristics of the pN_2 function be established definitely. In addition to the experiments reported in the tables, 5 other experiments have been made with essentially the same results. The data from these 20 experiments, 11 of which included combined nitrogen series, were placed on a comparable basis by calculating the *relative* total nitrogen and % N in the plants using the air controls ($pN_2 = 0.80$ atm.) as the base, 100. The plot of the data in Fig. 1 shows that in a given experiment inoculated plants grown under a pN_2 greater than 0.10 atm. may contain more or less nitrogen than the air controls, the relative values varying from 80 to 120; the mean value for all the experiments was 90 to 100 for these pressures. On the other hand for pN_2 less than 0.10 atm. the relative values range from 35 to 65 with a mean value of 45. Final total nitrogen content of the plants supplied with combined nitrogen exhibited the same type of variation about the 100% value but the mean values were 98 to 104% and apparently independent of the pN_2 throughout the range under investigation.

It was noted in the course of these and other experiments that one of the best indicators of inhibition of the fixation process was a decline in the % N in the plant. In some respects this datum is more sensitive to factors which affect the nitrogen fixation system than is total nitrogen. For example, two plant cultures which differ by a comparatively small amount at the start of an experiment are given different treatments. At the end of the test the difference in total nitrogen content appears to be significant, and this would be interpreted as arising from treatment, when actually it is only an expression of the difference in the original cultures. This is a source of error

TABLE III

INFLUENCE OF pN_2 ON NITROGEN FIXATION BY CLOVER IN THE PRESENCE OF HE AND A

pN_2, atm.	Gas added	Dry weight, mg.	Total N, mg.	% N
		Expt. XI, Inoculated		
0.80	...	570	13.4	2.35
.40	He	430	8.9	2.05
.20	He	560	13.7	2.49
.10	He	500	11.7	2.33
		NH_4NO_3		
0.80	...	580	19.2	3.31
.40	He	710	25.4	3.58
.20	He	600	18.3	3.05
.10	He	620	17.2	2.77
		Expt. XII, Inoculated		
0.80	...	424	8.90	2.10
.20	He	379	8.13	2.15
.11	He	300	5.64	1.89
.06	He	268	4.32	1.61
		Expt. XIII, Inoculated		
0.80	...	1455	25.15	1.73
.25	...	1818	26.90	1.48
.12	...	1840	32.40	1.76
.06	...	923	13.20	1.43
.25	He	1780	29.80	1.67
.12	He	1530	30.00	1.96
.06	He	1010	16.15	1.60
.32	A	1465	25.9	1.77
.16	A	1430	26.4	1.85
		Expt. XIV, Inoculated		
0.80	...	310 330	4.94 5.78	1.59 1.75
.40	He	202	4.10	2.04
.20	He	200	4.00	2.00
.11	He	200	4.20	2.10
.40	A	300	4.89	1.63
.20	A	375	6.10	1.62
		NH_4NO_3		
0.80	...	245	13.45	5.50
.20	He	260	14.15	5.43
.11	He	210	12.95	6.17
.40	A	220	10.26	4.67
.20	A	385	17.35	4.50
		Expt. XV, Inoculated		
0.80	...	510	15.1	2.96
.15	He	558	14.1	2.52
.10	He	490	12.1	2.46
.07	He	412	9.3	2.26
.04	He	320	7.50	2.36
		NH_4NO_3		
0.80	...	573	19.2	3.35
.15	He	590	19.5	3.30
.10	He	600	20.2	3.37
.07	He	520	18.7	3.60
.04	He	610	18.0	2.93

Expt.	Date	Days at pN_2 shown	N at start, mg.
XI	12/22/34–2/11/35	24	1.05
XII	2/1/35–3/7/35	15	1.50
XIII	6/17/35–9/12/35	57	3.50
XIV	4/17/35–6/11/35	32	1.10
XV	12/9/35–2/4/36	29	2.05

that must be constantly guarded against in experiments in which final total growths are taken rather than growth rates. However, in these experiments it was noted that even though replicates might vary considerably in total nitrogen (final growth) the percentage nitrogen was much more stable; frequently the duplicate with the lower total nitrogen had the higher % N, *i. e.*, there is no correlation between total nitrogen and % N if replicates only are considered. On the other hand, under circumstances in which fixation is obviously restricted, *e. g.*, very low pN_2, the percentage nitrogen in the plant is definitely decreased. This suggests an additional criterion for distinguishing between those factors which affect the total nitrogen content through specific effect on the fixation system and those which affect the total nitrogen only through effects on the

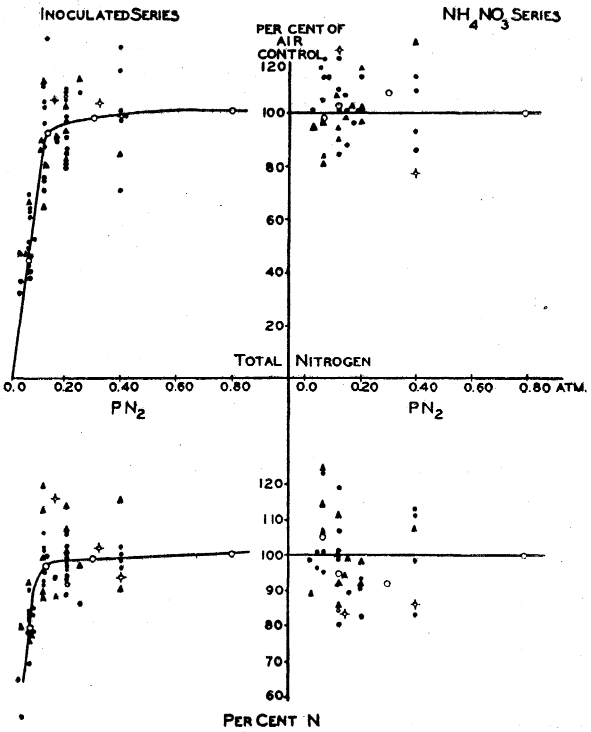

Fig. 1.—Comparison between the pN_2 functions of clover plants using free and combined nitrogen. Value for air controls (pN_2 = 0.80 atm.) taken as 100 in each case. ●, No added gas; ▲, helium; -ϕ-, argon; ○, mean of all points in each pressure group.

general growth of the plant. Thus a partial control is available for experiments in which for technical reasons growth rate studies are not particularly suitable.

Plot of the % N in the plants from 20 experiments on a relative basis confirmed the conclusions drawn from the total nitrogen data. As can be seen in Fig. 1 no consistent change in the % N occurs in inoculated plants until the pN_2 of the atmosphere is decreased to less than 0.10 atm., then a significant decline is observed. The scatter of the points for pressures greater than 0.10 atm. is usually within ±10% of the 100% line. With plants furnished combined nitrogen, % N in the plants did not appear to change significantly with pN_2 over the entire range, although the scatter of the points was greater.

Discussion

The qualitative observations made from a study of the figures were verified by a statistical analysis of the data from the pooled experiments. The different pressures used were grouped as follows: group 1, 0.04 to 0.07 atm.; 2, 0.10 to 0.12 atm.; 3, 0.20 to 0.40 atm.; 4, 0.80 atm.; and the data from the several experiments subjected to analysis of variance.[5] In the inoculated series 11 experiments were available in which all four pressure groups were represented; in the combined nitrogen series groups 1, 2 and 3 (6 experiments) and groups 2, 3 and 4 (7 experiments) were analyzed separately since all four groups were not represented in all experiments. The analyses show: (1) in the inoculated series the observed differences in total nitrogen and in % N among pressure groups 2, 3 and 4 are not statistically significant, but the differences between group 1 and the remainder are highly significant; (2) in the combined nitrogen series all the observed differences could have arisen from random sampling. The principal statistical constants given in Table IV likewise point to this conclusion.

In consideration of the following statistical analysis of the data, it appears that at pressures of nitrogen greater than 0.10 atm. most of the active points of the enzyme system concerned with the fixation are saturated so that the fixation is independent of the pN_2; below this pressure the quantity of nitrogen adsorbed, and hence fixed, is dependent on the pN_2.

TABLE IV

COMPARISON OF MEANS OF DIFFERENT pN_2 GROUPS

Inoculated

Function	No. of expts.	Pressure, mg. 1[a]	2	3	4	Standard error,[b] mg.
Total N	11	10.99	20.60	22.32	22.52	1.615
% N	11	1.61	1.90	1.88	1.94	0.038
			NH_4NO_3			
Total N	6	31.32	33.02	32.93	...	2.770
	7	...	20.80	22.38	20.73	1.315
% N	6	3.28	3.03	2.85	...	0.158
	7	...	3.42	3.33	3.69	.183

[a] Pressures: 1, 0.05–0.07 atm.; 2, 0.10–0.12 atm.; 3, 0.20–0.40 atm.; 4, 0.80 atm.

[b] Of difference between two means, *i. e.*, difference between two means must be twice this before it can be regarded as significant.

Because of variation in the plants it is not possible to characterize definitely the exact nature of the curve in the region in which complete saturation is replaced by partial saturation since relatively large differences are necessary in order that they fall outside the limits of experimental error. Likewise, control of the pN_2 under the experimental conditions described is probably restricted to about ±0.01 to 0.02 atm. In spite of the limitations the data in Table IV show that it is improbable (38:1 odds): (1) that the true mean of the 0.10–0.12 atm. series is less than 18.32 mg. (observed mean minus twice standard deviation) and (2) that the true mean of the air control groups is greater than 24.80 mg. This means that under the most unfavorable assumptions, a 75% saturation at pN_2 of 0.10 to 0.12 atm. is indicated. Considerably higher saturation, (up to 100%) is more probable; this is borne out by consideration of the % N data. The curves for the inoculated series in Fig. 1 were drawn through the mean values for each pressure group with the result that the transition regions are not well defined; it is not improbable that the true curve of the pN_2 function approximates a typical Langmuir adsorption isotherm.

Burk[2,6] on the basis of both total growth (respiration) and rate of respiration has shown that fixation of nitrogen by the *azotase* complex in the free living nitrogen-fixing bacteria *Azotobacter* is a function of the pN_2 until the latter becomes relatively large—up to 5 to 10 atmospheres—and that the rate is almost directly proportional to the pN_2 up to 0.5 atm. The dissociation constant (K_{N_2}, equivalent to substrate concentration at which rate is 50% of maximum) of the enzyme–nitrogen

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(5) Fisher, "Statistical Methods for Research Workers," third edition, Oliver and Boyd, London, 1930.

(6) Burk, *J. Phys. Chem.*, **34**, 1195 (1930).

complex was found to be 0.215 ± 0.002 atm., a value which Burk states is somewhat high in comparison with other gases for different enzyme systems. In our own work the data observed were total growth and not growth rates, hence K_{N_2} cannot be precisely determined from these values. However, since under the experimental conditions used, the rate will roughly follow the final observed total growth, an approximation of K_{N_2} is possible. It would appear that K_{N_2} for the symbiotic system is below 0.10 atm. possibly in the neighborhood of 0.05 atm. Whether this difference between the dissociation constants represents a real difference in these two biological nitrogen-fixing systems is still open to question, but further experiments concerned with the character of the enzyme complex should be able to supply an answer.

Summary

The relation of the partial pressure of nitrogen to fixation of the free element by the symbiotic system in red clover has been studied over the range of pN_2 from 0.04 to 1.56 atm. in the presence of no added gas, helium and argon. Statistical analyses of data from 11 experiments indicate that the fixation of nitrogen is essentially independent of pN_2 when the latter exceeds 0.10 to 0.20 atm. but decreases rapidly with pN_2 as the latter is diminished below 0.10 atm. This pN_2 function is characteristic of the nitrogen fixing process since it is not observed in plants supplied with combined nitrogen. The implications of these observations for the mechanism of the symbiotic fixation process are discussed.

MADISON, WISCONSIN RECEIVED JANUARY 29, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Mechanism of the Dehydration of Calcium Sulfate Hemihydrate

BY HARRY B. WEISER, W. O. MILLIGAN AND W. C. EKHOLM

During the past few years several papers have appeared which reopen the question of the chemical individuality of the so-called calcium sulfate hemihydrate or plaster of Paris and the mechanism of its dehydration. Linck and Jung[1] deduced from dehydration data that plaster of Paris loses its water after the manner of zeolites. Balarew[2] at different times has been on all sides of the question. At first[2a] he claimed that the dehydration isobar would indicate that the water is present in the form of a true hydrate; later[2b] he stated that the dehydration curves show the water to be held in a new way "half-hydratic and half-zeolitic"; finally,[2c] he concluded that the water is lost in the manner of zeolites. Gibson and Holt[3] concluded from pressure–temperature curves that the water is lost continuously as in a zeolite. Parsons[4] claimed that all the water in gypsum may be lost by heating without the intermediate formation of a hemihydrate.

Jung,[5] Ramsdell and Partridge[6] and Caspari[7] reported that the x-ray diffraction pattern of calcium sulfate hemihydrate and its dehydration product[8] are identical, in agreement with the view that the hemihydrate is a zeolite. Onorato[9] and Gallitelli[10] found the hemihydrate and dehydrated hemihydrate to have the same type of structure but recognized minor differences in the powder x-radiograms. Feitknecht[11] likewise observed differences in the two patterns provided care was taken to prevent rehydration of the dehydrated hemihydrate. Feitknecht believed that Jung's dehydrated sample must have rehydrated before x-ray examination was made.

From the above survey it appears to be an open question whether "calcium sulfate hemihydrate" is a true chemical hydrate which gives a definite x-radiogram and decomposes to "dehydrated hemihydrate" which gives a different x-radiogram

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[1] Linck and Jung, *Z. anorg. allgem. Chem.*, **137**, 407 (1924).

[2] (a) Balarew, *ibid.*, **156**, 258 (1926); (b) *Kolloid.-Z.*, **48**, 63 (1929); (c) Balarew and Koluschewa, *ibid.*, **70**, 288 (1935).

[3] Gibson and Holt, *J. Chem. Soc.*, 638 (1933).

[4] Parsons, Univ. Toronto Studies, Geol. Ser., No. 24, 1927, p. 24.

[5] Jung, *Z. anorg. allgem. Chem.*, **142**, 73 (1925).

[6] Ramsdell and Partridge, *Am. Mineral.*, **14**, 59 (1929).

[7] Caspari, *Nature*, **133**, 648 (1934).

[8] It should be pointed out that van't Hoff, Henrichsen and Weigert [*Sitz. akad. Wiss.*, 570 (1901)] prepared a "soluble" form of calcium sulfate by treating gypsum with nitric acid containing 2.38 moles of water per mole of nitric acid, above 50°. This material was named "soluble anhydrite" to distinguish it from the ordinary "insoluble" anhydrite. Although the term "soluble anhydrite" is usually applied to the product formed by the dehydration of calcium sulfate hemihydrate below 200°, Balarew[2b] believes this to be distinct from the "soluble anhydrite" of van't Hoff. Both Balarew and Ramsdell and Partridge[6] prefer to apply the term "dehydrated hemihydrate" to the dehydration product, and this terminology is used in this paper.

[9] Onorato, *Periodico Min.*, **3**, 138 (1932).

[10] Gallitelli, *ibid.*, **4**, 1, 132 (1933).

[11] Feitknecht, *Helv. Chim. Acta*, **14**, 85 (1931).

or whether the system is zeolitic, yielding upon dehydration a product identical in structure with the hydrated material. In the experimental portion of this paper there will be given the results of isobaric dehydration and x-ray diffraction studies which indicate that calcium sulfate hemihydrate is not a zeolite but behaves in all essential respects like a true chemical hydrate.

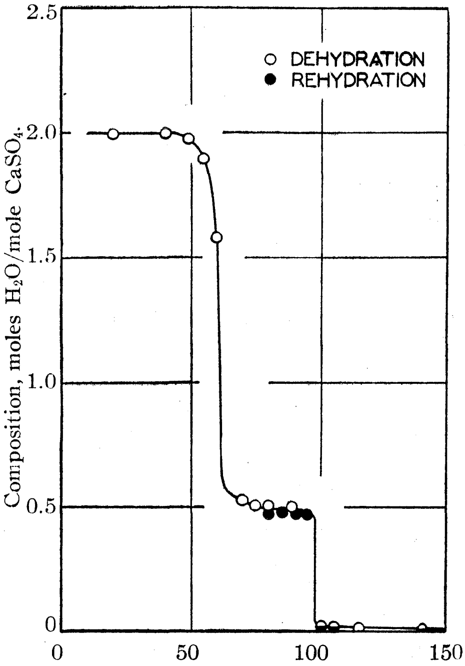

Fig. 1.

Experimental

Isobaric Dehydration.—The source of the calcium sulfate used in the experiments was clear, transparent selenite. Five samples of this material were dehydrated by raising the temperature progressively in an apparatus already described[12] at a constant aqueous vapor pressure of 23.6 mm. (water at 25°). One dehydrated sample was rehydrated by the reverse procedure. The temperature of the oven was maintained constant within ±1° for short periods of time and to within ±2° for longer periods. The samples were held at the various temperatures for days or weeks, weighing at intervals until equilibrium was attained. In some cases, the samples were held as long as five hundred hours at a given temperature. Figure 1 shows the complete dehydration–rehydration isobar for one sample. Figure 2 shows the hemihydrate portion of the dehydration for four samples. The points on the curve represent the average of values which differ by not more than ±0.006 mole of water per mole of calcium sulfate.

X-Ray Diffraction Examination.—A preliminary study was made of the x-ray diffraction patterns for (*a*) $CaSO_4 \cdot 2H_2O$ (selenite); (*b*) hemihydrate prepared by heating (*a*) to 95°; (*c*) dehydrated hemihydrate obtained by heating (*a*) to 145°, in a vacuum; and (*d*) anhydrite. Since the dehydrated hemihydrate is highly hygroscopic,[13] great care must be taken in preparing the samples for x-ray analysis. While still hot the samples were placed in thin tubes of Lindemann glass which were subsequently heated overnight in a vacuum and sealed. The sealed tubes were examined microscopically for possible leaks before placing in the diffraction apparatus. For the preliminary work the General Electric outfit (Kα Mo radiation) was employed. The films were standardized with sodium chloride in the usual way. The results are given in the form of diagrams in Fig. 3. It is apparent that each sample gives a different x-radiogram but the patterns for the hemihydrate and the dehydrated hemihydrate resemble each other rather closely.

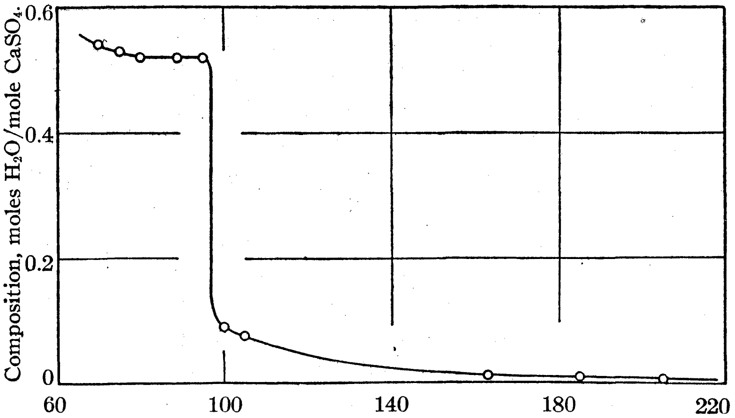

Fig. 2.

In order to make a quantitative study of the differences between the similar patterns of the hemihydrate and dehydrated hemihydrate, diffraction patterns were obtained with a Seemann

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[12] Weiser and Milligan, *J. Phys. Chem.*, **38**, 513 (1934).

[13] (a) Bower, *Bur. Standards J. Research*, **12**, 241 (1934); (b) Hammond and Withrow, *Ind. Eng. Chem.*, **25**, 653 (1933).

crystal analysis apparatus using Kα Cu radiation filtered through nickel foil. A precision Debye–Scherrer camera, 115.3 mm. in diameter, was employed. For purposes of calibration, pure nickelous oxide[14] prepared by igniting nickel nitrate in a current of nitrogen was mixed with the samples.

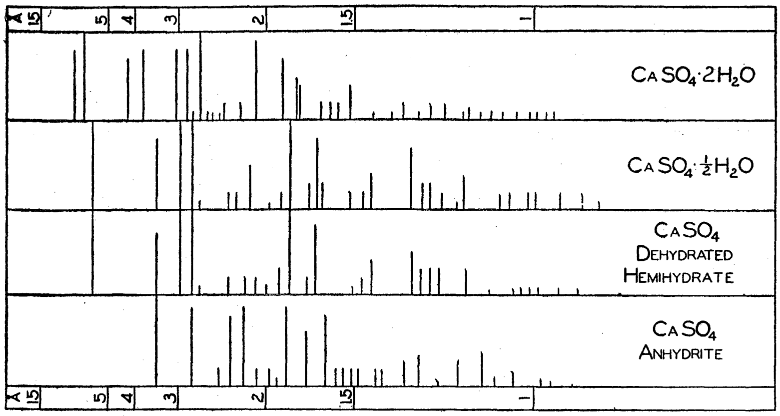

Fig. 3.

Fairly long exposures were required because of the low symmetry of the material, the small primary particle size, the large size and small aperture of the camera, and the need for obtaining a large number of lines. The usual exposure time was thirty to thirty-five hours at 60 m. a. and 40 k. v. Some typical negatives are reproduced in Fig. 4 and the data are shown diagrammatically in Fig. 5.

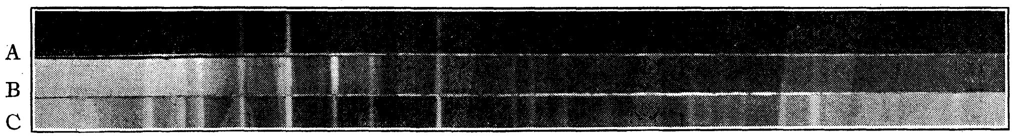

Fig. 4.—A, NiO; B, $CaSO_4\cdot 0.5H_2O$; C, $CaSO_4$ (Dehydrated hemihydrate).

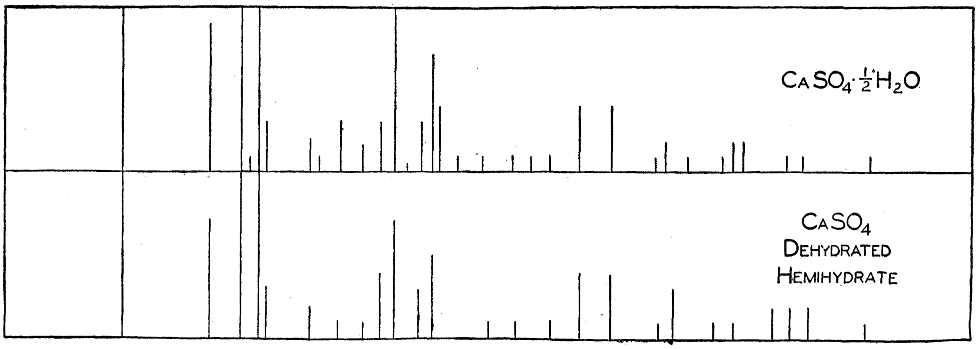

Fig. 5.

For purposes of comparison the corrected data are given in Table I. The interplanar spacings in Å. are denoted by d_{hkl} and the visually estimated, relative intensities by I.

Additional samples for x-ray examination were prepared by dehydrating selenite for twenty-four hours in a vacuum at 134, 159, 180 and 219°. The average composition of these samples was found to be $CaSO_4\cdot\pm 0.01H_2O$. To avoid any possibility of rehydration, the same procedure for filling and sealing the sample tubes was used as described above. All the patterns, using molybdenum radiation, were identical with those for dehydrated hemihydrate. This indicates the absence of any detectable amount of undecomposed hemihydrate or anhydrite. The samples dehydrated at 159 and 219° were allowed to rehydrate in air for several days. The compositions became, respectively, 0.63 and 0.60 mole of water per mole of calcium sulfate. After rehydrating the sample dehydrated to 134°, it was examined by x-rays, giving a pattern identical with that of hemihydrate.

Discussion of Results

The dehydration isobars for calcium sulfate hemihydrate are typical of those for a definite hydrate which adsorbs a small amount of water and gives a dehydration product which likewise adsorbs water. Since the hemihydrate and es-

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(14) Cairns and Ott, THIS JOURNAL, **55**, 527 (1933).

TABLE I

x-RAY DIFFRACTION DATA

	Hemihydrate $CaSO_4 \cdot 0.5H_2O$			Dehydrated hemihydrate $CaSO_4$	
	d_{hkl}	I		d_{hkl}	I
	6.000	10		6.000	10
	3.468	9		3.468	7
	3.002	10		3.012	10
	2.898	1			
	2.797	10		2.793	10
	2.703	3		2.711	3
(NiO)	2.407	7	(NiO)	2.407	7
	2.337	2		2.335	3
	2.272	1			
	2.131	2		2.138	1
(NiO)	2.084	9	(NiO)	2.084	9
	2.002	1		1.995	1
	1.905	3		1.870	4
	1.848	10		1.844	7
	1.792	1			
	1.732	3		1.741	3
	1.692	7		1.692	5
	1.662	4			
	1.602	1			
	1.527	1		1.506	1
(NiO)	1.474	10	(NiO)	1.474	10
	1.441	1		1.432	1
	1.394	1			
	1.353	1		1.349	1
	1.296	4		1.292	4
(NiO)	1.257	5	(NiO)	1.257	5
	1.238	4		1.237	4
(NiO)	1.203	5	(NiO)	1.203	5
	1.167	1		1.161	1
	1.153	2		1.142	3
	1.122	1			
	1.079	1		1.090	1
	1.068	2		1.065	1
	1.056	2			
(NiO)	1.042	3	(NiO)	1.042	3
				1.026	2
	1.011	1		1.009	2
	0.9969	1		0.9918	2
(NiO)	.9563	4	(NiO)	.9563	4
	.9418	1		.9441	1
(NiO)	.9321	4	(NiO)	.9321	4

pecially the dehydrated hemihydrate are known to adsorb water, the evidence seems conclusive that when $CaSO_4 \cdot 2H_2O$ is dehydrated isobarically, a definite hydrate $CaSO_4 \cdot 0.5H_2O$ which adsorbs a small amount of water is first formed and this in turn dehydrates in stepwise fashion to give dehydrated hemihydrate, calcium sulfate, which adsorbs water that is not removed completely at a vapor pressure of 23.6 mm. until well above the decomposition temperature. There is no indication that the water is present in the zeolitic form unless one wishes to apply the term "zeolitic" to the very small amount of water adsorbed first by the very finely divided hemihydrate and later by the resulting dehydrated hemihydrate. The failure of some investigators to obtain a clearly defined reversible step-curve for the decomposition of the hemihydrate is probably due to their failure to wait until equilibrium was established at each temperature.

The conclusions drawn from the dehydration data are supported by the x-ray diffraction studies. Since distinct characteristic differences exist between the x-ray patterns of hemihydrate and dehydrated hemihydrate, it would follow that the two are definite chemical individuals. The close agreement between many strong reflections shows that the type of lattice and the size of the unit cell are similar and that the hemihydrate lattice does not rearrange very much upon loss of the one-half molecule of water. This is the only way in which the hemihydrate resembles a zeolite. The characteristic changes in the pattern which take place on dehydration and rehydration show, however, that the water molecules in the hemihydrate are in a fixed position in the lattice and that the compound is not a zeolite.

The x-ray observations confirm qualitatively those of Feitknecht[11] but since the latter reported his data only in rough graphical form it is impossible to make a quantitative comparison. Since Jung,[5] Ramsdell and Partridge[6] and Caspari[7] believed the patterns of hemihydrate and dehydrated hemihydrate to be the same and Gallitelli[10] and Onorato[9] state that the structures are the same but recognize minor differences in the powder photographs, it would appear that these investigators failed to recognize the existence or the significance of the small but characteristic differences upon dehydration. This may be due to the small size of the cameras employed, the use of molybdenum radiation in some cases, and the failure to use a reference material for standardizing the films. However, there can be no doubt that significant differences exist between the x-radiograms of the two substances when use is made of a relatively large camera, copper radiation, and a standardizing material, and when special care is taken to avoid rehydration of the dehydrated hemihydrate.

Summary

1. Contrary to the conclusions of Linck and Jung, Balarew, Gibson and Holt, and others, the dehydration curve of calcium sulfate hemi-

hydrate gives a definite step indicating that the compound is a true chemical hydrate and not a zeolite.

2. Contrary to the conclusions of Jung, Ramsdell and Partridge, Caspari, Gallitelli, Onorato and others, calcium sulfate hemihydrate and "dehydrated hemihydrate" do not have identical structures. The x-radiograms of the two substances are similar, showing that the structures are similar; but the existence of definite characteristic differences between the two patterns indicates that the water molecules in the hemihydrate occupy fixed position in the lattice. These observations likewise support the view that calcium sulfate hemihydrate is a chemical individual and that the process of dehydration is not zeolitic in character.

HOUSTON, TEXAS RECEIVED APRIL 27, 1936

[CONTRIBUTION FROM THE GATES AND CRELLIN CHEMICAL LABORATORIES OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 546]

Strong Oxidizing Agents in Nitric Acid Solution. I. Oxidation Potential of Cerous–Ceric Salts

BY ARTHUR A. NOYES AND CLIFFORD S. GARNER

Plan of these Investigations

In connection with the recent investigations made by Noyes, Hoard, Pitzer and Dunn[1,2] of argentic salts in nitric acid solution, electromotive force measurements were made by Noyes and Kossiakoff[3] to determine the oxidation potential of argentous–argentic salts (Ag^{I}, Ag^{II}); and the result (1.914 volts) was compared with those of other strong oxidizing agents for which reliable data exist. As these data are rather limited, it seemed desirable to carry out researches on the oxidation potential of other powerful oxidizing substances; and it is the purpose of this series of papers to present the results obtained with cerous–ceric salts (Ce^{III}, Ce^{IV}), with thallous–thallic salts (Tl^{I}, Tl^{III}), and with cobaltous–cobaltic salts (Co^{II}, Co^{III}) in nitric acid solution.

The method of measurement was much the same as that used for argentous–argentic salts by Noyes and Kossiakoff, to whose article reference should be made for certain details of procedure. The conditions are simpler, however, in the case of ceric nitrate or thallic nitrate, in that these substances, unlike argentic nitrate, do not undergo at room temperature spontaneous reduction to cerous or thallous salt.

In this first paper are presented the results of measurements on cerous–ceric cells. Such cells were first measured by Baur and Glaessner.[4] They used cells containing cerous and ceric salts in nitric and sulfuric acid solutions; but carried out the work at "room temperature," and eliminated the liquid potential only to the extent that this is accomplished by inserting a saturated solution of potassium chloride between the cerium and the calomel electrodes. A satisfactory value therefore cannot be calculated for the oxidation potential from their data.

More recently, Kunz[5] studied the formal potential of cerous–ceric salts in 0.5 and 1.0 formal sulfuric acid solutions.

In order to determine the value in nitrate solution, which is likely to form complexes to a less extent, and to eliminate largely the liquid potential, we measured at 25 and at 0° cells of the type

$$\mathrm{Pt} + \mathrm{H_2}\,(1\ \mathrm{atm.}),\ \mathrm{HClO_4}\,(c'),\ \left\{\mathrm{HNO_3}\,(c) + \frac{\mathrm{Ce^{IV}}\,(c_2)}{\mathrm{Ce^{III}}\,(c_1)}\right\},\ \mathrm{Pt}$$

These experiments will now be described.

Apparatus and Materials

Preparation and Analysis of Solutions.—In preparing the stock solutions of cerous and ceric nitrate, C. P. hydrated cerous nitrate was used to make up a solution approximately 0.1 *f* in cerous nitrate and 1 *f* in nitric acid (to prevent subsequent hydrolysis). A 17-cm. layer of this solution gave no absorption spectrum, showing the absence of other rare-earth elements. The solution was then divided into two nearly equal portions.

A solution of ceric nitrate was prepared by electrolytic oxidation of one of these portions with a current of 2 amperes at 6–8 volts, till samples removed and titrated with ferrous sulfate solution showed that the oxidation was nearly complete.

The ceric nitrate solution thus prepared was analyzed as

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[1] Noyes, Hoard and Pitzer, THIS JOURNAL, **57**, 1221–1229 (1935).

[2] Noyes, Pitzer and Dunn, *ibid.*, **57**, 1229–1237 (1935).

[3] Noyes and Kossiakoff, *ibid.*, **57**, 1238–1242 (1935).

[4] Baur and Glaessner, *Z. Elektrochem.*, **9**, 534 (1903).

[5] Kunz, THIS JOURNAL, **53**, 98 (1931).

follows. Samples were weighed out, and, after adding the proper amount of water and sulfuric acid, the solutions were titrated with standard ferrous sulfate solution potentiometrically, using a vacuum-tube voltmeter. The amount of ceric cerium was thus obtained. The total cerium was determined by titration after oxidation of the cerium with ammonium peroxysulfate, using silver nitrate as a catalyst.[6] The nitric acid content was determined, after removing the cerium, by titration with standard sodium hydroxide solution, using phenolphthalein as indicator. To remove the cerium, the sample was shaken with mercury and a little potassium chloride till all the cerium was reduced to the cerous state; then sodium oxalate was added, the mixture was filtered, and the acid determined in the filtrate, tests having shown that no appreciable amount of nitric acid was adsorbed on the precipitate. The solution was diluted by weight to give a stock solution exactly 1.000 f in nitric acid, and check analyses were made. The ceric nitrate stock solution prepared in this manner was 0.1057 f in ceric nitrate and 0.004181 f in cerous nitrate.

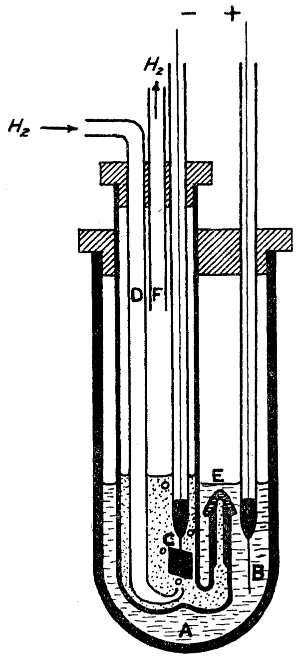

Fig. 1.

The other portion of the original cerous nitrate solution was analyzed in much the same way. It was diluted by weight so as to be exactly 1.000 f in nitric acid, and then again analyzed. The resulting stock solution of cerous nitrate was 0.08292 f in cerous nitrate and contained no ceric nitrate.

The solutions of perchloric acid were prepared by dilution of C. P. 60% perchloric acid, and were standardized against a sodium hydroxide solution.

Tank hydrogen was purified by passing it successively through concentrated potassium hydroxide solution and concentrated sulfuric acid, and over solid potassium hydroxide and an electrically heated platinum wire.

The Electrolytic Cell.—The assembled electrolytic cell is shown in Fig. 1. A large test-tube served as a container A for the cerous–ceric mixture, in which was immersed the hydrogen half-cell and a platinum wire electrode B. Measurements were made with the platinum wire bright and with it platinum-blacked; there was no difference in potential, although the latter electrode came to equilibrium with the solution much more rapidly. The hydrogen half-cell vessel contained the perchloric acid solution into which dipped a platinized platinum foil electrode C and a tube D through which the hydrogen was bubbled in; the vessel was also equipped with a short vertical capillary side-arm provided with a ground glass cap E which prevented liquid diffusion while allowing electrolytic contact. Before entering the half-cell the hydrogen passed through a glass coil and a vessel containing perchloric acid of the same concentration as that used in the half-cell. In addition a small "bubbler" was provided at the hydrogen outlet F to ensure a hydrogen atmosphere in the half-cell. The apparatus was immersed in a thermostat maintained at 25.00 ± 0.01°, or in one kept at 0°.

Method of Potential Measurements.—A Leeds and Northrup Type K potentiometer was used in conjunction with a high-sensitivity galvanometer for the measurements of the electromotive force. The Weston standard cell used was carefully checked at 25° against a new laboratory standard.

Cerous–ceric mixtures containing varying amounts of nitric acid were prepared from the stock solutions and a standard nitric acid solution by weighing. While each mixture was attaining thermal equilibrium in the cell, the hydrogen electrode was checked at 25° against a 1 N hydrochloric acid calomel electrode which had been prepared with purified chemicals in the presence of air.[7] The hydrogen half-cell was then placed in the electrolytic cell, and the potential observed over a period of one to fifty hours. In all cases equilibrium was attained within one hour, and readings were constant thereafter to 0.3 mv. or better; stirring had no effect on the potential. The hydrogen half-cell was checked against the calomel electrode after each run; the calculated value being always obtained to within 0.1 mv.

Calibrated volumetric apparatus, thermometers and weights were employed in this research, and all weighings were corrected to vacuum.

Measurements at 0°.—One of the cells which had been measured at 25° was placed in a 0° thermostat, and measurements of the electromotive force were made over a period of several days. The readings were constant to 0.2 mv., and upon returning the cell to the 25° thermostat, it gave a value for the potential within 0.1 mv. of that previously determined.

The Observed and Computed Electromotive Forces

In Table I are recorded the electromotive forces observed at various concentrations of the substances involved, the corrections computed for reducing these to standard concentrations and eliminating the liquid potential, and the final formal electrode potential thereby obtained.

The first column of the table shows the temperature, 25 or 0°. In the next five columns are given the weight formalities f (the concentrations in formula weights per kilogram of water) of the substances in the cells. In the next two columns are the mean ionic strength μ of the cerous–ceric mixtures, and the observed electromotive forces $E_{\text{obsd.}}$. The activity coefficients α of the two

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(6) Willard and Young, THIS JOURNAL, **50**, 1322, 1379 (1928).

(7) The value −0.2689 volt is the molal electrode potential of the hydrochloric acid calomel electrode for the case in which oxygen is not excluded. See Randall and Young, THIS JOURNAL, **50**, 989 (1928). The activity coefficients of hydrochloric acid solutions were taken from this same source.

TABLE I

OBSERVED AND COMPUTED ELECTROMOTIVE FORCES AT 25 AND 0°

Temp., °C.	HNO_3 c	$HClO_4$ c'	$Ce(NO_3)_3$ c_1	$Ce(NO_3)_4$ c_2	Ce^{III}/Ce^{IV} c_1/c_2	Mean ionic strength, μ	$E_{obsd.}$	E_C	E_L	E_H	E^0
25	2.000	2.000	0.03284	0.03932	0.8350	2.59	1.6001	−0.0046	−0.0096	+0.0244	1.6103
	(α, 0.759)		.03284	.03932	0.8350		1.6002	− .0046	− .0096	+ .0244	1.6104
		(α', 1.295)								Mean	1.6104
25	1.000	1.000	.06513	.02387	2.728	1.82	1.5915	+ .0258	− .0023	− .0047	1.6103
	(α, 0.706)		.06016	.03055	1.969		1.5997	+ .0174	− .0023	− .0047	1.6101
		(α', 0.803)	.04504	.05083	0.8861		1.6197	− .0031	− .0023	− .0047	1.6096
			.04468	.05133	.8705		1.6202	− .0036	− .0023	− .0043	1.6100
			.02768	.07413	.3734		1.6412	− .0253	− .0023	− .0047	1.6089
			.02288	.08146	.2809		0.6488	− .0326	− .0023	− .0051	1.6088
			.01808	.08703	.2077		1.6569	− .0403	− .0023	− .0051	1.6092
										Mean	1.6096
25	0.5000	1.000	.02191	.02624	.8351	0.89	1.6330	− .0046	− .0147	− .0051	1.6086
	(α, 0.708)		.02191	.02624	.8351		1.6328	− .0046	− .0147	− .0051	1.6084
		(α', 0.803)								Mean	1.6085
										General Mean	**1.6095**
0	1.000	1.000	.04468	.05133	.8705	1.83	1.6106	− .0033	− .0021	− .0040	**1.6012**
	(α, 0.706)	(α', 0.803)									

acids are given below their concentrations, the coefficients being interpolated from the data of Pearce and Nelson[8] for perchloric acid at 25° and from those of Abel, Redlich and v. Lengyel[9] for nitric acid at 25°. In the next three columns are the values of the electromotive force corrections computed as described below, and in the last column are the values of the formal oxidation potential E^0 referred to the standard molal hydrogen electrode H_2 (1 atm.), H^+ (activity 1 m.); by formal oxidation potential being meant the oxidation potential when the total concentrations, represented by Ce^{IV} and Ce^{III}, of the oxidized and reduced cerium (without reference to their ionization) are both 1.0 *f*.

This formal oxidation potential E^0 (for the reaction $Ce^{IV} + E^{-I} = Ce^{III}$) has been derived by adding to the observed electromotive force $E_{obsd.}$ (which is that of the cell formulated in the first section of this paper) the three following quantities:

(1) $E_C = (RT/2F) \ln (c_1/c_2)$, in order to provide for equiformal concentrations of cerous and ceric cerium, their total concentrations c_1 and c_2 being used in this Nernst equation in place of the ion activities.

(2) $E_L = (2T_H - 1)(RT/F) \ln (\alpha c/\alpha' c')$, in order to eliminate the small liquid potential arising from the different ion activities αc and $\alpha' c'$ of the nitric and perchloric acids; it being assumed that the ion mobilities of the two acids are equal in the given concentration range. The mean transference number T_H of the cation of the two acids has been estimated[10] to have the value 0.85 at 25° and the value of 0.86 at 0°.

(3) $E_H = (RT/F) \ln (\alpha' c'/\sqrt{p_{H_2}})$, in order to refer the value to the molal hydrogen electrode standard at 25°, p_{H_2} being the partial pressure of the hydrogen gas in atmospheres.

Discussion and Summary

It is seen from Table I that the formal cerous–ceric oxidation potential E^0 changes only slightly (at most by 1.5 mv.) on varying the ratio Ce^{III}/Ce^{IV} over ten-fold at constant ionic strength. Moreover, varying the acid concentration from 0.5 to 2.0 *f* and the ionic strength correspondingly has only a small effect on the value of E^0. This shows that nitrate complexes are formed only slightly, if at all, and that a hydrolytic reaction such as $Ce^{++++} + H_2O = CeOH^{+++} + H^+$ does not occur appreciably at these concentrations. Hence the value **1.6095** ± 0.0007 volt may be regarded as the cerous–ceric oxidation potential in nitric acid at 25°, independent of the concentration of that acid between 0.5 and 2.0 formal.

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[8] Pearce and Nelson, THIS JOURNAL, **55**, 3080 (1933).

[9] Abel, Redlich and v. Lengyel, *Z. physik. Chem.*, **132**, 204 (1928).

[10] This estimate at 25° is based on the considerations that the two acids have equal conductances at 2.0 *f*, that the nitric acid solution contains less than 10% as much cerium as acid, so that its conductance does not differ greatly from that of pure nitric acid, and that the latter has the values recorded in "International Critical Tables" (Vol. VI, pp. 241, 310 (1929)). For the 0° measurement, the same activity values were used as at 25°, since none are available at 0°.

The value of this potential at 0° was found to be **1.601** volts (in 1.0 *f* HNO_3).

It is interesting to note that in sulfate solution Kunz[5] obtained much smaller values, namely, 1.461 and 1.443 volts at 25° in 0.5 *f* and in 1.0 *f* H_2SO_4, respectively. This indicates that complex formation between the ceric ion and sulfate ion (or hydrosulfate ion) takes place to a large extent. It is probable therefore that the value obtained in nitric acid represents much more nearly the *molal* oxidation potential of cerous–ceric *ions*.

It may also be noted that the cerous–ceric potential in nitrate solution is of the same order as that (1.59 volts)[11] for the reaction $MnO_4^- + 4H^+ + 3E^- = MnO_2(s) + 2H_2O(l)$. Correspondingly, on adding permanganate solution to a nitric acid solution of cerous nitrate, manganese dioxide was found to form; and on adding ceric nitrate solution to freshly precipitated manganese dioxide, the color of permanganate was developed.

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[11] Brown and Tefft, THIS JOURNAL, **48**, 1128 (1926).

PASADENA, CALIFORNIA RECEIVED MAY 12, 1936

[CONTRIBUTION FROM THE GATES AND CRELLIN CHEMICAL LABORATORIES OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 547]

Strong Oxidizing Agents in Nitric Acid Solution. II. Oxidation Potential of Thallous-Thallic Salts

BY ARTHUR A. NOYES AND CLIFFORD S. GARNER

Previous and Proposed Investigations

The thallous–thallic oxidation potential has been studied by several investigators. Its determination was first undertaken by Spencer and Abegg[1] who studied the potential in nitric, hydrochloric and sulfuric acids, and in the presence of various salts with the view of investigating complex-ion formation. Their measurements were made at 25° against a 0.1 *N* calomel half-cell as a reference electrode, and their potentials were not corrected for liquid-junction potentials. Grubb and Hermann[2] later obtained values for the thallous–thallic potential in sulfuric acid solutions. Measurements by them were made at 18° against either a normal calomel electrode or a mercurous sulfate electrode, and liquid-junction corrections were not applied. Partington and Stonehill[3] recently measured at 25° cells of two types

$$\mathrm{Pt}, \left\{ \mathrm{H_2SO_4}\,(c) + \begin{matrix} \mathrm{Tl_2SO_4}\,(c_1) \\ \mathrm{Tl_2(SO_4)_3}\,(c_2) \end{matrix} \right\}, \mathrm{H_2SO_4}\,(c), \mathrm{H_2}\ (1\ \text{atm.}) + \mathrm{Pt}$$

and

$$\mathrm{Pt}, \left\{ \mathrm{H_2SO_4}\,(c) + \begin{matrix} \mathrm{Tl_2SO_4}\,(c_1) \\ \mathrm{Tl_2(SO_4)_3}\,(c_2) \end{matrix} \right\}, \mathrm{Hg_2SO_4}\ (\text{satd.}), \mathrm{Hg}, \mathrm{Hg_2SO_4}\,(\text{satd.}), \mathrm{H_2SO_4}\,(c), \mathrm{H_2}(1\ \text{atm.}) + \mathrm{Pt}$$

These investigations showed that the oxidation potential of thallous–thallic salts varies greatly with the nature of the anion present, doubtless owing to the formation of anion complexes; and as these complexes are probably produced in minimum quantity with monobasic oxyacids, such as nitric acid and perchloric acid, thereby yielding a molal potential approximating most closely that of the simple thallous and thallic ions, we have measured and describe in this paper cells of the type

$$\mathrm{Pt} + \mathrm{H_2}\,(1\ \text{atm.}), \mathrm{HClO_4}\,(c'), \left\{ \mathrm{HNO_3}\,(c) + \begin{matrix} \mathrm{Tl^{III}}\,(c_2) \\ \mathrm{Tl^{I}}\,(c_1) \end{matrix} \right\}, \mathrm{Pt}$$

During the progress of our investigation an article upon the thallous–thallic potential in perchloric acid solution has been published by Sherrill and Haas,[4] thereby making possible a comparison of the potential in the two monobasic oxyacids.

Apparatus and Materials

Preparation and Analysis of the Solutions.—A weighed quantity of c. p. thallous nitrate, dried in an oven at 140°, was dissolved in a definite weight of distilled water, and the resulting solution was divided into two nearly equal portions.

(1) From one of these portions a thallic nitrate solution was prepared by oxidation with a gas mixture containing 5% by volume of ozone (Noyes, Hoard and Pitzer[5]), thereby avoiding the introduction of foreign substances into the solution. To it had previously been added the amount of strong nitric acid (freed from nitrogen dioxide by bubbling air through it) required to leave the oxidized solution 0.5 *f* in nitric acid. It was thought that this acid would suffice to prevent the hydrolysis of the thallic nitrate formed, but during the oxidation dark-brown thallic hydroxide precipitated, and it was necessary to add more nitric acid to the oxidized mixture. The excess of ozone was blown out with oxygen, and the thallic nitrate solution was analyzed in the following way.

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[1] Spencer and Abegg, *Z. anorg. Chem.*, **44**, 379 (1905).

[2] Grubb and Hermann, *Z. Elektrochem.*, **26**, 291 (1920).

[3] Partington and Stonehill, *Trans. Faraday Soc.*, **31**, 1357 (1935).

[4] Sherrill and Haas, THIS JOURNAL, **58**, 952 (1936).

[5] Noyes, Hoard and Pitzer, *ibid.*, **57**, 1223 (1935)

TABLE I

OBSERVED AND COMPUTED ELECTROMOTIVE FORCES AT 25 AND 0°

Temp., °C.	HNO_3 c	$HClO_4$ c'	$TlNO_3$ c_1	$Tl(NO_3)_3$ c_2	Tl^{I}/Tl^{III} c_1/c_2	Mean ionic strength, μ	$E_{obsd.}$	E_C	E_L	E_H	E^0
25	2.000	2.000	0.07264	0.04720	1.5392	2.17	1.2096	+0.0055	−0.0096	+0.0244	1.2299
	(α, 0.759)	(α', 1.295)	.06499	.05819	1.1194		1.2138	+ .0014	− .0096	+ .0244	1.2300
										Mean	1.2300
25	1.000	1.000	.04999	.00406	12.314	1.09	1.2048	+ .0323	− .0023	− .0056	1.2292
	(α, 0.706)	(α', 0.803)	.04133	.01643	2.5148		1.2273	+ .0119	− .0023	− .0056	1.2313
			.03574	.02445	1.4617		1.2346	+ .0049	− .0023	− .0056	1.2316
			.02874	.03442	0.8351		1.2407	− .0023	− .0023	− .0056	1.2305
			.02146	.04484	0.4786		1.2489	− .0095	− .0023	− .0056	1.2315
			.00514	.06817	0.0754		1.2708	− .0332	− .0023	− .0056	1.2297
										Mean	1.2306
25	0.5000	1.000	.01624	.01455	1.1155	0.55	1.2499	+ .0014	− .0147	− .0056	1.2310
	(α, 0.708)	(α', 0.803)	.00691	.02788	0.2479		1.2677	− .0179	− .0147	− .0056	1.2295
										Mean	1.2303
										General Mean	**1.2303**
0	1.000	1.000	.02874	.03442	0.8351	1.09	1.203	− .0021	− .0021	− .0051	**1.193**
	(α, 0.706)	(α', 0.803)									

To a weighed sample solid potassium chloride and mercury were added, the mixture was shaken for two minutes and filtered through a Jena glass filter. The filtrate with washings was then titrated with standard sodium hydroxide solution to determine the nitric acid content. It was necessary to reduce the thallic salt in this way, since otherwise it separated out as the hydroxide and obscured the end-point. The content in thallic nitrate was determined on separate samples by reducing the thallic thallium to thallous thallium with sulfur dioxide, blowing out the excess of sulfur dioxide with carbon dioxide, and determining the thallium by two independent methods. However, it was found that the large amount of nitrate present interfered with these determinations; so the samples were first fumed with concentrated sulfuric acid to convert the nitrate to sulfate. Two determinations were made by the iodate method using the iodine monochloride end-point,[6] and these agreed to better than 0.1% with two determinations by the bromate method using methyl orange as an oxidation indicator.[7] The absence of thallous thallium in the thallic nitrate solution was proved by making a sample 5 *f* in hydrochloric acid, adding a small amount of iodine monochloride solution and shaking with carbon tetrachloride; no iodine color was perceptible. The thallic nitrate stock solution thus prepared was 0.1835 *f* in thallic nitrate and 2.430 *f* in nitric acid.

(2) To the other portion of the thallous nitrate solution was added enough nitric acid to make the resulting solution of the same acidity as the thallic nitrate stock solution. Analyses for both thallium and acid checked the values obtained by the direct synthesis of the solution. The thallous nitrate stock solution was 0.1284 *f* in thallous nitrate and 2.430 *f* in nitric acid.

The Electrolytic Cell.—The electrolytic cell used for the electromotive force measurements was that described in the preceding paper. The platinum wire electrode gave the same potential whether it was bright or platinum-blacked; however, equilibrium was more rapidly attained in the latter case.

Method of Potential Measurements.—The equipment used and the method of making the electromotive force measurements were those previously described in detail. The potential of a given cell was observed over a period of one to seventy hours. Equilibrium was reached within an hour, and subsequent readings were constant to 0.1 mv., stirring having no effect on the potential.

Measurements at 0°. One of the cells which had been measured at 25° was transferred to a 0° thermostat, and its potential observed over a period of three days. Equilibrium was much more slowly attained than at 25°, and the readings were sensitive only to about 0.5 mv. The cell was afterward returned to the 25° thermostat, and gave substantially the same electromotive force as before. The probable error of the formal potential at 0° is about one millivolt.

The Observed and Computed Electromotive Forces

In Table I are shown the concentration data, the observed electromotive forces, $E_{obsd.}$, the corrections applied to these, and the computed formal oxidation potentials E^0 resulting thereby, all in just the same form in which these quantities are presented in Table I of the preceding article. The activity coefficients α and α' of the two acids are as before taken from the data of Pearce and Nelson[8] and of Abel, Redlich and v. Lengyel,[9] the same values being used at 0° (where data are lacking) as at 25°.

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[6] Swift and Garner, THIS JOURNAL, **58**, 113 (1936).

[7] Kolthoff, *Rec. trav. chim.*, **41**, 172 (1932); Zintl and Rienäcker, *Z. anorg. allgem. Chem.*, **153**, 278 (1926); see also Noyes, Pitzer and Dunn, THIS JOURNAL, **57**, 1231 (1935).

[8] Pearce and Nelson, *ibid.*, **55**, 3080 (1933).

[9] Abel, Redlich and v. Lengyel, *Z. physik. Chem.*, **132**, 204 (1928).

Summary and Discussion

Measurements have been described above of the electromotive forces at 25 and 0° of cells of the type

$$\text{Pt} + \text{H}_2\,(1\text{ atm.}),\ \text{HClO}_4\,(c'),\ \left\{ \text{HNO}_3\,(c) + \frac{\text{Tl}^{\text{III}}\,(c_2)}{\text{Tl}^{\text{I}}\,(c_1)} \right\},\ \text{Pt}$$

From these measurements presented in Table I the formal oxidation potential E^0 of the reaction $\text{Tl}^{\text{III}} + 2\text{E}^{-\text{I}} = \text{Tl}^{\text{I}}$ has been computed to have the value **1.2303** ± 0.0007 volt at 25° and the value **1.193** ± 0.001 volt at 0° in nitric acid solution. This value is shown to remain substantially constant when the ratio $\text{Tl}^{\text{I}}/\text{Tl}^{\text{III}}$ is varied one hundred-fold and when the concentration of nitric acid is varied from 0.5 to 2 *f*. This constancy of the potential shows that neither hydrolysis of the thallic nitrate (by a reaction like $\text{Tl}^{+++} + \text{H}_2\text{O} = \text{TlOH}^{++} + \text{H}^+$), nor formation of nitrate complexes occurs to a considerable extent with thallic salts in nitric acid solutions between 0.5 and 2.0 formal.

This value, 1.230 volts, of the formal potential is slightly lower than those found by Sherrill and Haas[4] for the thallous–thallic potential in perchloric acid solution, who obtained at 25° 1.260 volts for the formal potential in 1.0 *f* perchloric acid and 1.247 volts for the extrapolated molal potential for thallous–thallic ions.

Noteworthy is the fact that the thallous–thallic potential in sulfuric acid solution, determined by Partington and Stonehill[3] to be 1.20 to 1.22 volts, is of about the same magnitude as the potentials in nitric and perchloric acids indicating that the formation of sulfate complexes by thallic sulfate is not very extensive.

PASADENA, CALIF. RECEIVED MAY 12, 1936

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND THE PHYSICO-CHEMICAL LABORATORY OF THE NEW YORK STATE EXPERIMENT STATION][1]

The Electron Diffraction Study of Paraldehyde

BY D. C. CARPENTER AND L. O. BROCKWAY

Paraldehyde has been shown[2] to exist as the trimer $(\text{CH}_3\text{CHO})_3$ in the gaseous state and in solution in phenol, and metaldehyde as the tetramer $(\text{CH}_3\text{CHO})_4$ in phenol solution. In the present work the configuration of paraldehyde has been established by electron diffraction methods as a staggered six-membered ring of alternate carbon and oxygen atoms with a hydrogen atom and a methyl group attached to each of the ring carbon atoms, the methyl carbon atoms being approximately coplanar with the ring oxygen. The technique of the electron diffraction method of determining the structure of molecules has been described,[3] and the method now represents one of the most direct and feasible means of determining bond angles and distances.

Experimental

The sample of paraldehyde used in this study was purified by repeated fractional distillation and boiled at 124.0 ± 0.2°. Smits and deLeeuw[4] record the boiling point as 123.7°.

The low vapor pressure of paraldehyde at room temperature prevented the use of the ordinary unheated gas nozzle. In this investigation the sample was placed in a small glass bulb which was sealed to a copper tube leading through an all-metal high vacuum valve and up into the apparatus where it terminated in a nozzle just below the electron beam. The sample bulb, connecting tubes, valve and nozzle were all heated by spirals of resistance wire enclosing the entire path of the vapor. The valve was constructed so that a stiff spring pressing on the valve stem compensated for relative expansion of the valve parts and the valve was vacuum tight both at ordinary and elevated temperatures. Four thermocouples were used to follow the temperatures of the various parts of the assembly. This arrangement for handling vapors at high temperatures differs from those used by other investigators in which the gas stream flows continuously and is regulated by changes of the temperature of the sample holder. Here the gas flow is controlled by a quick-acting valve.

Fifteen photographs of paraldehyde were obtained in three sets with the temperature of the sample ranging from 103 to 115°. The exposure

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(1) Published as paper No. 542 from the Gates Chemical Laboratory and approved by the Director of the New York State Experiment Station for publication as Journal Article No. 141.

(2) W. Burstyn, *Sitzber. Wiener Akad.*, 511 (1902).

(3) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(4) A. Smits and H. L. deLeeuw, *Z. physik. Chem.*, **77**, 269 (1911).

times were adjusted so that the inner rings could be measured on some photographs and the outer rings on others. The de Broglie wave length of the electrons was 0.0606 Å. as determined by calibration with gold foil. The distance from gas orifice to photographic film was 10.43 cm.

The photographs show seven rings of which the second and fifth are very strong. The fourth is close to the third and weaker than the third and fifth rings. The sixth ring is weaker than the fifth and seventh. Measurements of the diameters were made by two observers and the corresponding values of s (equal to $(4\pi \sin \theta/2)/\lambda$) are given in Table I.

TABLE I

No. of readings	Max.	Min.	Visual intensity	S (obsd.)	S (calcd.)	l_{C-O}
12	1		20	3.73	3.50	(1.342)
9		2		4.68	4.40	(1.333)
15	2		30	6.13	5.65	(1.315)
15		3		7.70	7.40	(1.375)
15	3		10	9.05	9.12	1.440
15		4		10.14	10.10	1.425
15	4		5	11.27	10.75	(1.364)
15		5		12.71	12.60	1.418
15	5		10	14.07	14.00	1.423
3		6		15.45	15.35	1.416
3	6		1	16.62	17.00	(1.463)
6	7		1	18.82	18.90	1.436
				Weighted mean		1.427

C–O = 1.43 ± 0.02 Å.

Discussion

The estimated intensities of the visual maxima and the corresponding s values were used in the calculation of a radial distribution curve.[5] The data of Table I lead to the curve shown in Fig. 1. This curve shows two pronounced peaks corresponding to the most important interatomic distances in the molecule. The first peak occurs at 1.47 Å., exactly the value which would be predicted for models of the ring type shown in Fig. 2, in which there are six C–O and three C–C single bonds. The covalent radii lead to the values 1.43 and 1.54 Å., respectively. If these values are weighted according to the number and scattering power of the atoms involved, the single peak corresponding to the two unresolved distances should occur at 1.47 Å. the observed value. Accordingly, the single bonded ring structure is very probable.

A determination of the bond angle can be made by use of the second peak which occurs at 2.36 Å. This peak corresponds to the interaction of atoms bonded to the same atom. The ratio 2.36 to 1.47 is 1.61, which leads to the bond angle of 108° in close approximation to the tetrahedral angle of 109°28′. Similar values of the bond angle between carbon and oxygen have been found in other compounds, such as dimethyl ether and dioxane, and we accept the tetrahedral angle as being correct in the calculation of theoretical intensity curves.

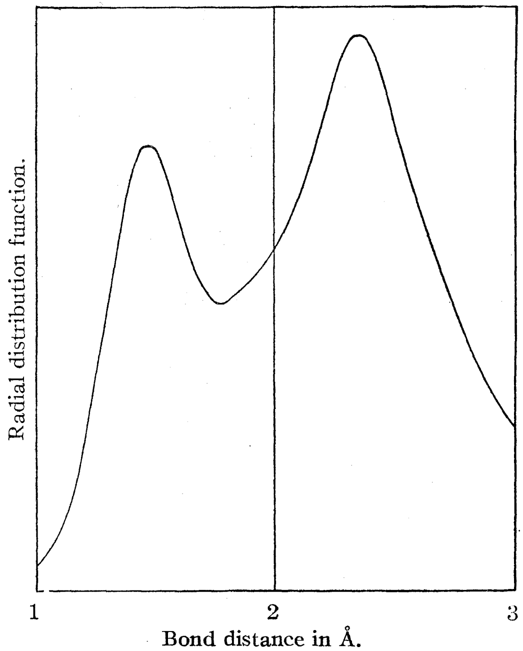

Fig. 1.—Radial distribution curves for paraldehyde.

Four ring models of the paraldehyde molecule are possible, corresponding to elevating the methyl groups successively above the plane of the –C–O–C–ring as shown in Fig. 2. Calculations of the theoretical intensity of scattering, $I = \Sigma_i \Sigma_j Z_i Z_j (\sin sl_{ij}/sl_{ij})$ where $s = (4\pi \sin \theta/2)/\lambda$ were made for each of the four models for s values up to 20. The distances between bonded atoms were taken as follows: C–O, 1.43 Å.; C–C, 1.54 Å.; C–H, 1.06 Å.; and the bond angles were taken as 109° 28′. The calculated curves are shown in Fig. 3. The observed positions of the maxima and minima are indicated at the bottom of the figure. The s values for the maxima and minima of the first theoretical curve (all methyl groups in the plane of the ring) are listed in the sixth column of Table I. The four curves all show the qualitative intensity features observed in the photographs. Particularly characteristic is the strong fifth maxi-

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[5] L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

mum. Differences in the four models are evident in the fourth and sixth rings. The fourth ring is displaced outward in going from model 1 to model 4, and models 3 and 4 are in definite disagreement with the photographs on this account. Similarly these last two models show an inward displacement of the sixth ring which is not observed.

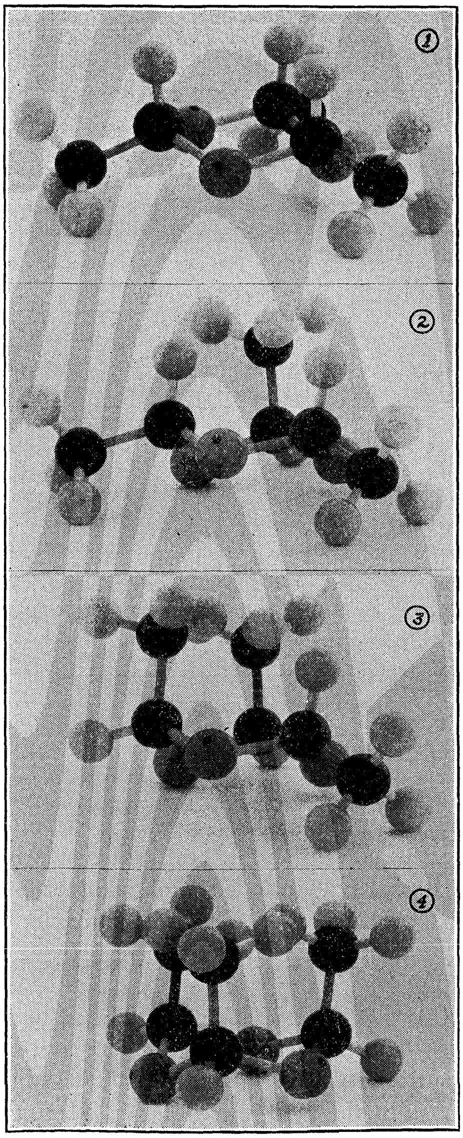

Fig. 2.—Models of paraldehyde molecule.

The values for the C–O distances in the last column of Table I are derived by multiplying the ratio of S(calcd.) to S(obsd.) by the assumed value for the distance. In arriving at the weighted mean value we reject the values from the two innermost rings and from the fourth and sixth maxima. In the former case the contrast effect of the dense central image leads to interatomic distance values which are too small and in the latter case the notable asymmetry of maxima results in the expected shift explained by the St. John effect.[3] While these rings are not suitable for exact determination of the interatomic distances, they are valuable in confirming the ring structure of the molecule since the corresponding theoretical curve and the photographs show the same asymmetric features. The dimensions of the molecule are determined as 1.43 ± 0.02 Å. for the C–O bond distance and 1.54 ± 0.02 Å. for the C–C bond distance with the staggered ring arrangement of six alternating carbon and oxygen atoms well established.

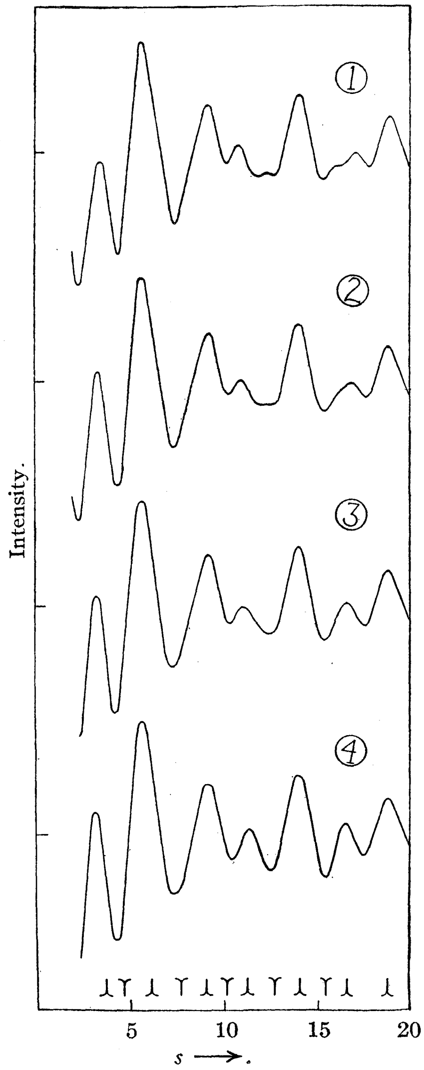

Fig. 3.—Theoretical intensity curves for paraldehyde models.

The close similarity in the theoretical intensity curves corresponding to models 1 and 2 makes it impossible to distinguish on the basis of our data between the model with all of the methyl groups nearly in the plane of the ring and the model having one methyl group above the ring. A comparison can be made with the structure of metaldehyde determined by x-ray crystal studies.[6] Metaldehyde, which is the tetramer of acetaldehyde, has an eight-membered ring of alternating carbon and oxygen atoms with four methyl groups attached to the four carbon atoms and all four of the methyl groups lie in the plane of the carbon atoms in the ring. The molecules are packed together in such a way that the closest approach of methyl carbon atoms on adjacent molecules is 3.90 Å. with an average separation for the intermolecular methyl groups of 4.02 Å. Hydrogen atoms on these methyl groups are separated by 2.14 Å. In models 3 and 4 of paraldehyde which have two and three methyl groups above the ring the calculated separation of methyl carbons is 2.33 Å. and of the methyl hydrogens is 1.85 Å.; comparison of these distances with those observed in the metaldehyde crystals again eliminates these two models of paraldehyde. The observed configuration of the metaldehyde molecules makes model 1 of paraldehyde (all methyl groups nearly in the plane of the ring) seem most probable.

Electron diffraction pictures were taken of the vapor of metaldehyde and the photographs show that the gaseous molecule cannot be represented by any single configuration. This is to be explained by the ease with which the eight-membered ring can be distorted from the configuration found in the crystalline form of metaldehyde without stretching or bending the bonds between adjacent atoms. This labile nature of the ring is not found in the crystal because the interactions between molecules in the condensed state are strong enough to hold the molecules in a single equilibrium configuration. The six-membered ring of paraldehyde does not exhibit any such labile character because of the strains set up in any distortion of the smaller ring.[7]

We are indebted to Professor Linus Pauling for proposing the investigation and for many valuable suggestions and criticisms.

Summary

Paraldehyde has been studied by the electron diffraction method and found to consist of a staggered six-membered ring of alternate carbon and oxygen atoms having a C–O distance of 1.43 ± 0.02 Å. The bond angles are all tetrahedral and the three methyl groups are placed symmetrically about the molecule in nearly the same plane as the ring (*i. e.*, as fixed by the tetrahedral angles) with the possibility that only one of the methyl groups may be elevated above the plane of the ring. The methyl carbon atoms are attached to the carbon atoms of the ring by bonds having a length of 1.54 ± 0.02 Å.

GENEVA, N. Y.
PASADENA, CAL.

RECEIVED MAY 11, 1936

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[6] L. Pauling and D. C. Carpenter, THIS JOURNAL, **58**, 1274 (1936).

[7] An electron diffraction study of paraldehyde vapor has been reported by Ackermann and Mayer (*J. Chem. Phys.*, **4**, 377 (1936)). These authors used electrons of only 6400 volts energy corresponding to a wave length of 0.15 Å. and obtained three maxima. While their observed *s* valves for the first and second maxima and minima are from 3 to 10% lower than those reported in this paper the discrepancy may well be due to the differences in technique. As reported above, when the shorter wave-length (0.06 Å.) is used the apparent positions of the innermost rings is affected by the very dense central spot and they lead to unreliable interatomic distance values. This effect is evidently less serious when the inner rings occur at greater angles. The conclusions of Ackermann and Mayer are in fair agreement with the present results based on photographs showing seven maxima.

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND THE PHYSICO-CHEMICAL LABORATORY OF THE NEW YORK STATE EXPERIMENT STATION][1]

The Crystal Structure of Metaldehyde

BY LINUS PAULING AND D. C. CARPENTER

Metaldehyde is described by Groth[2] as crystallizing in tetragonal needles with the axial ratio $a:c = 1:0.2761$. A preliminary x-ray investigation of the crystal was carried out by Hassel and Mark,[3] who determined the size of the unit of structure and reported the space group to be either C_{4v}^9 or C_4^5, the location of the atoms in the unit not being found. We have reinvestigated this crystal, finding the space group to be C_4^5—I_4, and making a complete determination of the atomic arrangement. The unit of structure contains two molecules of the tetramer, $(CH_3CHO)_4$, each molecule consisting of an eight-membered –O–C–O–C– ring with H and CH_3 attached to each carbon atom of the ring. The interatomic distances and bond angles were found to be the same as in paraldehyde,[4] $(CH_3CHO)_3$.

The Unit of Structure and Space-Group Symmetry

Metaldehyde was recrystallized from absolute alcohol by the method of slow cooling, and dried on a Büchner funnel. The crystals were in the form of needles with dimensions about 0.5 × 0.5 × 20 mm. Laue photographs taken with crystal orientations differing only by rotation through a multiple of 90° about the needle axis were found to be identical, verifying the tetragonal symmetry of the crystal. Several Laue photographs were prepared with the incident beam in the plane normal to the *c*-axis. Each of these photographs showed a horizontal plane of symmetry, but none showed a vertical plane of symmetry (photographs with the incident beam parallel to [100] and [110] of the unit of structure, among others, were prepared). Consequently the point-group symmetry of the crystal cannot be that of D_{4h}, D_4, C_{4v}, or D_{2d}, but must be instead that of C_{4h}, C_4, or S_4. Of these C_{4h} and S_4 are eliminated by our observation of a strong pyroelectric effect along the needle axis, the liquid-air method[5] being used. The crystal is thus definitely allocated[6] to the point group C_4.

The pronounced prismatic cleavage of the crystal was strikingly shown by its behavior on cooling with liquid air, the strains resulting from temperature gradients during cooling causing each crystal to separate into a large number of fibers.

Oscillation and rotation photographs were prepared with [001] as axis of rotation, Mo $K\alpha$ radiation filtered through zirconia being used. These led to the values $a_0 = 10.40$ Å. and $c_0 = 4.11$ Å. for the edges of the unit of structure, in approximate agreement with the values of Hassel and Mark, $a_0 = 10.34$ Å., $c_0 = 4.10$ Å. All of the reflections on a complete set of oscillation photographs about [001] and on a completely-indexed Laue photograph were found to be compatible with this unit (the axes of which are 45° from those used by Groth). No reflections (hkl) with $h + k + l$ odd were observed; the lattice is accordingly body-centered. Of the body-centered space groups isomorphous with C_4 all but C_4^5 are eliminated by the observation that all types of prism planes give reflections; C_4^5—I_4 is accordingly the space group of the crystal.

The Atomic Arrangement

There are 8 CH_3CHO in the unit of structure (density calculated, 1.31; observed, 1.27). As pointed out by Hassel and Mark, these are formally combined by the four-fold axes into polymers $(CH_3CHO)_4$. It seems highly probable that these groups have a structure closely similar to that of paraldehyde, each oxygen atom being attached to two carbon atoms by single bonds. We made the preliminary assumptions that the interatomic distances have the values C—C = 1.54 Å. and C—O = 1.43 Å. and the bond angles all have the tetrahedral value 109° 28′, as in paraldehyde. There are only two configurations of the molecule compatible with these assumptions. In one of these the four methyl groups are directed along the *c*-axis, and in the other they

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[1] Published as paper No. 543 from the Gates Chemical Laboratory and approved by the Director of the New York State Experiment Station for publication as Journal Article No. 142.

[2] P. Groth, "Chemische Krystallographie," Vol. III, p. 47.

[3] O. Hassel and H. Mark, *Z. physik. Chem.*, **111**, 357 (1924).

[4] D. C. Carpenter and L. O. Brockway, THIS JOURNAL, **58**, 1270 (1936).

[5] A. J. P. Martin, *Mineral. Mag.*, **22**, 519 (1931).

[6] Hassel and Mark prepared only complete rotation photographs, and so were unable to distinguish between the point groups C_4 and C_{4v} and the space groups C_4^5 and C_{4v}^9.

are directed outward from the center of the ring. (The four-fold axis eliminates intermediate configurations.) The first of these is at once ruled out by the consideration of interatomic distances in the c direction, in which molecules are only 4.11 Å. apart. The metaldehyde molecule accordingly has the configuration shown in Fig. 1. The atomic arrangement is then completely determined by one additional parameter φ, corresponding to rotation of the molecule about the four-fold axis through its center (see Fig. 6).

The intensity data used in evaluating this parameter and in verifying the assumed values for the others were obtained in the following way. Using the same crystal and the same exposure, oscillation photographs about [001] were prepared with the incident beam covering the ranges 0–15, 15–30, 30–45, 45–60, 60–75, 75–90 and 90–105° with the axis [100] (the first and last photographs being identical). Microphotometer records of the equatorial reflections were then prepared with a Krüss microphotometer, and interpreted in terms of intensities with the aid of similar records of a set of 0–15° photographs taken with different exposure times. The intensity values so obtained for thirty prismatic forms are given in Table I, together with relative values of F calculated from them by use of the equation

$$F_{hkl} = \left(\frac{2I_{hkl} \sin 2\vartheta}{1 + \cos^2 2\vartheta}\right)^{1/2} \qquad (1)$$

in which I_{hkl} is the observed intensity and ϑ the angle of reflection.

TABLE I

EQUATORIAL REFLECTIONS FOR METALDEHYDE

	Intensity of reflection		
hkl	Obsd.	Calcd.	F, obsd.
110	275	230	5.0
200	33	18	2.1
220	78	62	−3.8
130	60	74	−4.1
310	13	0	1.6
400	51	63	−3.8
330	36	32	−3.2
240	11	9	1.9
420	46	57	−3.8
150	19	8	−2.7
510	25	18	−3.0
350	13	8	2.4
600	9	3	−2.0
260	8	9	1.9
620	20	21	3.0
550	9	11	2.2
710	10	7	2.3
170	9	6	2.2
460	8	5	−2.0
370	5.6	5	1.8
730	7	7	2.0
800	4	2	−1.6
820	8	10	2.2
750	7	6	−2.2
480	10	14	2.6
190	9	10	−2.6
930	8	14	2.5
680	8	1	−2.5
860	3.6	3	−1.7
2.10.0	9	13	−2.8

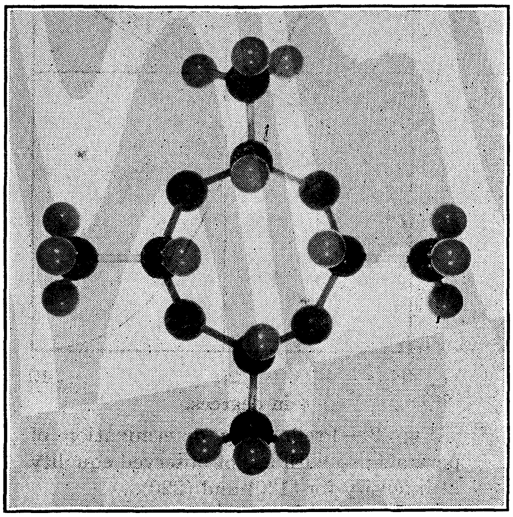

Fig. 1.—Configuration of metaldehyde molecule.

The observed intensity values were compared with intensity values calculated by replacing F_{hkl} in Equation 1 by

$$F_{hkl} = \Sigma_j f_j e^{2\pi i(hx_j + ky_j + lz_j)} \qquad (2)$$

Pauling–Sherman f-values[7] being used for f_j, and the coördinates x_j y_j z_j being calculated as a function of φ for the molecular model described above.

The observed approximate equality in intensity of reflection from {130} and {220} limits φ to values in the neighborhood of 16° (Fig. 2). The comparisons of {150} with {510} ($F_{150}/F_{510} = 0.87$) and {260} with {620} ($F_{260}/F_{620} = 0.63$) shown in Fig. 3, as well as other similar comparisons, lead to values near 16° 40′ for φ.

In order to investigate the possibility that the molecular parameter values differ slightly from those assumed, a two-dimensional Fourier analysis of the distribution of scattering power in the crystal projected on the plane (001) was made, using the equation

$$\rho(x,y) = \text{constant}\ \Sigma_h \Sigma_k F_{hk0} \cos 2\pi(hx + ky) \qquad (3)$$

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[7] L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

the sum being extended over all planes (*hk*0) for which reflections were observed. The experimental *F*-values for the corresponding forms are given in Table I, together with their assumed algebraic signs, these being as calculated for $\varphi = 16° 40'$ and the original molecular model. The resultant distribution function $\rho(x,y)$ is shown in Fig. 4. It is seen that the function corresponds to well-defined molecules of the type described. In order to obtain some information as to the reliability of the distribution function and especially as to the effect of breaking off the Fourier series, the calculations were repeated three times: first, with use of the *F* values of Table I except for omission of the form {2.10.0}; second, the same except for omission also of the forms {860} and {680}; and third, with inclusion of all forms, the *F*-values of Table I being multiplied by a factor decreasing from 1 for forms with sin ϑ/λ less than 0.75 to 0.20 for the forms with largest sin ϑ/λ, in order to force a gradual termination of the series. The atomic coördinates given by the four treatments deviate from their average values by a mean of 0.002, or 0.02 Å. The average values of the atomic coördinates given by the four treatments are

$$\begin{aligned} \mathrm{O}:&\ x = 0.074,\ y = 0.143\\ \mathrm{C_1}:&\ x_1 = 0.149,\ y_1 = 0.050\\ \mathrm{C_2}:&\ x_2 = 0.291,\ y_2 = 0.091 \end{aligned}$$

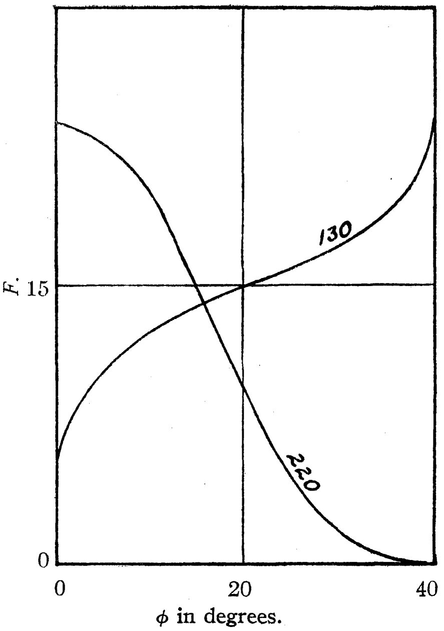


Fig. 2.—Preliminary determination of parameter φ with use of observed equality of intensity for (130) and (220).

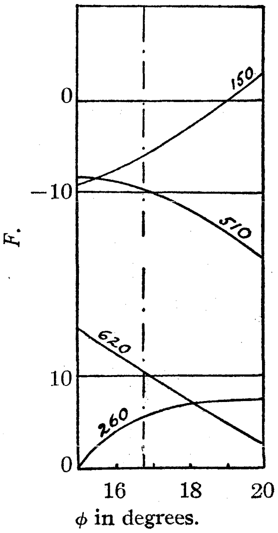


Fig. 3.—Determination of parameter φ.

These correspond to the projected interatomic distances C–O = 1.24 Å. and 1.28 Å. and C–C = 1.53 Å. (all ±0.03 Å.), in excellent agreement with the originally assumed values C–O = 1.27 Å. and C–C = 1.54 Å.

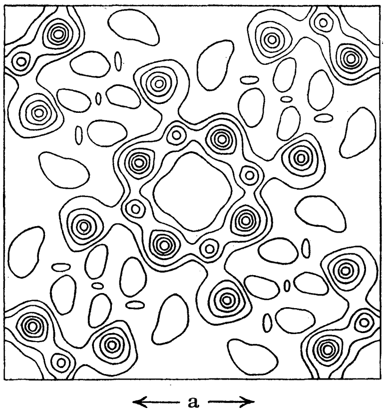


Fig. 4.—Distribution function $\rho(x,y)$ for metaldehyde (projection on (100)).

The value of φ given by the distribution function is about 17° 30′, and that given by our original treatment is 16° 40′. Inasmuch as the projected interatomic distances agree with those originally assumed to within 0.02 Å., we shall accept the original molecular model as verified by experiment, and take for φ the average of the two determined values, 17° 0′ ± 30′. The atomic arrangement of the crystal is then described by the parameters

$$\begin{aligned} \mathrm{O}:&\ x = 0.074,\ y = 0.140,\ z = -0.163\\ \mathrm{C_1}:&\ x_1 = 0.151,\ y_1 = 0.047,\ z_1 = 0.000\\ \mathrm{C_2}:&\ x_2 = 0.293,\ y_2 = 0.090,\ z_2 = 0.000 \end{aligned}$$

The values of the *z* parameters are those corresponding to the original model. Verification of these values is provided by the general agreement of calculated and visually estimated observed intensities of layer-line reflections (Table II).

TABLE II

LAYER-LINE REFLECTIONS FOR METALDEHYDE

First layer line				Second layer line	
	Intensity			Intensity	
hkl	Obsd.	Calcd.	*hkl*	Obsd.	Calcd.
121	40	71	222	10	10
211	10	10	312	60	50
301	9	8	402	15	17
231	18	17	142	25	27
321	18	32	332	7	5
141	10	12	242	8	5
411	40	55	422	27	24
341	18	8	512	20	22
431	40	55	152	6	8
501	46	39	352	15	18
251	20	15	532	8	4
521	15	17	602	4	1
161	0	2	622	8	17
611	9	10	262	9	8
451	9	13	552	3	2
361	6	15	192	4	1
631	5	7	772	3	1
701	0	1			
271	6	8			
721	15	23			
471	5	9			
901	6	9			
921	9	7			
491	2	4			
1.10.1	3	6			

Description and Discussion of the Structure

The crystal of metaldehyde is found to consist of molecules with the configuration shown in Fig. 1 arranged as shown in Fig. 5. The single-bond distances 1.43 Å. (C–O) and 1.54 Å. (C–C) and the tetrahedral bond angle 109° 28′ for both carbon and oxygen are verified within the accuracy of the investigation (±0.03 Å. and ±3°, respectively). The molecules are piled in columns along the *c*-axis. We expect the forces between adjacent molecules in a column to be large, because of the apposition of the negatively charged face of each molecule (formed by the four oxygen atoms of the staggered ring) to the positively charged face of the next molecule (formed by the hydrogen atoms attached to the ring carbon atoms).[8] On the other hand, the forces between columns are small, the molecules in one column presenting their relatively inactive methyl groups to those of the surrounding columns. In consequence the crystal cleaves easily into fibers.

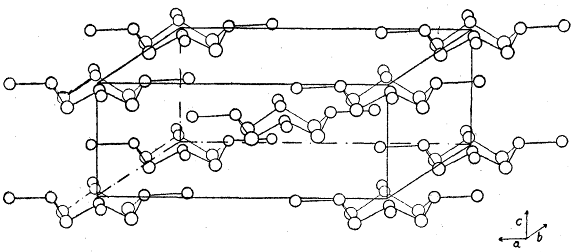
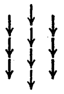


Fig. 5.—Arrangement of metaldehyde molecules in the unit cell.

It is interesting that the translation by $c_0/2$ of each column relative to its four nearest neighbors brings the molecule dipole into an electrostatically stabilized configuration



in which the positive poles of one column are closer to the negative poles of neighboring columns than to their positive poles.

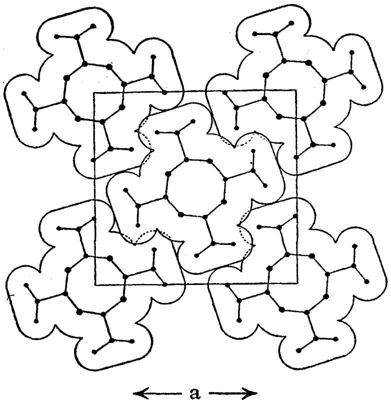


Fig. 6.—Packing diagram of metaldehyde molecules in the unit cell.

The packing of the molecules is shown in Fig. 6, drawn with packing radii of 1.0 Å. for hydrogen and 1.5 Å. for oxygen, the C–H distance being taken as 1.06 Å. and the methyl groups being assumed to rotate about the C–C bonds. Each methyl group is approximately equidistant from eight methyl groups of surrounding molecules, there being two at a distance of 3.90 Å., four at 4.03 Å., and two at 4.11 Å. (directly above and below), corresponding to a packing radius for the methyl group of 2.01 ± 0.06 Å. The variation observed in the methyl–methyl distances is not accidental; it is clearly the result of the shape of the methyl group. Interatomic distances between hydrogen atoms are found to be very closely equal, showing that a hydrogen atom attached to carbon can be assigned a packing radius and con-

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[8] The parallel dipole moments of the molecules give rise to the observed pyroelectric effect.

sidered to behave as a sphere (so far as contacts in directions away from the carbon atom are concerned). This point of view has been especially emphasized by Mack[9] in connection with his interesting work on the packing of organic molecules. In metaldehyde, assuming rotation of methyl groups, the hydrogen–hydrogen distances corresponding to the methyl–methyl contacts mentioned above are 2.16 Å. (two), 2.15 Å. (four), and 2.11 Å. (two), giving for hydrogen the packing radius 1.07 ± 0.01 Å.

There may also be contact between oxygen and hydrogen atoms. Each oxygen atom is 2.68 Å. from two hydrogen atoms attached to ring carbons of the molecule below, and 2.70 Å. from a hydrogen atom in an adjacent column. These distances correspond to a packing radius for oxygen of 1.6 Å., which is somewhat larger than the ionic crystal radius 1.40 Å.

It is interesting to note that metaldehyde, like paraldehyde, contains no aldehyde groups, the oxygen atoms being ethereal in type.

We are indebted to Dr. S. Weinbaum for much assistance in the course of this investigation.

Summary

The tetragonal crystal metaldehyde is shown by x-ray examination to have a body-centered unit of structure with $a_0 = 10.40$ Å. and $c_0 = 4.11$ Å., containing two molecules of the tetramer, $(CH_3CHO)_4$. The atomic arrangement involves all atoms in general positions of the space group C_4^5–I_4, with the following parameter values: oxygen, $x = 0.074$, $y = 0.140$, $z = -0.163$; ring carbon, $x_1 = 0.151$, $y_1 = 0.047$, $z_1 = 0.000$; methyl carbon, $x_2 = 0.293$, $y_2 = 0.090$, $z_2 = 0.000$. The molecule contains an eight-membered –C–O–C– ring, with the carbon–oxygen distance 1.43 ± 0.03 Å., and methyl groups attached to ring carbon atoms, with the carbon–carbon distance 1.54 ± 0.03 Å. The bond angles of oxygen and carbon have the value 109.5 ± 3°. A discussion of the packing of the molecules and of the packing radii of the methyl group and hydrogen atom is given.

PASADENA, CALIF.
GENEVA, N. Y.

RECEIVED MAY 11, 1936

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[9] E. Mack, Jr., THIS JOURNAL, **54**, 2141 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE B. F. GOODRICH COMPANY]

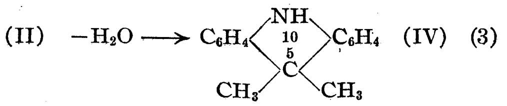
The Preparation of Acridanes by the Grignard Reaction

BY W. L. SEMON AND DAVID CRAIG

In previous publications[1a] *o*-*t*-butyldiphenylamine (III) has been identified as one of the two main products from the reaction of methylmagnesium iodide with methyl N-phenylanthranilate (I). The other product[1b] is shown here to be 5,5-dimethylacridane (IV) formed as indicated in reactions 1 and 3 by the dehydration of *o*-anilinophenyldimethylcarbinol (II).

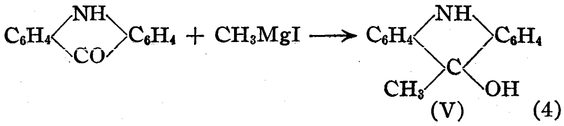
$$C_6H_5—NH—C_6H_4\text{-}o—CO—OCH_3\ (I) + CH_3MgI \longrightarrow$$
$$C_6H_5—NH—C_6H_4\text{-}o—C(OH)(CH_3)_2 \qquad (II) \quad (1)$$

$$(II) + CH_3MgI \longrightarrow$$
$$C_6H_5—NH—C_6H_4\text{-}o—C(CH_3)_3 \qquad (III) \quad (2)$$



$$(II)\quad -H_2O \longrightarrow C_6H_4\langle\overset{NH}{\underset{C(CH_3)_2}{\ }}\rangle C_6H_4 \qquad (IV) \quad (3)$$

The acridane (IV) has not previously been described and identified although some may have been contained in the material isolated following the action of sodium on commercial acridine.[2] The 5,5-diphenylacridane[3] and certain amino derivatives of acridane[4] have been prepared by reactions similar to the ones used here. While this method of formation is strong evidence for the accuracy of the formula assigned to IV, it is not beyond the realm of possibility that the product might have been *o*-isopropenyldiphenylamine. A more conclusive proof for the presence of an *o*,*o*′-carbon bridge was found in the synthesis of IV from compounds such as acridone or 5-methylacridine already containing the heterocyclic nucleus. This was accomplished by reactions 4 and 6



$$C_6H_4\langle\overset{NH}{\underset{CO}{\ }}\rangle C_6H_4 + CH_3MgI \longrightarrow C_6H_4\langle\overset{NH}{\underset{C(CH_3)(OH)}{\ }}\rangle C_6H_4 \qquad (V) \quad (4)$$

$$V + CH_3MgI \longrightarrow IV$$

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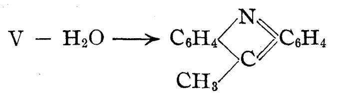
[1] (a) Craig, THIS JOURNAL, **57**, 195 (1935); (b) Semon, British Patent 405,797, Jan. 30, 1933, and French Patent 750,474, May 29, 1933.

[2] Bergmann and Blum-Bergmann, *Ber.*, **63**, 759 (1930).

[3] (a) Baeyer and Villiger, *ibid.*, **37**, 3191 (1904); (b) Gilman, THIS JOURNAL, **51**, 2260 (1929); (c) Kehrmann, and Tschui, *Helv. Chim. Acta*, **8**, 28 (1925).

[4] Goldstein and others, *ibid.*, **11**, 486 (1928), and previous papers especially *ibid.*, **11**, 478 (1928).



$$V - H_2O \longrightarrow C_6H_4\begin{matrix}N\\ C\\ CH_3\end{matrix}C_6H_4 \quad (VI) \qquad (5)$$

$$VI + CH_3MgI \longrightarrow IV \qquad (6)$$

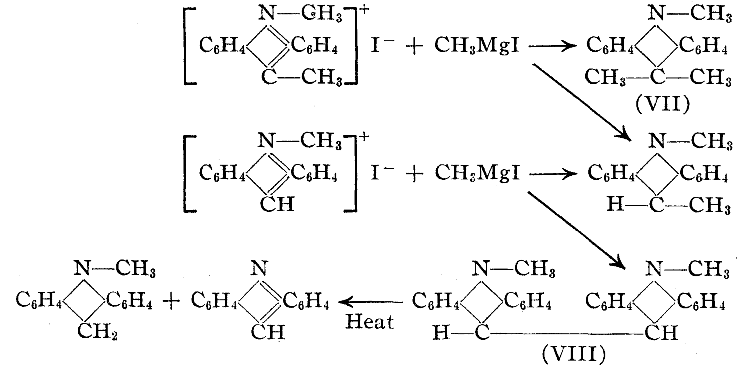
In some respects reaction 4 is similar to reaction 2 and might indicate the direct replacement of oxygen by Grignard reagent;[5] however, a two-stage reaction such as the 1,4-addition of methylmagnesium iodide to an unsaturated intermediate is not precluded[6] as a means for explaining the formation of III, or of IV from reaction 6.

Higher homologs of IV have been prepared by these same reactions. Thus ethylmagnesium bromide reacts with I to yield an oil analyzing satisfactorily for *o*-anilinophenyldiethylcarbinol. On dehydration there is obtained 5,5-diethylacridane and an isomer, possibly *o*-pentenyldiphenylamine. The formation of *o*-*t*-heptyldiphenylamine was not observed. The isolation of the two isomers emphasized the desirability for preparing the acridane by a reaction similar to reaction 4. Both the 5,5-diethylacridane and the 5,5-di-*n*-butylacridane were thus prepared from caridone and the appropriate alkylmagnesium halides.

In all of the cases discussed so far the alkylmagnesium halide has reacted with =NH or –N= to form N-magnesium halides. These have been hydrolyzed to the corresponding NH compounds as is usual in the process of working up such reaction mixtures.[7]

Where the nitrogen has an alkyl group attached as in the 5-alkylacridinium salts, the reaction with alkylmagnesium halide becomes more complex. Freund and Bode[8] reported 5,5-diethyl-10-methylacridane formed by the reaction of 5-ethylacridine methiodide with ethylmagnesium bromide and of 5,10-di-methylacridane by a similar reaction. Further, Stevens, *et al.*,[9] reported 5,5,10-trimethylacridane as a product from the reaction of methylmagnesium iodide with 5-methylacridine methiodide or with 5-cyano-5,10-dimethylacridane. However, the compounds reported were not well characterized and that described as trimethylacridane is probably, in the light of the present work, a mixture of this compound (m. p. 100–102°) and of 5,10-dimethylacridane (m. p. 140–141°). Freund and Bode[8a] failed to mention the formation of acridine from the reaction of methylmagnesium iodide and acridine methiodide and did not record the isolation of any high melting compound. We have subsequently isolated such a material and assigned formula VIII as it is probably the N,N′-dimethyl homolog of diacridane. The melting point of this compound, due to decomposition, varied with the rate of heating and the product of pyrolysis contained acridine and 10-methylacridane, thus behaving in a manner quite similar to the unsubstituted diacridane.[10]

Reaction 7 accounts for the products obtained when acridine methiodide and 5-methylacridine methiodide were treated with methylmagnesium iodide.



(7)

The further observation that the original acridine is reformed when the corresponding methiodide is treated with Grignard reagent indicates the reversible character of the formation of acridinium salts; thus the consumption of alkyl halide by some reagent such as the Grignard favors the decomposition and explains the formation of the ethane which is evolved as a gas in the course of the reaction.

The low yields and many products observed from the reaction of acridinium salts and Grignard reagent indicate that the products may not be formed in a single reaction but rather in a series of concurrent ones. If we generalize in re-

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[5] (a) See footnote 11, Ref. 1; (b) Maxim and Mavrodineanu, *Bull. soc. chim.*, [5] **2**, 591 (1935); (c) Aston, Ailman, Scheuermann and Koch, THIS JOURNAL, **56**, 1164 (1934); (d) Robinson and Robinson, *J. Chem. Soc.*, **123**, 532 (1923).

[6] Gilman, Kirby and Kinney, THIS JOURNAL **51**, 2252 (1929); Hoffman, Farlow and Fuson, *ibid.*, **55**, 2000 (1933).

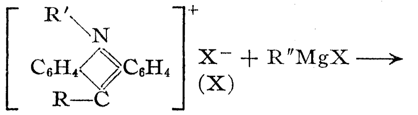
[7] For the formation of additive compounds of Grignard reagents with acridines, see Senier, Austin and Clarke, *J. Chem. Soc.*, **87**, 1469 (1905).

[8] (a) Freund and Bode, *Ber.*, **42**, 1746–1766 (1909); (b) see also Richter-Anschütz, "Chemie der Kohlenstoffverbindungen," Akademische Verlagsgesellschaft, Leipzig, 1931, Vol. III, p. 262.

[9] Stevens, *et al.*, *J. Chem. Soc.*, 2568–2572 (1931).

[10] Lehmstedt and Hundertmark, *Ber.*, **63**, 1239 (1930).

gard to a reaction such as reaction 8, it may be seen that the Grignard reagent may add in two



(8)

different ways in a 1,4-manner and in a larger number of ways if the less likely 1,2-addition is to be considered. The MgX portion may therefore be attached through N or through C. Where the attachment is to N there should be formed 5,5,10-trisubstituted acridane; where the attachment is to C there is formation of a new more complex Grignard reagent along with generation of alkyl halide which may occur in at least two ways. Further, the various Grignards now present may react with the alkyl halides and unsaturates to give a multiplicity of products which may account for the evolution of hydrocarbon noted. Specifically if the C attached MgX derivative reacts with X there is formed a complex salt which gives rise to a diacridane derivative of the type VIII already mentioned. Further, since acridines may be liberated from the acridinium salts by Grignard reagents as previously mentioned the possibility of these reacting further should not be overlooked. Pseudo-salt formation as an alternate for reaction 8 explains all of the products so far isolated but does not predict quite as many products in the case of higher homologs. The extent to which the formation of reduction products was due to unreacted magnesium was not determined.

Properties of 5,5-Dimethylacridane.—5,5-Dimethylacridane (IV) shows the typical reactions of a diarylamine. It dissolves readily in concentrated sulfuric acid and less readily in concentrated hydrochloric acid to form colorless solutions from which the free base precipitates on dilution with water. It forms N-acetyl, N-phenyl, N-methyl and N-metallic derivatives, showing the presence of a secondary amino group. One interesting reaction that indicates its similarity to many other hydrocarbon substituted diarylamines is the formation of 5-methylacridine by heating with hydrochloric acid, an essential reversal of the reaction by which it is formed from methylmagnesium iodide and 5-methylacridine. This reaction also occurs on refluxing IV with its N-sodium salt. The absence of an unsaturated side chain in the molecule is shown by the remarkable stability of IV on prolonged refluxing with aqueous potassium permanganate. 5,5-Dimethylacridane in a manner entirely similar to other diarylamines readily forms fairly stable yellow double compounds with acridine and 5-methylacridine.[11]

Experimental Part

5,5-Dimethylacridane (IV).—This compound prepared as previously described[1a] was reported as melting at 122–124°. After further recrystallization it was found to melt at 125–126°. Addition of 17 g. (0.088 mole) of 5-methylacridine to a solution of 0.3 mole of methylmagnesium iodide in 100 cc. of *n*-butyl ether at 100° produced no apparent reaction. When the mixture was heated to boiling, a vigorous reaction set in. After refluxing for thirty minutes the mixture was poured into ice water containing 30 cc. of glacial acetic acid. A solid precipitated which proved to be 5-methylacridine hydroiodide, yield 11.5 g. The butyl ether layer was separated, dried and upon distillation gave 3.5 g. of a product boiling at 155° at 1 mm. Recrystallization gave 2.5 g. of pure 5,5-dimethylacridane of the same melting point as the material prepared from methyl N-phenylanthranilate. This compound was also prepared by adding 18 g. (0.092 mole) of acridone to 0.3 mole of methylmagnesium iodide in di-*n*-butyl ether. Reaction began at 80° but, due to the insolubility of the acridone, it was not complete even after refluxing for thirty minutes. There were isolated from the crude reaction product, 6 g. of 5-methylacridine and 2.5 g. of 5,5-dimethylacridane or yields of 44 and 17%, respectively, of these compounds based upon the unrecovered acridone (14 g.).

Anal. Calcd. for $C_{15}H_{15}N$: C, 86.07; H, 7.23; N, 6.70. Found: C, 86.0, 86.3; H, 7.28, 7.29; N, 6.96, 6.80.

The acetyl derivative was prepared by reaction of IV with acetyl chloride and crystallization from hexane. It melted at 153–154°. The benzoyl derivative was prepared by reaction with benzoyl chloride and, when crystallized from *o*-dichlorobenzene, melted at 294–297°.

5,5-Dimethylacridane is easily soluble in concentrated sulfuric acid from which it is precipitated by the addition of water. This property is useful for separating IV from other compounds which may be either less soluble in concentrated acid, or soluble and more strongly basic so that soluble, stable salts remain unhydrolyzed on dilution. 5,5-Dimethylacridane dissolves less readily in concentrated hydrochloric acid. A solid hydrochloride is not formed under these conditions. The free base precipitates on the addition of water. The solutions both in sulfuric and in hydrochloric acid are colorless, thereby distinguishing the compound from an acridine. The reaction of IV with iodobenzene according to Goldberg's[12] method gave an N-phenyl derivative, m. p. 123°, after crystallization from alcohol. The mixed melting point of this derivative and of the parent compound was lower than either. 5,5-Dimethylacridane reacted with sodium or sodamide much like diphenylamine and formed the N-sodium derivative.

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(11) Blum, *Ber.*, **62**, 891 (1929), described the corresponding double compounds of diphenylamine with these acridines as well as the double compound of 5-methylacridine with 5-methylacridane.

(12) Goldberg, *ibid.*, **40**, 4541 (1907).

Forty grams of 5,5-dimethylacridane and 0.5 g. of sodamide were heated gently until the evolution of ammonia was complete. The temperature was then raised to the refluxing point and maintained for forty-five minutes. A combustible gas was evolved slowly. The product was cooled and shaken with 100 cc. of benzene and the mixture extracted with three 50-cc. portions of 5% sulfuric acid. On making the extracts alkaline 2 g. of 5-methylacridine separated. After crystallizing from a mixture of benzene and hexane it melted at 117–119°. Heating a mixture of 5,5-dimethylacridane (0.3 mole), hydrogen chloride (0.15 mole) and diphenylamine (0.45 mole) in an autoclave for three hours at 250° gave 5-methylacridine and a combustible gas, presumably methane. The acid was neutralized and the non-aqueous portion distilled. The bright yellow double compound of 5-methylacridine with 5,5-dimethylacridane separated on crystallization from hexane. The melting point, 124°, was depressed not at all or only a few degrees by the addition of varying quantities of 5,5-dimethylacridane.

Anal. Calcd. for $C_{15}H_{15}N \cdot C_{14}H_{11}N$: C, 86.52; H, 6.52; N, 6.96. Found: C, 86.65; H, 6.51; N, 7.04.

The same compound was also prepared by mixing equimolecular quantities of the components dissolved in hot hexane or alcohol solution and cooling. Plates were secured from alcohol and needles from hexane. The corresponding double compound of 5,5-dimethylacridane with acridine melted at 135–136° when crystallized from hexane. The acridine components can be separated readily from these double compounds by repeated extraction with dilute sulfuric or nitric acid. Hydrochloric acid is less suitable because of the low solubility of the acridine hydrochlorides in water.

5,5-Dimethylacridane showed no signs of reaction with boiling aqueous potassium permanganate during four hours, the starting material being recovered unchanged.

During some experiments on the melting and freezing of 5,5-dimethylacridane it was found that a low melting (m. p. 92–93°) form could be obtained by careful cooling. It was unstable in the presence of the high melting form.

5,5,10-Trimethylacridane, 5,10-Dimethylacridane and Related Compounds.—The trimethyl derivative was prepared by treating the sodium salt of IV with methyl iodide in refluxing toluene. The sodium iodide was washed out with water and the oil fractionally distilled. Unreacted IV was then separated from its N-methyl derivative by crystallizing from a mixture of hexane and benzene. The N-methyl derivative melted at 100–102°.

Anal. Calcd. for $C_{16}H_{17}N$: C, 86.04; H, 7.68; N, 6.28. Found: C, 85.88; H, 7.64; N, 6.49.

In order to repeat the work of Stevens, *et al.*,[9] 0.072 mole of finely powdered 5-methylacridine methiodide[13] (m. p. 265–267°) was added to 0.30 mole of methylmagnesium iodide in 100 cc. of ether during five minutes. Reaction took place rapidly with the disappearance of the red color of the methiodide and with the evolution of a gas. The mixture was refluxed for forty minutes and then hydrolyzed with dilute acetic acid. Benzene (100 cc.) was added and the ether distilled. The residue was filtered, yielding 4.5 g. of solid material that was not identified. The benzene layer was distilled and yielded 10.5 g. of material at 160–170° (1.5 mm.). This on crystallization from a mixture of benzene and hexane gave 1.5 g. of crystals of m. p. 140–141° and 1.5 g. of less pure product of m. p. 138–140°. This product is 5,10-dimethylacridane.

Anal. Calcd. for $C_{15}H_{15}N$: C, 86.07; H, 7.23; N, 6.70. Found: C, 86.05; H, 7.13; N, 6.99.

The mother liquor was extracted with dilute hydrochloric acid to remove colored by-products and on evaporation yielded 1 g. of crystals melting at 92–98°. These on crystallization from hexane melted at 100–102°, alone or mixed with the above described 5,5,10-trimethylacridane.

The 5,10-dimethylacridane just described was identified by mixed melting point with the compound prepared from the addition of 0.1 mole (32.1 g.) of acridine methiodide (m. p. 206–209°, dec.) to a well-cooled solution of 0.3 mole of methylmagnesium iodide in 100 cc. of ether. Reaction occurred with the evolution of a gas, presumably ethane, and precipitation of a solid. The mixture was hydrolyzed with ice and dilute acetic acid in the usual way. A considerable amount of solid (12 g.) was filtered off. From the filtrate there were obtained acridine and 5,10-dimethylacridane; yield 8.5 g. A small amount of impurity in the latter compound may have been 10-methylacridane.[14]

The solid after crystallizing twice from toluene melted with decomposition at about 280°.

Anal. Calcd. for $C_{28}H_{24}N_2$: C, 86.55; H, 6.23; N, 7.21. Found: C, 86.87; H, 6.08; N, 7.43.

Three grams of this solid was heated to reflux for three minutes, during which time the temperature reached 350°. The product was treated with 50 cc. of concentrated hydrochloric acid and filtered to remove a small amount of insoluble matter. Several volumes of water were added. The oil thus precipitated soon crystallized and was then filtered off. Four tenths gram of acridine was recovered from the filtrate by distilling the organic bases precipitated by the addition of sodium hydroxide. The product that was filtered off was dissolved in benzene. In order to remove traces of acridine the benzene solution was extracted repeatedly with dilute hydrochloric acid and finally with water. Distillation of the benzene solution produced 0.7 g. of crude 10-methylacridane. It melted at 91–93° after recrystallizing twice from petroleum ether.

Anal. Calcd. for $C_{14}H_{13}N$: C, 86.11; H, 6.72; N, 7.17. Found: C, 86.10; H, 6.82; N, 7.31.

A reaction of methylmagnesium iodide with acridine hydroiodide under the conditions used for acridine methiodide gave approximately a 15% yield of acridane along with some unreacted acridine. Attempts to isolate 5-methylacridine from the products were not successful.

5,5-Diethylacridane.—Thirty grams (0.132 mole) of methyl N-phenylanthranilate in 150 cc. of ether was added to 0.6 mole of ethylmagnesium iodide in 150 cc. of ether during twenty-five minutes. The heat of reaction caused the mixture to boil. A greenish-yellow color developed and a small amount of precipitate appeared. Stirring was continued for forty minutes during which time more of the precipitate formed. The mixture was allowed to stand at room temperature for three days, hydrolyzed with dilute

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[13] Hamer, *J. Chem. Soc.*, 1002 (1930).

[14] Bergmann, Blum-Bergmann and Christiani, *Ann.*, **483**, 80 (1930).

acetic acid in the usual way and distilled. The product boiled at 175° (2 mm.); yield 27 g. (79%).

Anal. Calcd. for $C_{17}H_{21}NO$: C, 79.94; H, 8.30; N, 5.49. Found: C, 79.76; H, 8.39; N, 5.66.

These values are in agreement with the empirical formula of *o*-anilinophenyldiethylcarbinol.

The product was dehydrated by dissolving in concentrated sulfuric acid and pouring into water. Distillation of the oil obtained and crystallization from hexane separated it into a white solid, m. p. 90–91°, and an oil, b. p. 150–155° (2 mm.).

Anal. Calcd. for $C_{17}H_{19}N$: C, 86.02; H, 8.07; N, 5.91. Found for the solid: C, 85.99; H, 8.19; N, 6.08. Found for the oil: C, 86.01; H, 8.10; N, 5.89.

The oil contained a small amount of the solid and was probably largely an *o*-pentenyldiphenylamine. The solid was shown to be 5,5-diethylacridane by its synthesis as follows: 18 g. (0.092 mole) of acridone was added rapidly to 0.3 mole of ethylmagnesium bromide in 150 cc. of *n*-butyl ether at 100°. A vigorous reaction ensued causing the temperature to rise to 120°. The mixture was refluxed and stirred for two hours. When this was poured into water a greenish precipitate separated which was filtered off after the addition of 25 cc. of acetic acid and standing overnight; yield 7 g.; m. p. 250–270°. The ether layer was separated and distilled. A fraction, b. p. 150°(2 mm.)–165° (3 mm.), weighing 11 g. and a residue of 5 g. was obtained. The fraction, b. p. 150°(2 mm.)–165° (3 mm.) gave 7 g. (34% yield) of 5,5-diethylacridane which when recrystallized from hexane melted at 90–92° alone or mixed with the solid product obtained from methyl N-phenylanthranilate.

5,5-Di-*n*-butylacridane.—This compound was prepared in refluxing ethyl ether from 13 g. (0.067 mole) of acridone and 0.4 mole of *n*-butylmagnesium bromide. The initial reaction took place rapidly. After thirty minutes the ethyl ether was distilled off and the mixture refluxed in *n*-butyl ether for thirty minutes. The mixture was hydrolyzed in the usual manner with acetic acid and the product distilled and crystallized from hexane; m. p. 87–88°, b. p. 173–183° (2 mm.). The yield of pure product was 4 g. (24%).

Anal. Calcd. for $C_{21}H_{27}N$: C, 85.94; H, 9.28; N, 4.78. Found: C, 85.96; H, 9.16; N, 4.86.

Summary

1. The preparation of 5,5-dialkylacridanes by the reaction of acridines, acridinium iodides, acridone and methyl N-phenylanthranilate with Grignard reagents is described.

2. The following new compounds were prepared: 5,5-dimethylacridane, 5,5,10-trimethylacridane, 5,5-diethylacridane, *o*-anilinophenyldiethylcarbinol, 5,5-di-*n*-butylacridane and the double compounds of acridine and 5-methylacridine with 5,5-dimethylacridane.

3. The properties of 5,5-dimethylacridane are described in considerable detail.

AKRON, OHIO RECEIVED FEBRUARY 28, 1936

[CONTRIBUTION FROM THE LABORATORIES OF THE WM. S. MERRELL COMPANY]

The Synthesis of Dibenzoyl Disulfide

BY R. S. SHELTON AND T. H. RIDER

Amberg and Brunsting[1] recently investigated the use of dibenzoyl disulfide,[2] and found it of considerable value as an antipruritic. Their favorable preliminary clinical report suggested that a detailed study of the properties and methods of preparing dibenzoyl disulfide might be of interest and value, especially as applied to the commercial production of a medicinally pure product.

A check of the previous literature[3] on this product failed to give a method of preparation which was economically feasible.

It was found early in this investigation that sodium thiobenzoate is easily formed by the reaction of benzoyl chloride with 35% aqueous sodium hydrosulfide. The thiobenzoate was not, however, oxidized to any great extent in the reaction mixture to the desired disulfide. The reaction was tried in alcoholic solution, but without much better result, due to the reaction of the alcohol with the acid chloride.

A further investigation of the oxidation of the thiobenzoate yielded satisfactory results. Engelhardt, Latschinoff and Malyscheff[4] had previously studied the oxidation of thiobenzoic acid by the action of air, cupric sulfate, ferric chloride, potassium triiodide and potassium ferricyanide. These and other oxidation agents were investi-

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(1) S. Amberg and L. A. Brunsting, *Proc. Staff Meet. Mayo Clinic*, **8**, 443 (1933).

(2) Dibenzoyl disulfide was referred to in the original clinical report[1] as "benzoyl persulphide," an inaccurate nomenclature since it does not distinguish between the di-, tri- or tetra-sulfides, all of which are known [I. Block and M. Bergmann, *Ber.*, **53**, 961 (1920)].

(3) E. Fromm, *Ann.*, **348**, 144 (1906); A. Weddige, *J. prakt. Chem.*, **2**, 459 (1871); E. Moness, W. A. Lott, F. F. Berg and W. G. Christiansen, Portland Meeting, American Pharmaceutical Association, August, 1935; Wöhler and Liebig, *Ann.*, **3**, 267 (1832); A. Engelhardt, P. Latschinoff and S. Malyscheff, *Z. chem.*, **11**, 353 (1868); I. Block and M. Bergmann, *Ber.*, **53**, 961 (1920); J. v. Braun, *ibid.*, **36**, 2259 (1903); A. Binz and Th. Marx, *ibid.*, **40**, 3855 (1907); S. Mosling, *Ann.*, **118**, 305 (1861); L. Szperl, *Roczniki Chemji*, **10**, 510 (1930); *C. A.*, **25**, 503 (1931).

(4) A. Engelhardt, P. Latschinoff and S. Malyscheff, *Z. chem.*, **11**, 353 (1868).

gated and concentrated hydrogen peroxide was found to give the best results. It was found also that thiobenzoic acid is oxidized more smoothly than the sodium salt, and that oxygen was very useful in aiding the oxidation of the thiobenzoate as it was formed in the reaction mixture. From these preliminary findings, a method was developed,[5] easily applicable to large-scale production, in which thiobenzoic acid is oxidized as completely as possible by air and oxygen at the time of its formation in the reaction mixture, and after acidification the oxidation of the filtrate is completed with concentrated hydrogen peroxide.

$$\mathrm{C_6H_5COCl + 2NaHS \longrightarrow C_6H_5SOSNa + NaCl + H_2S}$$

$$\mathrm{2C_6H_5COSNa\ (also\ C_6H_5COSH) + H_2O_2 \xrightarrow{[O]} C_6H_5COSSCOC_6H_5 + H_2O}$$

Experimental

A 22-liter flask is fitted with a motor stirrer, inlet tubes for oxygen, a tube connected to the water pump to aid in the removal of hydrogen sulfide and a dropping funnel. The flask is placed in an ice-bath, and to it is added 10.6 liters of commercial 35% sodium hydrosulfide solution. The stirrer and suction pump are adjusted, the flow of oxygen started, and through the dropping funnel 7.4 liters of benzoyl chloride are added slowly over a period of five or six hours. The first 500 cc. of benzoyl chloride must be added slowly, allowing sufficient intervals of time for the materials to react completely. Failure to observe these precautions results in a violent reaction which is difficult to control. After the addition of the benzoyl chloride has been completed, an excess of sodium hydrosulfide solution is added to make sure that the reaction has gone to completion. A completed reaction is evidenced by the cessation of hydrogen sulfide evolution. The reaction mixture is then allowed to stand overnight.

The following day the precipitate (about 4700 g.) is filtered, washed thoroughly with water to remove adhering chlorides and dried in a stream of air. Any thiobenzoic acid which has escaped oxidation and which may have adhered to the precipitate is oxidized completely by this process. The filtrate and washings are cooled in an ice-bath, then acidified with concentrated sulfuric acid. Air or oxygen is bubbled through the cool solution, and 1200 cc. of 30% hydrogen peroxide added in 25-cc. portions over a period of three or four days.

It is important that during this time the solution be kept acid, and that the oxidation by means of air and oxygen be continued until no more precipitate is formed. The precipitate is then filtered, washed with about 5 liters of water and added to the original crop of dibenzoyl disulfide. The crude material is then broken up in small portions and air dried for several days.

Many solvents were investigated in a study of the purification of the crude dibenzoyl disulfide, but none was found to give a pure white material from one recrystallization. Purification is best accomplished as follows. The crude dibenzoyl disulfide is dissolved in ethylene dichloride at 60° in the ratio of 3 kg. to 6 liters of solvent. The resulting solution is faintly pink. It is important that the temperature of the solvent at the time of solution be 60° or less since the disulfide assumes a decided permanent pink color above that temperature. One liter of saturated sodium bicarbonate solution is added, and the mixture stirred vigorously for an hour. This is done in the absence of heat, as the prolonged heating of benzoyl disulfide in the presence of alkalies results in its decomposition, *i. e.*

$$\mathrm{C_6H_5COSSCOC_6H_5 + 2NaOH \longrightarrow C_6H_5COSNa + C_6H_5COONa + S + H_2O}$$

The alkali purification removes the benzoic acid which is present as an impurity. It was found that sodium bicarbonate gave less decomposition than dilute sodium hydroxide.[6] The layers are allowed to separate, and the ethylene dichloride layer is filtered. Two liters of alcohol (special denatured formula 3A is satisfactory) are added to the filtrate which is then cooled overnight at a temperature of from 0 to 5°. The precipitate is filtered and washed with about 300 cc. of ether. The filtrate is then cooled to −15° and a second crop is obtained, generally of sufficient purity to be added to the first crop. The total yield of purified dibenzoyl disulfide, after air drying, is about 5.5 kg. (yields of 5.9 kg. were obtained on some runs). Yields of about 80% of crude material were obtained; yields of purified material were about 65 to 70% of the theoretical.

Dibenzoyl disulfide is reported in the literature as a white to faintly pink crystalline solid, but there is lack of agreement as to its melting point. Dibenzoyl disulfide, purified by the method described, is a faintly pink (Norite did not remove this coloration) crystalline solid, melting with decomposition to a pink liquid between 128 and 129°, in a capillary tube preheated to 100°. Further recrystallization from ethylene dichloride or carbon disulfide gave beautiful colorless plates melting at 129–130° in the preheated capillary tube or at 132° on the bar.[7]

Anal. Calcd. for $\mathrm{C_{14}H_{10}O_2S_2}$: C, 61.27; H, 3.67; S, 23.38. Found: C, 60.68; H, 4.21; S, 23.55.

Analytical Degradations of Dibenzoyl Disulfide[8]

In an effort to establish beyond doubt the structure of the product prepared by the above method, we have found that in addition to the routine sulfur analysis, it was advisable to work out a method of analytical degradation by which the benzoic acid could be recovered. While it was found possible to prepare benzanilide quantitatively by simple refluxing with aniline, it was impossible to free the benzanilide completely from sulfur without loss of the benzanilide. Dibenzoyl disulfide was found to be quite resistant to hydrolysis under most conditions, but the following method gave yields of from 98 to 99.2% of benzoic acid.

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[5] T. H. Rider and R. S. Shelton, U. S. Patent 2,028,246, January 21, 1936.

[6] Grateful acknowledgment is made to Dr. E. S. Cook for suggesting the use of sodium bicarbonate and for checking the method of preparation and purification.

[7] L. M. Dennis and R. S. Shelton, THIS JOURNAL, **52**, 3128 (1930).

[8] The method described was worked out by E. S. Cook and Karl Bambach.

Procedure for Analytical Degradation of Dibenzoyl Disulfide to Benzoic Acid.—Reflux 1 g. of dibenzoyl disulfide with 30 cc. of 40% w/v potassium hydroxide solution in a 100-cc. round-bottomed flask for three hours. Cool, transfer to a separatory funnel (rinsing out flask with water), acidify with concentrated hydrochloric acid, and allow to cool. Shake the benzoic acid into ether, using five portions (total of 120 cc.) and collect the ether extracts in another separatory funnel. Wash the ether with 25 cc. of approximately 0.1 *N* hydrochloric acid, and then wash this aqueous portion with 15 cc. of ether. Combine the ether extracts and filter through cotton into a beaker, washing the cotton with fresh ether. Evaporate the ether with the aid of a stream of air. (Evaporation may be hastened by placing the beaker in a water-bath at not over 40° until 30 cc. remains; then remove from water-bath and complete removal with air.) Treat the residue with a solution of 1.5 g. of sodium bicarbonate in 50 cc. of water. Warm the mixture and allow it to stand until all the benzoic acid has dissolved; the sulfur will be practically insoluble. Filter the liquid through a coarse filter paper into a separatory funnel and wash the paper thoroughly with water. Acidify the sodium benzoate solution with 10% hydrochloric acid, allow it to cool, and shake out the benzoic acid with chloroform, using five portions (total of 100 cc.). Collect the chloroform extracts in another separatory funnel. Wash the chloroform with 20 cc. of approximately 0.1 *N* hydrochloric acid, and then wash this aqueous portion with 10 cc. of chloroform. Filter the combined chloroform extracts through cotton into a tared beaker and evaporate the chloroform with the aid of a stream of air, placing the beaker in a water-bath at a temperature of not over 40° as before. Dry the benzoic acid overnight in a vacuum desiccator over sulfuric acid and weigh.

Summary

A new practical method for preparing medicinally pure dibenzoyl disulfide is described.

CINCINNATI, OHIO RECEIVED APRIL 6, 1936

[CONTRIBUTION FROM THE BURROUGHS WELLCOME AND CO., U. S. A., EXPERIMENTAL RESEARCH LABORATORIES]

Some N-Aryl Barbituric Acids

BY JOHANNES S. BUCK

In connection with a study of the hypnotic action of certain unsymmetrical alkylaryl ureas,[1] it was desirable to obtain a series of 1-aryl barbituric acids, having the aryl group the same both for the ureas and for the barbituric acids. Two series were therefore prepared, one having 5,5-diethyl groups and the other 5,5-ethyl-*n*-butyl groups, the N-aryl groups in both series being phenyl, *o*-, *m*- and *p*-tolyl, *o*-, *m*- and *p*-anisyl, *o*-, *m*- and *p*-phenetyl, and α- and β-naphthyl. Hjort and Dox[2] have previously described briefly four of the diethyl compounds, but they failed to crystallize the 1-phenyl-5,5-ethyl-*n*-butyl compound, and to obtain the 1-*p*-ethoxyphenyl-5,5-ethyl-*n*-butyl derivative. The complete series (24) is here described. The pharmacological examination will be published in another place.

Experimental

The ethyl diethylmalonate used was purchased. Ethyl *n*-butylethylmalonate was prepared in good yield by butylating ethyl ethylmalonate, in the usual way by means of sodium ethylate and *n*-butyl iodide. The ester boiled sharply at 109° (1.4 mm.) or 125–126° (11 mm.). When prepared by ethylating ethyl *n*-butylmalonate, no sharp boiling point could be obtained.

The barbituric acids were all prepared by the usual reaction. 0.05 mole (10.8 g. and 12.2 g.) of the dialkylmalonate was added to 0.2 atom (4.6 g.) of sodium dissolved in the minimum amount of absolute alcohol; 0.05 mole of the requisite urea was added and the mixture refluxed for four to five hours. The solution was then cooled, diluted with water, made just acid to Congo red, and most of the alcohol removed, by a current of air, on the steam-bath. The residue was extracted with ether and the ether washed three times with saturated sodium bicarbonate solution, to remove hydrolysis products (very little of the barbituric acid was lost). The washed ether was then extracted with 80 cc. of 10% sodium hydroxide solution, water being added if necessary. On acidification of the alkaline solution the barbituric acid separated, usually as an oil, and was extracted with ether or filtered off and recrystallized until pure, alcohol or slightly aqueous alcohol being the solvent, unless otherwise noted. A few of the ethyl-*n*-butyl compounds were very difficult to purify and required elaborate treatment.

The bicarbonate washings contain uncyclized compounds, which are usually small in amount. They can be isolated by acidifying the solution. Some were examined but are not recorded here. The residual ether contains unchanged urea, ester and decomposition products.

The barbituric acids are tabulated below. Variations in the foregoing procedure are indicated in footnotes. The compounds are all white, crystalline and tasteless. They are soluble in cold 5% sodium hydroxide solution, practically insoluble in water, slightly soluble to insoluble in petroleum ether (the low-melting ones are more soluble), moderately to readily soluble in ether, readily soluble to very soluble in alcohol, and from moderately soluble to

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(1) Hjort, deBeer, Buck and Ide, *J. Pharmacol.*, **55**, 152 (1935).

(2) Hjort and Dox, *ibid.*, **35**, 155 (1929).

TABLE I

1-ARYL-5,5-DIETHYL BARBITURIC ACIDS

Aryl radical	Appearance	M. p., °C.	Formula	Analyses, % N Calcd.	Found
Phenyl[a]	Small thick glittering plates	178	$C_{14}H_{16}O_3N_2$	10.76	10.83
o-Tolyl	Small glittering rect. plates	182	$C_{15}H_{18}O_3N_2$	10.22	10.13
m-Tolyl	Small striated prisms	133	$C_{15}H_{18}O_3N_2$	10.22	10.09
p-Tolyl[b]	Glittering prisms	155.5	$C_{15}H_{18}O_3N_2$	10.22	10.28
o-Anisyl	Nodules of small rect. plates	176.5	$C_{15}H_{18}O_4N_2$	9.65	9.66
m-Anisyl	Masses of fragmentary prisms	115–116	$C_{15}H_{18}O_4N_2$	9.65	9.73
p-Anisyl[c]	Thin flat prisms	129	$C_{15}H_{18}O_4N_2$	9.65	9.66
o-Phenetyl	Small flat rect. prisms	159	$C_{16}H_{20}O_4N_2$	9.21	9.18
m-Phenetyl	Small nodules of prisms	114	$C_{16}H_{20}O_4N_2$	9.21	9.08
p-Phenetyl[d]	Glittering small octahedra	160	$C_{16}H_{20}O_4N_2$	9.21	9.24
α-Naphthyl	Aggregates of small flat prisms	207	$C_{18}H_{18}O_3N_2$	9.03	9.01
β-Naphthyl	Nodules of tiny prisms	146	$C_{18}H_{18}O_3N_2$	9.03	8.97

[a] Hjort and Dox[2] give m. p. 177°. [b] M. p. given as 152–153°. [c] M. p. given as 126–127°. [d] M. p. given as 152–153°.

TABLE II

1-ARYL-5,5-ETHYL-*n*-BUTYL BARBITURIC ACIDS

Aryl radical	Appearance	M. p., °C.	Formula	Analyses, % N Calcd.	Found
Phenyl[a,b]	Powder of minute nodules	*ca.* 70	$C_{16}H_{20}O_3N_2$	9.72	9.83
o-Tolyl[c]	Small stout rhombs	135	$C_{17}H_{22}O_3N_2$	9.27	9.33
m-Tolyl[d,b]	Powder of minute nodules	*ca.* 89	$C_{17}H_{22}O_3N_2$	9.27	9.28
p-Tolyl[c]	Small stout rounded prisms	142	$C_{17}H_{22}O_3N_2$	9.27	9.33
o-Anisyl[e]	Slightly glittering small prism. nodules	139.5	$C_{17}H_{22}O_4N_2$	8.80	8.82
m-Anisyl[f]	Chalky small nodules	102.5	$C_{17}H_{22}O_4N_2$	8.80	8.82
p-Anisyl	Bulky obscure prism aggregates	124	$C_{17}H_{22}O_4N_2$	8.80	8.84
o-Phenetyl	Granular tiny prisms	131	$C_{18}H_{24}O_4N_2$	8.43	8.48
m-Phenetyl[g,b]	Chalky bulky tiny nodules	84–85	$C_{18}H_{24}O_4N_2$	8.43	8.36
p-Phenetyl[h]	Granular small stout prisms	100	$C_{18}H_{24}O_4N_2$	8.43	8.39
α-Naphthyl[i]	Glittering stout prisms	182	$C_{20}H_{22}O_3N_2$	8.28	8.42
β-Naphthyl	Dull white crusts	126	$C_{20}H_{22}O_3N_2$	8.28	8.32

[a] Not obtained crystalline by Hjort and Dox.[2] Reaction product was distilled (b. p. 203° at 0.5 mm.), rejecting the white sublimate first over. The distillate (stiff resin) was repeatedly recrystallized from carbon disulfide–heptane at 0°, a very tedious operation. The melting point is unsharp. The compound is very soluble in the usual solvents.

[b] These three compounds have recently been obtained crystalline, without the use of distillation, but distillation is preferable, and is essential in order to obtain seeding crystals.

[c] Repeatedly recrystallized from ether.

[d] As footnote [a]. B. p. 212° (0.6 mm.).

[e] After three recrystallizations from aq. alcohol, the product was partly dissolved in ether and the residue recrystallized from ether.

[f] Benzene used for extractions in place of ether.

[g] The reaction product was distilled (b. p. 225–230° at 1.2 mm.) rejecting the white sublimate first over. The distillate was dissolved in carbon disulfide, precipitated with petroleum ether, and kept at the b. p. (216° at 0.5 mm.) until about one-third had distilled over. The residue was crystallized from carbon disulfide–heptane and recrystallized from heptane, then ether, all at 0°. Many months were needed to obtain crystals.

[h] Hjort and Dox[2] obtained only an uncyclized product.

[i] After three recrystallizations from alcohol, the product was again extracted with ether and the ether extracted with another portion of sodium hydroxide solution. After acidification, the precipitate was recrystallized from alcohol, partly dissolved in ether, and the residue recrystallized from alcohol.

very soluble in benzene. The average yield, after drastic purification, is about one-half the weight of ester used, but considerable additional amounts may be recovered from the crystallization liquors. In general, the *m*-aryl compounds show greatly increased solubility and lower melting points, than the ortho and para isomers. The ethyl-*n*-butyl homologs melt lower than the corresponding diethyl compounds.

The ureas used are mostly described, with appropriate references, by Buck, Hjort and deBeer.[3] *p*-Phenetyl urea was purchased from the Eastman Kodak Co. α-Naphthyl urea[4] and β-naphthyl urea[4a] were made by the nitrourea–alcohol method.[5]

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(3) Buck, Hjort and deBeer, *J. Pharmacol.*, **54**, 188 (1935).

(4) Beilsteins "Handbuch der organ. Chem.," 4 Aufl., XII, p. 1238; (4a) *ibid.*, p. 1292.

(5) Buck and Ferry, THIS JOURNAL, **58**, 854 (1936).

The analyses (micro-Dumas) were carried out by Mr. W. S. Ide. The melting points are corrected.

Summary

A series of 1-aryl-5,5-diethyl barbituric acids, and a series of 1-aryl-5,5-ethyl-*n*-butyl barbituric acids, have been prepared, the substituent N-aryl groups in both series being phenyl, *o*-, *m*- and *p*-tolyl, *o*-, *m*- and *p*-anisyl, *o*-, *m*- and *p*-phenetyl, and α- and β-naphthyl. The aryl radicals were selected in order that comparisons might be made, pharmacologically, with a series of alkylaryl ureas having these radicals.

Tuckahoe, New York Received April 23, 1936

[261st Contribution from the Industrial Farm Products Research Division, Bureau of Chemistry and Soils, United States Department of Agriculture]

Biochemical Studies in the Genus Rhizopus. I. The Production of Dextro-Lactic Acid[1]

By G. E. Ward, L. B. Lockwood, O. E. May and H. T. Herrick

Introduction

The production of lactic acid by microörganisms has, in general, been regarded heretofore as an attribute of bacteria, and not characteristic of the fungi. The prevailing conceptions regarding the relation of lactic acid to microbiological metabolism were summarized by Raistrick[2] in 1932: "It is a striking fact that lactic acid has never been reported as a mould metabolic product, although it is produced in larger or smaller quantities by many bacteria." Raistrick and other authors who have made similar statements have probably had in mind the biochemical activities of organisms of genera such as Aspergillus, Penicillium and Fusarium, which, indeed, have never been known to yield lactic acid. However, several investigators have reported lactic acid production in varying quantities by certain organisms of the genera Rhizopus and Mucor.

Since an accurate summary of the literature has never before appeared, and since some of the work is not conveniently reached or translated, it is briefly summarized here. In 1894, Eijkmann[3] suggested that the small quantity of acid produced by *Mucor rouxii* (*rouxianus*) was probably lactic acid, and Chrzaszcz[4] later confirmed this view. Shortly thereafter there were issued patents[5] which described the production of lactic acid by a mold termed "Lactomyces." The culture was of doubtful authenticity, but was probably a Rhizopus. In 1911, Saito[6] reported that *Rhizopus chinensis* produced *l*-lactic acid when cultivated on glucose solutions, and in 1919, Ehrlich[7] stated that in cultures of certain Rhizopus species which produced principally fumaric acid, there occurred small quantities of *d*-lactic acid, succinic acid, and *l*-malic acid.

Takahashi and co-workers[8] showed that up to 38% of the fermented glucose was converted to *l*-lactic acid by certain species of Rhizopus. Varying quantities of fumaric acid, succinic acid, *l*-malic acid, formic acid, acetic acid and ethyl alcohol were also found in these cultures. In 1933, Takahashi and Asai[9] found that four species of Mucor produced traces of lactic acid, in addition to acetaldehyde, ethyl alcohol, pyruvic acid and succinic acid. Ethyl alcohol was the principal product of these fermentations.

In 1930, Kenji Miyaji[10] reported that a new Monilia species isolated from commercial cultures of soy sauce produced *d*-lactic acid and succinic acid when cultured on artificial media containing glucose.

The highest yields of *d*-lactic acid from carbohydrates by fungi heretofore obtained were recently reported by Kanel,[11] who found that a fungus resembling *Rhizopus japonicus* converted 38 to 40% of the consumed invert sugar or starch to this acid. Fumaric acid accumulated in older

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[1] Presented in part before the Section of Biological Chemistry of the American Chemical Society, April, 1935, New York City, N. Y.

[2] Raistrick, *Ergebnisse Enzymforsch.*, **1**, 362 (1932).

[3] Eijkmann, *Zentr. Bakt. Parasitenk.*, **16**, 97 (1894).

[4] Chrzaszcz, *ibid. II*, **7**, 326 (1901).

[5] Boullanger, British Patent 13,439 (1899); German Patent 118,063 (1901).

[6] Saito, *Zentr. Bakt. Parasitenk. II*, **29**, 289 (1911).

[7] Ehrlich, *Ber.*, **52**, 63 (1919).

[8] Takahashi and Sakaguchi, *J. Agr. Chem. Soc .(Japan)* ,**1**, 46 (1925); Takahashi, Sakaguchi and Asai, *Bull. Agr. Chem. Soc. (Japan)*, **2**, No. 5, 61 (1926).

[9] Takahashi and Asai, *Zentr. Bakt. Parasitenk. II*, **89**, 81 (1933).

[10] Kenji Miyaji, *Gifu Imp. Coll. of Agr. (Japan) Research Bull.*, 10 (1930).

[11] Kanel, *Microbiology (U. S. S. R.)*, **3**, 259 (1934).

TABLE I

SUMMARY OF METABOLIC ACTIVITIES OF ACID-PRODUCING RHIZOPI

Organism	*Rhizopus oryzae* 394			*R. oryzae* 395			*R. arrhizus* 519		
Nitrogen source	NH_4NO_3	$(NH_4)_2SO_4$	Urea	NH_4NO_3	$(NH_4)_2SO_4$	Urea	NH_4NO_3	$(NH_4)_2SO_4$	Urea
Age at harvest, days	16	16	16	16	16	16	21	21	21
Weight of mycelium, g.	0.35	0.64	0.87	0.32	0.59	0.80	0.09	0.08	0.14
Glucose consumed, g.[12]	8.3	10.2	10.8	8.3	9.7	10.6	8.8	9.9	9.9
Lactic acid found, g.[13]	4.90	5.51	4.58	5.11	5.25	4.98	3.34	4.08	3.19
Fumaric acid found, g.[14]	None	None	None	None	None	None	None	None	0.017
Calcium in solution, g.	1.25	1.46	1.29	1.29	1.40	1.31	0.86	0.96	0.71
Calcium as lactate, %	87	84	79	88	84	85	86	95	*practically* 100
Calcium as fumarate, %	None	None	None	None	None	None	None	None	Trace
Yield of lactic acid based on glucose consumed, %	59	54	42	62	54	47	38	41	32
Water of crystn. of desiccated zinc lactate, %	...	13.05	...	...	13.00	...	12.91	...	...
Sp. rot. of anhyd. zinc lactate, 4% soln.	...	−8.4°	...	...	−8.3°	...	−8.2°	...	...

Organism	*R. oryzae* 610			*R. tritici* 488			*R. oryzae* 585		
Nitrogen source	NH_4NO_3	$(NH_4)_2SO_4$	Urea	NH_4NO_3	$(NH_4)_2SO_4$	Urea	NH_4NO_3	$(NH_4)_2SO_4$	Urea
Age at harvest, days	21	21	21	20	20	20	21	21	21
Weight of mycelium, g.	0.73	0.91	1.20	Lost	Lost	Lost	0.46	0.78	1.12
Glucose consumed, g.[12]	7.3	10.4	10.6	7.0	9.0	9.0	6.2	9.0	10.5
Lactic acid found, g.[13]	2.97	4.32	4.22	1.74	3.90	2.96	[a]	2.05	2.00
Fumaric acid found, g.[14]	0.28	0.34	0.46	0.74	0.89	0.41	[a]	1.03	1.28
Calcium in solution, g.	0.98	1.25	1.26	0.77	1.17	0.87	[a]	1.08	1.12
Calcium as lactate, %	67	77	75	51	74	76	[a]	43	39
Calcium as fumarate, %	10	9	13	33	26	16	[a]	33	34
Yield of lactic acid based on glucose consumed, %	41	41	40	25	43	33	[a]	23	19
Water of crystn. of desiccated zinc lactate, %	...	13.28	...	...	12.81	...	Zinc lactate not isolated		
Sp. rot. of anhyd. zinc lactate, 4% soln.	...	−7.1°	...	...	−7.3°	...			

[a] Relatively poor development. Complete analysis not made.

cultures, in addition to small quantities of other unidentified acids.

Discussion

In the course of a survey of the biochemical activities of fungi of the genus Rhizopus conducted in this Division, it was found that certain organisms, when cultivated on a glucose-nutrient medium in the presence of calcium carbonate, induced a vigorous fermentation, with the formation of soluble calcium salts, which were found to consist principally of calcium *d*-lactate, with varying quantities of calcium fumarate. Two of the organisms (*Rhizopus oryzae* 394 and *R. oryzae* 395) were outstanding in their ability to convert glucose to *d*-lactic acid, the yields of up to 62% far exceeding those previously reported for fungi.

Ammonium nitrate, ammonium sulfate, and urea were satisfactory nitrogen sources, but none of the organisms developed well or utilized the glucose to an appreciable extent when sodium nitrate was supplied. When cultivated in the absence of calcium carbonate, the organisms generally utilized only a small quantity of the glucose, and developed in the medium only a slight acidity, usually equivalent to not more than 30 cc. of 0.1 *N* potassium hydroxide per flask (75 cc. of culture solution).

Certain strains (two strains of *Rhizopus sp.*, four strains of *R. nigricans*, one of *R. microsporus* and one of *R. chinensis*) produced very little acid under any of the conditions studied. Some strains, particularly one *R. nigricans* and the *R. chinensis*, formed appreciable quantities of ethyl alcohol when urea was used as the nitrogen source and calcium carbonate was absent.

A summary of the activities of organisms which were noteworthy in acid production is presented in Table I. Calcium carbonate was present in all these cases.

From the data presented, it is evident that several Rhizopi are able to convert the major portion of the glucose substrate to *d*-lactic acid, and that two organisms, *R. oryzae* 394 and *R. oryzae* 395, are outstanding in this respect. Fumaric acid is often formed in small quantities by the good lactic

(12) Shaffer and Hartmann, *J. Biol. Chem.*, **45**, 365 (1921).
(13) Friedmann and Graeser, *ibid.*, **100**, 291 (1933).
(14) Hahn and Haarmann, *Z. Biol.*, **87**, 107 (1927).

acid producers, and is formed in considerable amounts by certain other species, especially by *R. oryzae* 585. It should be mentioned that subsequent work has shown that fumaric acid production by *R. oryzae* 394 and *R. oryzae* 395 is a variable function, and small amounts may or may not be present, dependent upon such factors as temperature, age of the cultures, variations in the components of the medium, etc. Data involving this phenomenon and further physiological studies will be presented in a later communication.

All the products of the fermentation have not been identified. The species listed in Table I develop some acidity due to compounds other than lactic and fumaric acids. Many of the solutions give a positive Denigès test for malic acid, and occasionally there have been obtained traces of an acid melting at 177–180°, which suggests the presence of succinic acid. The acidity due to volatile acids is exceedingly small. It is conceivable that there might exist in these biological systems an equilibrium between succinic acid, fumaric acid, malic acid, and perhaps oxalacetic acid, such as has been the subject of recent intensive investigations of tissue metabolism. The authors are studying this question more fully from the standpoint of fungus metabolism.

The 62% yields of *d*-lactic acid given by *R. oryzae* 395 are not only reproducible, but the authors have occasionally attained a yield of 65 to 67% based on the glucose consumed.

Experimental Part

All the cultures were grown at 30° on approximately 15% solutions of commercial hydrated glucose (91.5% *d*-glucose, 8% moisture, 0.4% dextrins), with other nutrient constituents as $MgSO_4 \cdot 7H_2O$, 0.25 g. per liter; KH_2PO_4, 0.30 g. per liter; NH_4NO_3, $(NH_4)_2SO_4$, $NaNO_3$ or urea as nitrogen sources, to yield 0.5 g. of nitrogen per liter.

Each variation was studied in triplicate using 75 cc. of nutrient solution in 200-cc. Pyrex Erlenmeyer flasks. Each variation of nitrogen source was studied with and without the addition of calcium carbonate at the rate of 4 g. per flask. The calcium carbonate was sterilized separately, and added to the sterile nutrient solution at the time of inoculation.

At the conclusion of the incubation period, the culture liquors were analyzed for residual glucose, calcium ion, lactic acid and fumaric acid, as indicated in Table I.

In addition to the examination of its zinc salt, the lactic acid was also identified by the preparation of ethyl lactate (b. p. 154°) and the vacuum distillation of the acid itself (b. p. 119° at 12 mm.).

By virtue of its favorable partition coefficient, the fumaric acid could be separated qualitatively from lactic acid in the first ether extracts of the acidified culture solution, and could then be purified by recrystallization from water. The melting point (285° dec.), neutralization equivalent (58), and melting point of the *p*-nitrobenzyl ester (150°) proved its identity.

In conclusion, the authors wish to mention that the study of the 14 species of Rhizopus reported here represents only the beginning of an investigation of the biochemical activities of the entire genus. About eighty species of the authors' collection have not yet been investigated, it having been considered desirable to study in more detail the production of *d*-lactic acid by the vigorous organisms already encountered.

Summary

Several species of Rhizopus are able to convert glucose to *d*-lactic acid when cultivated in the presence of calcium carbonate. The yields of 62%, based on glucose consumed, are noteworthy in view of the 40% yields which are the highest previously reported. The lactic acid is accompanied by variable quantities of unidentified acids, and may or may not be associated with variable quantities of fumaric acid.

Washington, D. C. Received April 23, 1936

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Tetrachloroethane-1,2-d_2 (*sym*-Dideuteriotetrachloroethane)

BY FRITZ W. BREUER

Studies on organic compounds of deuterium, in progress in this Laboratory,[1] have been extended to the chlorination of acetylene-d_2 to give *sym*-dideuteriotetrachloroethane. A well controlled combination of the gases was effected by a negative catalyst. In common with other deuterium compounds the difference in density ($d^{20}{}_{4}$) 1.6118 as compared with 1.5943 for ordinary *sym*-tetrachloroethane, prepared in precisely the same way in the same apparatus, is most pronounced. Assuming the same molecular volume for the "light" and "heavy" compound the calculated density is 1.6136. The boiling point is about 0.5° higher than that of the ordinary compound, and it was found that the vapor pressures differ considerably.[2] Refractive indices ($n^{20}{}_{\mathrm{D}}$) of the deuterio and known compounds are 1.4824 and 1.4940, respectively. In the Raman spectrum[3] all lines predicted for the new substance are actually observed. The observation of Urey and Price[4] of the slow interaction of aluminum carbide and deuterium oxide finds its analog in the low rate of evolution of "heavy" acetylene from calcium carbide. In the catalyzed reaction of ordinary and deuterioacetylene with chlorine no appreciable difference in rates was noticed.

Experimental Part

Most of the methods described for the synthesis of *sym*-tetrachloroethane were tested for their suitability to small scale preparations involving the least risk of explosions. Finally the industrially used procedure utilizing the combination of acetylene and chlorine on a freshly prepared deposit of certain metal chlorides on a carrier was chosen. It was worked out carefully using ordinary water first.

Apparatus and Procedure.—The general assembly of the apparatus is shown diagrammatically in Fig. 1. The principal parts are an acetylene generating flask (a) with dropping funnel (a′), a storage system of four 500-ml. bulbs (b, b′, b″, b‴) interconnected by three-way stopcocks, and using redistilled mercury as a confining liquid, a leveling bulb with customary air trap; two reaction tubes (c, c′) made of heavy-walled (bomb) tubing, diameter 15 mm, length 15 and 30 cm., respectively, with cap joint for the gas inlets and standard tapered[5] glass joint for the attachment of receivers (d, d′) of the conventional type for the immersion in a cooling bath, and a terminal bubble counter (e). The all-glass chlorine purifying train consisted of a platinized asbestos–manganese dioxide catalyzer tube, heated electrically to 450°, gas wash bottles containing saturated potassium permanganate solution and concd. sulfuric acid, a pressure regulator (f) for the adjustment of the gas velocity and a capillary flow control with bubble counter (g). The catalyst, a mixture of 7.5 parts of ferric oxide, 7.5 parts of reduced iron, 15 parts of aluminum oxide, 5.5 parts of antimony metal (powdered) and 15 parts of clean quartz sand, which components had been either ignited or dried *in vacuo* at 110°, was suspended on ignited asbestos and packed rather loosely in the reaction tubes. They were wrapped with wire gauze and after attaching to the assembly the formation of the metal chlorides was started by a slow stream of chlorine. Part of the more volatile chlorides was expelled.

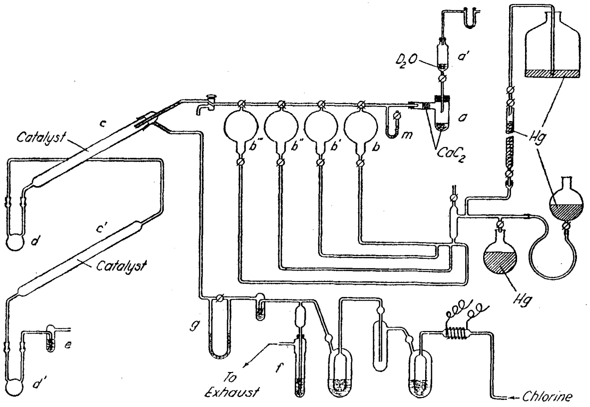

Fig. 1.

A constant and controllable rate of acetylene from the storage flasks to the reaction tubes was secured by a device consisting of a 12-liter carboy, filled with a 7-cm. layer of redistilled clean mercury and a heavy walled siphon tube with a set of two capillary stopcocks for the adjustment and shutting of the mercury flow.

Especially pure calcium carbide kindly supplied by Carbide and Carbon Chemicals Corporation, a light brown material, was crushed with exclusion of moisture and the inner cores powdered in an atmosphere of dry nitrogen. Generator (a) was charged with 8 g. (0.13 mole) of carbide and covered with a 3-mm. layer of ignited quartz sand. In the side-arm a layer of powdered calcium carbide was se-

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[1] (a) Whitmore and co-workers, THIS JOURNAL, **56**, 749 (1934); (b) Breuer, *ibid.*, **57**, 2236 (1935).

[2] *Cf.* Lewis and MacDonald, *ibid.*, **55**, 3057 (1933), and Taylor and Junger, *ibid.*, **55**, 5057 (1933), for an explanation of vapor pressure differences of protium and deuterium compounds.

[3] To be published elsewhere by D. H. Rank of the Physics Department of the Pennsylvania State College.

[4] Urey and Price, *J. Chem. Phys.*, **2**, 300 (1934).

[5] See *Ind. Eng. Chem., News Edition*, **10**, 268 (1932).

cured between plugs of glass wool. The thoroughly dried acetylene generating and storage part of the system was outgassed most carefully through three-way stopcock (u), heating the carbide to 250°. Four cc. (0.22 mole) of deuterium oxide (d^{20}_4) 1.1071 was placed in dropping funnel (a′) and permitted to react slowly with the carbide. Formation of "heavy" acetylene and the simultaneous removal of mercury from the storage bulbs were controlled so that the gas pressure was kept close to atmospheric, as indicated by manometer (m). Deuterium oxide was added in small portions whenever no change in pressure was noted during one-half hour. After sixty hours all of the "heavy" water had reacted, while the same volume of ordinary water had been used up in very considerably less time. Unreacted deuterium oxide was expelled by heating the generator to an oil-bath temperature of 170°, and brought into reaction with fresh carbide in the side arm. By simultaneously cooling the bulbs (b, etc.) with dry ice and keeping the generator at 170° most of the gas was transferred in the storage system and a nearly theoretical yield of acetylene-d_2 was obtained.

For the chlorination process a 100-watt incandescent bulb with metal reflector was placed at a distance of approximately 40 cm. from the reaction tube (c) and 16 cc. of chlorine per minute passed through the tubes prior to admitting the acetylene at a rate of 4 cc. per minute. Combination of the gases started immediately as indicated by the warming of tube (c) and the formation of a liquid reaction product. As a matter of precaution tube (c′) was heated slightly by the flame of a wing-top burner. Very little gas passed through the terminal bubble counter (e), until the acetylene storage flasks were emptied (fifteen hours). The reaction products were expelled completely in receiver (d), which was kept at −10°, by repeated heating of tube (c) in a stream of chlorine, finally to the sublimation temperature of ferric chloride. No material had formed in reaction tube (c′). A yield of 14.5 g. of tetrachloroethane-1,2-d_2 (78% of the theoretical amount, based on deuterium oxide) was obtained.

Purification and Physical Constants.—Receiver (d) was attached by standard tapered glass joint to the pot of a partial reflux type fractionating column (length of packed[6] section 37 cm., inner diameter 0.7 cm.) with sealed on pot and multiple receiver, and transferred at 60 mm. pressure. Using a reflux ratio of 10:1 two fractions boiling at 68.8–70.7°, and 70.7° were collected, and the latter refractionated at 89 mm. to give three cuts with boiling ranges of 77.5–79.5°, 79.5–80° and 80°. From the middle fraction (8.5 g.) the density, boiling point, melting range and refractive index were determined by a technique described in an earlier paper.[1b]

	$CDCl_2CDCl_2$	$CHCl_2CHCl_2$
d^{20}_4	1.6118	1.5943
n^{20}_D	1.4924	1.4940
B. p., °C. (737 mm.)	145.7 ± 0.05	145.2 ± 0.05

The melting curves of both deuteric and ordinary compounds indicate that these substances are not quite pure; nevertheless it was found that the "heavy" compound melts 0.2–0.5° higher than its protio analog. Preliminary measurements of vapor pressure differences of the "light" and "heavy" compound, taken at 5° intervals over the range +20–80° indicate that the vapor pressure of the deuteric compound is from 9–6% lower.

Grateful acknowledgment is made to the Carbide and Carbon Chemicals Corporation for the very pure sample of calcium carbide and to Dr. D. H. Rank of the Physics Department of The Pennsylvania State College for the permission to mention some of his as yet unpublished results. Particular thanks are due Dean Frank C. Whitmore of the School of Chemistry and Physics who made possible and greatly encouraged the present work.

Summary

Tetrachloroethane-1,2-d_2 has been prepared and some of its physical constants have been determined.

STATE COLLEGE, PA.

RECEIVED MAY 4, 1936

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[6] Wilson and others, THIS JOURNAL, **55**, 2795 (1933).

[CONTRIBUTION FROM BROOKLYN POLYTECHNIC INSTITUTE, BROOKLYN, N. Y.]

Vapor Pressures of Saturated Aqueous Solutions. Monoammonium and Diammonium Acid Phosphates

BY EDWARD J. ROEHL

In connection with other current research work, the author has determined the vapor pressure curves for saturated aqueous solutions of monoammonium and diammonium acid phosphates over a temperature range.

A search of the literature failed to reveal data for the diammonium salt, and the only record for the monoammonium salt seems to be that of Edgar and Swan[1] over the limited temperature range of from 19 to 30°.

Experimental Method

The isoteniscope of Smith and Menzies[2] was employed. The bulb of the isoteniscope had a capacity of about 15 ml., and was connected to a 10-liter bottle as reservoir. The manometer was of the closed end type described by Roehl[3] and was read by means of a cathetometer. The usual precautions as to temperature control, stirring, etc., were employed. A saturated solution of the salt was used as the confining liquid. The two ammonium phosphates were prepared by crystallizing commercial C. P. chemicals repeatedly from water. In all cases, duplicate determinations were made upon separate samples, and in several cases other duplicate determinations were made on samples which had been still further purified by recrystallization. The curves were checked for both falling and rising temperatures.

The experimental data for the monoammonium salt were found to fit the equation given over a range of temperature from 19–90°

$$\log P = -2240/T + 8.862$$

with a mean deviation of 0.8% in pressure. The data for the diammonium salt can be represented by the equation given from 19–55°

$$\log P = -2240/T + 8.807$$

with a mean deviation of 0.4% in pressure.

The only available data, those of Warren,[4] give the following values for the ammonia pressure of the solid salts, and which would correspond to the ammonia pressures for the saturated solutions.

PRESSURES IN MM. OF MERCURY

	80.24°	100°	125°
$NH_4H_2PO_4$	....	0.00	0.05
$(NH_4)_2HPO_4$	1.36	5.0	30.0

This indicates that the ammonia pressure over the saturated solution has not reached an appreciable value for the monoammonium salt at 100° and for the diammonium salt at 55°.

It was found that the data for the two salts gave parallel straight lines when plotted as log P against $1/T$, and that the two lines were parallel to the vapor pressure curve for water. A search of the literature was made and all the data possible to locate for saturated aqueous solutions plotted as log P against $1/T$. It was found that all the curves were straight lines and all parallel to the water curve. Thus the data can be represented by the equation

$$\log P = -2240/T + B$$

and in Table I there are given the material, the temperature range, and the values for the constant B.

TABLE I

Material	Temperature range, °C.	Constant B
H_2O[5]	20–100	8.895
Na_2CO_3[6]	30–100	8.800
$NaCl$[6,7]	20–95	8.760
Na_2SO_4[6,7]	20–100	8.835
KCl[1,7]	20–45	8.812
$KClO_3$[6]	55–100	8.864
K_2SO_4[7]	20–55	8.880
$K_2Cr_2O_7$[7]	20–50	8.885

The values obtained from the equations check the observed data with a mean deviation of 1%.

Summary

The vapor pressures for the saturated aqueous solutions of monoammonium acid phosphate have been determined over a temperature range of from 19 to 90°; and for the diammonium acid phosphate from 19 to 55°. Empirical equations were derived to express the data.

On plotting the data and all the data possible to locate in the literature for saturated aqueous solu-

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[1] Edgar and Swan, THIS JOURNAL, **44**, 570 (1922).

[2] Smith and Menzies, *ibid.*, **32**, 1412 (1910).

[3] Roehl, *ibid.*, **52**, 1020 (1932).

[4] Warren, *ibid.*, **49**, 1904 (1927).

[5] "Int. Crit. Tables," Vol. III, p. 212.

[6] Landolt–Börnstein, Vol. II, p. 1392.

[7] Leopold and Johnston, THIS JOURNAL, **49**, 1974 (1927).

tions, as log P against $1/T$, it was found that the curves were all straight lines and all parallel to the curve for water. At present there seems to be no explanation for this unexpected result.

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RECEIVED MAY 6, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK AND CO., INC.]

The Synthesis of 3-Hydroxy-2-(3)-benzofuranone and of 4-Hydroxymandelic Acid

BY KURT LADENBURG, KARL FOLKERS AND RANDOLPH T. MAJOR

A number of hydroxy acids were recently investigated in regard to the treatment of urinary infections. Mandelic acid was the most effective of these,[1] and this was due in part to the fact that it was excreted unchanged in the urine. It seemed quite possible that the introduction of a phenolic hydroxyl group into this acid might increase its antiseptic action. 2-Hydroxymandelic acid appeared promising, since salicylic acid has been found to pass through the body into the urine largely unchanged,[2] and because it seemed possible that this hydroxymandelic acid might also be excreted partly unchanged. It was of further interest to determine the influence of the 4-hydroxy group in the bactericidal efficiency of the mandelic acid molecule.

There is but little information on 2-hydroxymandelic acid in the chemical literature. Plöschl[3] treated salicylaldehyde with hydrocyanic acid in solution. The crude 2-hydroxymandelonitrile was then treated with concentrated hydrochloric acid for hydrolysis to 2-hydroxymandelic acid. The acid product was a sirup, which like the nitrile was neither purified, nor analyzed. Later Baeyer and Fritsch[4] obtained crude 2-hydroxymandelic acid by reduction of 2-hydroxyphenylglyoxylic acid with sodium amalgam. They were unable to crystallize the crude sirupy acid, and finally converted it to the crystalline 2-hydroxyphenylacetic acid by further reduction with hydriodic acid. Rosenmund and Schindler[5] mentioned the reaction of 2-hydroxymandelic acid with acetyl chloride to give a diacetyl derivative of m. p. 68°, but gave neither the source nor a description of their 2-hydroxymandelic acid.

Plöschl's preparation of 2-hydroxymandelic acid was repeated carefully several times. The result was always a very small yield of a colored sirup, which would not crystallize. According to Plöschl, the aqueous solution of the acid on evaporation yielded an oil which crystallized, but a description of the solid was not given. This solid, supposed to be the lactone of 2-hydroxymandelic acid (3-hydroxy-2-(3)-benzofuranone),[6] was obtained in these experiments, but in all cases, the products were so impure and unsatisfactory that a more detailed examination of the reactions was made.

2-Hydroxymandelonitrile was found to be an oil, which was stable for only about twelve hours at about 0°. Its distillation under high vacuum was hardly satisfactory due to decomposition. To convert certain nitriles to the acids, it has frequently been advantageous to proceed first to the imino ether hydrochloride, then to the ethyl ester and finally to the acid. Consequently, three experiments were made in which the nitrile was treated with dry hydrogen chloride and ethanol. At the ester stage, only one of the three products could be induced to crystallize partially. The analytical data indicated that the crystals were 3-hydroxy-2-(3)-benzofuranone, the lactone of 2-hydroxymandelic acid.

These results suggested that in the one case the reaction designated as A had proceeded to a greater extent than reaction B so that there was sufficient lactone present to crystallize and be isolated.

If this were true, then the lactone should be isolated without difficulty when ethanol was omitted from the reaction. This contention was verified by experiment, and this reaction has provided an excellent method of preparing the pure 3-hydroxy-2-(3)-benzofuranone.

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[1] Rosenheim, *Lancet*, **228**, 1032 (1935). See also, Lyon and Dunlop, *Brit. Med. J.*, No.. 3909, 1096 (1935); Holling and Platt, *Lancet*, **230**, 769 (1936); Cubitt, *ibid.*, **230**, 922 (1936); *Proc. Staff Meetings of the Mayo Clinic*, **11**, 231 (1936).

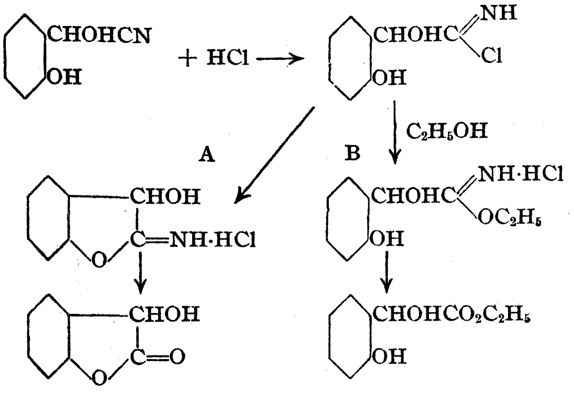
[2] Sollmann, "Manual of Pharmacology," 4th ed., W. B. Saunders and Co., 1932, p. 626.

[3] Plöschl, *Ber.*, **14**, 1316 (1881).

[4] Baeyer and Fritsch, *ibid.*, **17**, 974 (1884).

[5] Rosenmund and Schindler, *Arch. pharm.*, **266**, 282 (1928).

[6] The International Rules numbering has been used for the benzofuran nomenclature.



Certain properties of 3-hydroxy-2-(3)-benzofuranone are described in the experimental section. In particular, and as might be expected, the pure lactone partially hydrolyzed to 2-hydroxymandelic acid when dissolved in water; and when an alkaline solution of the acid was acidified, the lactone was partially formed from the liberated acid.

The isomeric 4-hydroxymandelic acid has been described in the literature, but each of the four methods,[7] by which it was obtained have certain disadvantages. For this research, 4-hydroxymandelic acid was synthesized from 4-hydroxybenzaldehyde through the intermediates: nitrile, imino ether hydrochloride and ethyl ester. This method was found to be quite satisfactory.

Aqueous solutions of 2-hydroxymandelic acid (and its lactone) and 4-hydroxymandelic acid have been tested *in vitro* against *E. Typhi* and *Staphylococcus aureus* by Dr. W. L. Sampson of the Merck Institute for Therapeutic Research. By comparing these two acids with mandelic acid, it was found that the phenolic hydroxyl group did not augment the bactericidal power of the acid.

Experimental

All analyses were micro determinations carried out by Mr. D. Hayman and Mr. S. Adler.

For satisfactory results, the details of the following preparations must be carefully observed.

2-Hydroxymandelonitrile.—Ten grams of pure salicylaldehyde was dissolved in a 10% aqueous solution of 8.6 g. of sodium bisulfite. To this was added 50 ml. of ether, and the liquids were cooled to 0–5° and stirred mechanically. A 20% aqueous solution of 4.1 g. of sodium cyanide was added from a dropping funnel, after which the stirring was continued for one hour. The layers were separated, and the aqueous layer extracted with ether. The combined ethereal solutions were washed twice with 30 ml. of 10% sodium bisulfite solution each time. After removal of the ether *in vacuo* at 20°, *ca.* 35 ml. of dry benzene was added, and then removed *in vacuo* at 20–25°. The residue was pumped out for two to three hours at 1 mm. pressure. The yield of nitrile was 10 to 11 g. (82–90%). It was a light green tinted viscous oil. The yield was increased by further extraction of the aqueous layer.

All efforts to crystallize this oil were unsuccessful. It could be kept only about twelve hours at temperatures of 0 to 10° or lower, and after this the slow decomposition and resinification increased until the oil had become a deep red thick resin. The odor of hydrocyanic acid was noticeable.

A carefully pumped out (1 mm. pressure or lower) analytical specimen of the freshly prepared nitrile gave, on immediate analysis: found, C, 63.71, 63.57; H, 5.01, 5.10; N, 9.0. Calcd. for $C_8H_7NO_2$: C, 64.40; H, 4.73; N, 9.40.

When a sample of the freshly prepared nitrile was placed in a still of the alembic type at a pressure of 10^{-3} to 10^{-5} mm., a few drops distilled on warming the flask to about 50°. However, this slight warming caused a marked increase in the pressure of the system. Hydrocyanic acid was detected and vapors (probably salicylaldehyde) were condensed in the trap. This warming also increased the resinification of the sample. The few drops of distillate on immediate analysis gave, found: C, 64.31; H, 5.28.

3-Hydroxy-2-(3)-benzofuranone (Lactone of 2-Hydroxymandelic Acid).—Ten grams of freshly prepared nitrile that had been well pumped out at 1 mm. was dissolved in 50 ml. of anhydrous ether. This solution was cooled in an ice-bath, and dry hydrogen chloride bubbled through until a little over the theoretical amount was absorbed. The red solution was kept at 10° overnight, and then the ether was decanted from the salt. The flask was placed in a desiccator over sodium hydroxide and evacuated to 5 mm. for four hours. To the imino ether hydrochloride was added 400 ml. of water, and the flask was shaken mechanically until the solution was almost clear. A red lump of tar remained. The solution was filtered and allowed to stand at 25° for five hours. It was again filtered to remove flocculent material, and then extracted with ether five times. The residue that remained after removal of the ether by distillation was pumped out until it crystallized. The lactone was recrystallized from dry benzene until the constant value, m. p. 107–108°, was reached. The yield was 30% (based on salicylaldehyde).

Anal. Calcd. for $C_8H_6O_3$: C, 64.00; H, 4.03. Found: C, 64.23, 64.32; H, 4.27, 4.29.

Titration experiments indicated that 3-hydroxy-2-(3)-benzofuranone partially hydrolyzed when dissolved in warm water. When an aqueous solution of the lactone was treated with the required amount of calcium hydroxide dissolved in a large amount of water, an insoluble calcium salt formed. *Anal.* Calcd. for $C_{16}H_{14}O_8Ca$: Ca, 10.71. Found: Ca, 10.18, 9.97.

When the lactone was dissolved in 0.5% sodium hydroxide solution, and allowed to stand at 25°, a brown insoluble precipitate formed. This precipitate contained only a trace (0.14%) of sodium.

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(7) (1) The direct hydrolysis of *p*-hydroxymandelonitrile to the acid [Henry, *Chem. News*, **85**, 301 (1902)]. (2) The reduction of *p*-hydroxyglyoxylic acid [Ellinger and Kotake, *Z. physiol. Chem.*, **65**, 409 (1910)]. (3) The reaction of nitrous acid on *p*-hydroxyphenylaminoacetic acid [Fromherz, *ibid.*, **70**, 356 (1910)]. (4) The hydrolysis of 4-α-dibenzoyloxyphenylacetamide [Alay and Rabout, *Bull. soc. chim.*, [4] **11**, 392 (1912)].

Anal. Found: C, 64.17; H, 5.00. The filtrate on acidification, extraction, etc., yielded a red oil.

Anal. Found: C, 60.21; H, 4.23.

When the lactone was dissolved in a 1% sodium carbonate solution and refluxed one hour, hydrolysis was complete, as was evidenced by a lack of extractable material. The alkaline solution, after acidification, extraction, etc., yielded a partially crystalline residue.

Anal. Found: C, 59.48; H, 4.83. Calcd. for the lactone: C, 64.00; for the acid, C, 57.12. Thus, these residues were mixtures of the lactone and the acid.

Obviously, the lactone partially hydrolyzed to the acid in water solution and, conversely, the acid, liberated in solution from its salt, partially formed the lactone.

4-Hydroxymandelonitrile.—Ten grams (0.082 mole) of 4-hydroxybenzaldehyde was dissolved in a warm 10% solution of 10 g. of sodium bisulfite, and cooled to 0°. The solution was covered with 50 ml. of ether, and with mechanical stirring, a 20% solution of 4.2 g. (0.086 mole) of sodium cyanide was added over a period of thirty minutes. After stirring thirty minutes longer at 0°, the layers were separated, and the aqueous one extracted further with ether. The combined extracts were washed with a 10% sodium bisulfite solution, dried over calcium chloride and then distilled at 25° or lower *in vacuo*. The nitrile was dried at 1 mm. for one to two hours. This yield of nitrile was 90%; m. p. 99–102°.[8]

Ethyl 4-Hydroxymandelate.—Eleven grams of the nitrile was dissolved in 50 ml. of anhydrous ether, and 4.6 ml. of absolute ethanol was added. Dry hydrogen chloride was bubbled through the solution at 0–5° until a little over the theoretical amount had been absorbed. After standing overnight at 10°, the ether was decanted from the imino ether hydrochloride. The salt was dried and freed of excess hydrogen chloride in a vacuum desiccator. The yield of the salt was 11.5 g.

The crude imino ether hydrochloride was shaken mechanically with 300 ml. of water until the solution was almost clear. The insoluble material was filtered, and the solution was allowed to stand at 25° for five hours. The solution was then extracted with ether, and on solvent removal, there remained 5.5 g. (34.2% as based on 4-hydroxybenzaldehyde) of ethyl 4-hydroxymandelate of m. p. 124–126°. On recrystallization (with norite) from dry benzene the constant value of m. p. 128.5–129° was obtained.

Anal. Calcd. for $C_{19}H_{12}O_4$: C, 61.19; H, 6.17. Found: C, 61.09; H, 6.25.

4-Hydroxymandelic Acid (Monohydrate and Anhydrous).—Three and one-half grams of the pure ethyl ester was dissolved in 110 ml. of 2% sodium hydroxide solution, and the mixture refluxed for one hour. The light brown solution was cooled and acidified with hydrochloric acid. The first ether extract removed all the colored impurities and about 0.1 g. of the acid (m. p. 79–82°). After twenty more ether extractions, and distillation of the solvent, there remained 2.4 g. (72%) of 4-hydroxymandelic acid monohydrate of m. p. 82–84°. On dissolving in benzene, and reprecipitating with petroleum ether, it melted at 83–84°.

Anal. Calcd. for $C_8H_8O_4 \cdot H_2O$: H_2O, 9.67. Found: H_2O, 9.66.

Anhydrous 4-hydroxymandelic acid (from the monohydrate by warming *in vacuo* at 60°) melted at 109.5–110.5°.[9]

Anal. Calcd. for $C_8H_8O_4$: C, 57.12; H, 4.80. Found: C, 57.42; H, 5.08.

Summary

Pure 3-hydroxy-2-(3)-benzofuranone has been made from salicylaldehyde. When this lactone was dissolved in water, it hydrolyzed partially to 2-hydroxymandelic acid. 4-Hydroxymandelic acid has been synthesized from 4-hydroxybenzaldehyde through the intermediate nitrile, imino ether hydrochloride and ethyl ester.

2- and 4-hydroxymandelic acids were not more bactericidal against *E. Typhi* and *Staphylococcus aureus in vitro* than mandelic acid.

RAHWAY, N. J. RECEIVED MAY 27, 1936

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[8] Buck, THIS JOURNAL, **55**, 3388 (1933), described analytically pure 4-hydroxymandelonitrile of m. p. 98°, which was obtained in 38% yield (pure) by a technique differing in detail from this procedure.

[9] By other methods, Fromherz[7] found m. p. 83–84° for the monohydrate and m. p. 107–108° (Ellinger and Kotake [7] m. p. 105–106°) for the anhydrous acid.

[Contribution from the Chemical Laboratory of the University of Illinois]

A New Synthesis of Mixed Benzoins. Second Paper

By Richard T. Arnold[1] and Reynold C. Fuson

The new synthesis of mixed benzoins by the condensation of suitable aromatic compounds with arylglyoxals[2] has been extended to a number of new cases, and has been found to be generally useful in the preparation of this type of substance. In Table I are listed the various benzoins which have been made, together with indications as to the conditions employed.

Preparation of the Arylglyoxals

The glyoxals were prepared in good yields by the method of Riley and Gray,[3] with an added modification as follows.

After the oxidation with selenium dioxide, the dioxane solution is decanted from the precipitated selenium and distilled under atmospheric pressure until nearly all of the dioxane has passed over. At this point, 100 cc. of a suitable hydrocarbon[4] is added, and the solution again distilled at atmospheric pressure until the distillate is no longer turbid. At this stage, the solution is transferred to a Claisen flask, and the distillation completed under diminished pressure. This modification was employed to prevent the formation of the glyoxal hydrate which normally contaminates the distillate. By use of this method with commercial xylene (b. p. 137–140°), *p*-bromophenylglyoxal (b. p. 115° (7 mm.); m. p. 51–52°), and *p*-chlorophenylglyoxal (b. p. 123–125° (17 mm.); m. p. 40–42°) were prepared in 64 and 55% yields, respectively. These compounds were identified by conversion into their hydrates which melted at 132°[13] and 121°, respectively.

Preparation of the Benzoins

The optimum conditions for this reaction are typified in the synthesis of *p*-bromobenzoin.

Table I

Benzoin	M. p., °C.	Yield, %	Time, hrs.	Solvent	Analyses, % Calcd. C	H	Found C	H	Diketone
$C_6H_5COC(OH)HC_6H_5$	133	90	20	C_6H_6					95°
$(CH_3)_3C_6H_2COC(OH)HC_6H_2(CH_3)_3$[5]	59– 60	48	15	CS_2	81.08	8.18	80.84	8.051	118–119[6]
$C_6H_5COC(OH)HC_6H_4OCH_3$	100[7]	48	5	CS_2					62– 63[7]
$C_6H_5COC(OH)HC_{10}H_7$	128	42	15	CS_2	82.4	5.4	82.3	5.7	87[8]
$C_6H_5COC(OH)HC_6H_4Cl$	116[11]	84	15	CS_2					73[10]
$ClC_6H_4COC(OH)HC_6H_5$	90–91[11]	35	15	C_6H_6					73[10]
$C_6H_5COC(OH)HC_6H_2(CH_3)_3$	93.5–94[12]	62	5	CS_2	80.3	7.14	80.0	7.4	134–136[2]
$(CH_3)_3C_6H_2COC(OH)HC_6H_5$	102–103[2]	63	7	C_6H_6					134–136[2]
$BrC_6H_4COC(OH)HC_6H_5$	108–109	70	15	C_6H_6	57.73	3.78	57.62	3.81	84– 85[10]
$C_6H_5COC(OH)HC_6H_4Br$	125–126	57	15	C_6H_5Br	57.73	3.78	57.93	3.94	84– 85[10]
$C_6H_5COC(OH)HC_6H_4CH_3$	116[11]	50	15	CS_2					31[10]
$CH_3C_6H_4COC(OH)HC_6H_5$	110[11]	42	15	CS_2					31[10]

Ten and sixty-five hundredths grams of *p*-bromophenylglyoxal was dissolved in 50 cc. of benzene and placed in a 125-cc. separatory funnel.

In a 500-cc., three-necked, round-bottomed flask surrounded with ice and equipped with a mercury-sealed stirrer were placed 200 cc. of dry benzene and 13.3 g. of aluminum chloride. The glyoxal solution was added dropwise to the benzene–aluminum chloride solution. The addition took approximately thirty minutes. The reaction was allowed to run at 0° for fifteen hours. The reaction mixture was then decomposed by adding slowly ice-cold 20% hydrochloric acid solution. The benzene solution was concentrated by removal of the solvent under diminished pressure. The process was performed in the absence of air,

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(1) Chemical Foundation Fellow in Organic Chemistry, 1935–1936.

(2) Fuson, Weinstock and Ullyot, This Journal, **57**, 1803 (1935).

(3) Riley and Gray, "Organic Syntheses," Vol. XV, John Wiley and Sons, New York, 1935, p. 67.

(4) For this purpose, the hydrocarbon should have a boiling point about 10–15° above the melting point of the glyoxal hydrate.

(5) Zinc chloride was used instead of aluminum chloride for a catalyst.

(6) Kohler and Baltzly, This Journal, **54**, 4015 (1932).

(7) McKenzie and Luis, *Ber.*, **65B**, 794 (1932).

(8) This benzil is new. *Anal.* Calcd. for $C_{18}H_{12}O_2$: C, 83.09; H, 4.63. Found: C, 82.93, 82.87; H, 4.73, 4.74.

(9) Jenkins, This Journal, **56**, 682 (1934).

(10) Hatt, Pilgrim and Hurran, *J. Chem. Soc.*, 93 (1936).

(11) Weissberger, *Ann.*, **478**, 112 (1934).

(12) Weinstock and Fuson, This Journal, **58**, 1233 (1936).

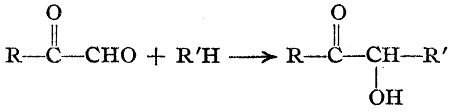
(13) Söderbaum, *Ber.*, **26**, Ref., 1015 (1893).

and was continued until the residual solution was reduced to a volume of 30 cc. To this was added 30 cc. of low-boiling petroleum ether, and the solution kept cold overnight. The precipitate was separated by filtration with suction and washed with four 25-cc. portions of cold, low-boiling petroleum ether. The material weighed 10.2 g. (70.2% of the theoretical amount), and melted at 105–106°. After one recrystallization from ethyl alcohol, the benzoin melted at 108–109°.

The general procedure involves the use of the hydrocarbon reactant as the solvent; in some cases, however, carbon disulfide has been found to give very satisfactory results.

The Structure of the Benzoin

In every case where the resulting benzoin is known, our product showed perfect agreement with the published descriptions of the compound anticipated. In cases where both benzoin isomers were prepared, both were oxidized by iodine[14] to give identical diketones. Most of these diketones are known substances.[10] It is important to note that in each instance only one benzoin was obtained, and that in every case the structure of the benzoin corresponded to that to be expected on the basis of the general equation



$$R-\overset{\overset{O}{\|}}{C}-CHO + R'H \longrightarrow R-\overset{\overset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-R'$$

Summary

Twelve benzoins have been prepared by condensation of arylglyoxals with aromatic hydrocarbons or their derivatives. The structures of the mixed benzoins have been shown to be those which would be predicted on the basis of the general equation as indicated above.

[14] Carson and McAllister, This Journal, **51**, 2822 (1929).

URBANA, ILLINOIS RECEIVED MAY 25, 1936

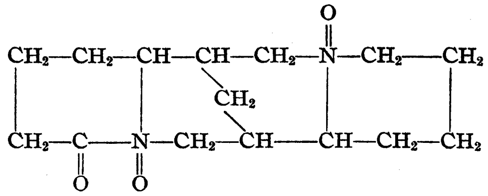
[CONTRIBUTION FROM THE PATHOLOGICAL DIVISION, BUREAU OF ANIMAL INDUSTRY]

Lupine Studies. XI. The Alkaloids of *Lupinus Barbiger* S. Wats.

BY JAMES FITTON COUCH

In a previous communication[1] the occurrence of sparteine in *Lupinus barbiger* was announced. At that time the presence of two other alkaloids of undetermined identity was indicated. This paper describes the isolation and identification of these alkaloids. *L. barbiger* is a perennial species ranging from Colorado, Utah, Arizona, and California.[2] Two lots of material, one from northern Arizona and one from Utah were examined in the course of this study and no significant differences between them were found.

Three well-defined alkaloids were isolated from this species: sparteine and two hitherto undescribed bases which have been named dilupine and trilupine. Lupinine and lupanine were sought for and found not to be present. The new alkaloids are of unusual interest. Trilupine, $C_{15}H_{24}O_3N_2$, proved to be an amine oxide derived from *d*-lupanine of which it is the di-N-oxide corresponding to the structure



By the action of hydrogen dioxide on sparteine the di-N-oxide of that base has been prepared[3] by a number of workers. Polonovski[4] has shown that geneserine is the amine oxide of eserine and analogous compounds have been prepared synthetically from other bases.[5] This is, however, the first instance in which amine oxides have been discovered in a lupine species. It was found that while gold chloride and platinum chloride would yield the corresponding double salts of trilupine if the mixtures were not heated for more than a short time, other acids and longer heating resulted

[1] J. F. Couch, This Journal, **54**, 1691 (1932).

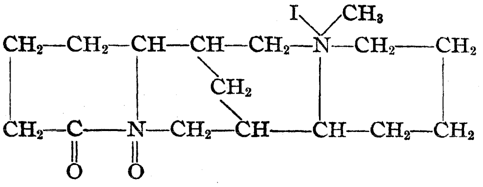
[2] W. W. Eggleston, in I. Tidestrom, "Flora of Utah and Nevada," *Contr. U. S. Nat. Herbarium*, **25**, 297 (1925), Govt. Printing Office, Washington.

[3] F. B. Ahrens, *Ber.*, **20**, 2218 (1887); Wackernagel and Wolffenstein, *ibid.*, **37**, 2220 (1904); A. Valeur and E. Luce, *Compt. rend.*, **168**, 1276 (1919).

[4] Max Polonovski, *Bull. soc. chim.*, **21**, 191 (1917).

[5] (a) Max and Michel Polonovski, *Compt. rend.* **180**, 1755 (1925); (b) M. Freund and E. Speyer, *Ber.*, **43**, 3310 (1910); (c) R. Wolffenstein, *ibid.*, **25**, 2777 (1892).

in the formation of salts of *d*-lupanine, the reaction involving removal of the oxide oxygen atoms. Freund and Speyer[5b] were able to prepare crystalline salts of the oxides of morphine, thebaine, codeine and ethylmorphine with mineral acids. When trilupine reacted with methyl iodide in the cold a compound was obtained that contains one oxygen atom less than is required from trilupine methiodide and which appears to be the methiodide of *d*-lupanine mono-N-oxide of the probable structure



Trilupine was converted into *d*-lupanine by treating the dihydrochloride, which is identical with *d*-lupanine dihydrochloride, with alkali, and shaking out the liberated base with chloroform, which yielded an alkaloid identical with *d*-lupanine. The latter was converted into trilupine by the action of calcium dioxide on *d*-lupanine dihydrochloride and the synthetic base agreed with the natural alkaloid in all respects.

The optical activity of trilupine might be expected to throw some light on the problem of the possible asymmetry of the nitrogen atoms in lupanine. The crystallized base had a specific rotation of 63.76° as compared with 84.35° for *d*-lupanine. Correcting for the content of water of crystallization and for the difference in molecular weight the comparable figure for trilupine is 83.12° or sufficiently close to the figure for *d*-lupanine to furnish no support for the view that the nitrogen atoms are asymmetrical.

Dilupine was not obtained in sufficient quantities to permit a thorough study. The analytical figures agree with the formula $C_{16}H_{26}O_2N_2$ for the free base while the analyses of the methiodide and the hydrobromide require a base of the formula $C_{16}H_{26}ON_2$, suggesting that dilupine may be the amine oxide of a C-methyl-lupanine. The base recovered from the hydrobromide was not identical with dilupine but had the nitrogen content required by a methyl-lupanine which supports this view. The question, however, must await further study for complete clarification.

The presence of the di-amine oxide of lupanine in the plant suggested that lupanine should also have been found if only as a decomposition product of trilupine. Careful search failed to reveal that alkaloid even in the residues from vacuum distillations.

Experimental

Material.—The plant material consisted of two lots of plants, one collected on the Kaibab Forest, Arizona, and the second at Hilltop, 10 miles north of Fairview, Utah. The first collection was made during the summer of 1928 and the second on July 11 and August 11, 1931. The plants had not formed seeds at the time of collection. The material was dried, shipped to Washington and ground to a coarse powder for use. The air-dried plant had moisture contents of 8.47 and 7.62% for the two collections. It was identified by W. W. Eggleston as *Lupinus barbiger* S. Wats.

Isolation of the Alkaloids.—The method used in extracting the alkaloids has previously been described;[6] 16.45 kg. of the first collection yielded 1.67% of alkaloid, freed from resinous impurities and calculated to moisture-free plant; 58.09 kg. of the second yielded 1.86%. The alkaloids were treated with an equal volume of ether which dissolved nearly half. The dissolved alkaloids, freed from ether, were then dissolved in petroleum ether, which took up all but a trace of resinous matter. The alkaloidal residue obtained by distilling off the solvent will be referred to as fraction A. The material not dissolved by ether was extracted with benzene which dissolved the larger portion of it. On distilling off the solvent fraction B was obtained. The material not dissolved by benzene was extracted with boiling ethyl acetate and, freed from solvent, the extract furnished fraction C. The undissolved matter was insoluble in a mixture of boiling acetone and 10% alcohol and consisted of resinous substances.

Fraction A was a brownish sirup of strong burnt-wool odor. It weighed 441 g. and gave a strong reaction for sparteine in the modified Grant test. It was submitted to distillation under reduced pressure but could not be separated into its constituents by that method. Fractions were obtained that had nearly the correct index of refraction and optical activity for sparteine, but were evidently contaminated with some other base. Separation was effected by dissolving the fractions that distilled below 195° at 1 mm. in dilute hydrochloric acid and adding aqueous mercuric chloride when the double chloride of sparteine and mercury crystallized and could be purified by recrystallization from hot 20% hydrochloric acid. The alkaloid was recovered from this compound by treating it with ammonia and extracting with chloroform. On distilling off the solvent the base remained as a light yellow sirup which distilled at 185° and 7 mm. with a small residue. It had $n^{27}\text{D}$ 1.5256, $(\alpha)^{30}\text{D}$ 5.95°, and depressed the freezing point of benzene conformably to the molecular weights 241, 244 and 240. The substance was positive to the Jorissen[7] and modified Grant[8] tests for sparteine.

Anal. Calcd. for $C_{22}H_{26}N_2$: C, 76.86; H, 11.19. Found: C, 76.51; H, 11.40.

Salts of Sparteine.—Picrate, m. p. 205–206°, did not depress the melting point of authentic sparteine picrate.

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[6] J. F. Couch, THIS JOURNAL, **56**, 2434 (1934).

[7] Jorissen, *Ann. chim. anal.*, **16**, 412 (1911).

[8] Couch, *Am. J. Pharm.*, **97**, 38 (1925).

Calcd.: N, 16.18. Found: N, 16.00. The platinum chloride melted at 248° (dec.) and did not depress the melting point of authentic sparteine platinum chloride.

The Dihydrobromide.—Five grams of the base, dissolved in 100 cc. of acetone, was treated with an excess of hydrobromide acid solution. Two layers formed and 1 volume of alcohol was added which produced a homogeneous solution. On standing overnight in an ice box the solution deposited a mass of colorless prisms. Recrystallized from alcohol these melted at 197°.

Anal. Calcd. for $C_{15}H_{26}N_2 \cdot 2HBr \cdot H_2O$; Br, 38.63; H_2O, 4.35. Found: Br, 38.51, 38.50; H_2O, 4.40, 4.54. $(\alpha)^{29}\mathrm{D}$ $-18.33°$ in water, $c = 1.2770$, $l = 4$, $a = 0.93°$. The free alkaloid regenerated from this salt showed $n^{27}\mathrm{D}$ 1.5259 and formed a picrate that melted at 206°. The methiodide readily separated from a mixture of the base with methyl iodide without warming. Recrystallized from alcohol it melted at 239–240°.

Anal. Calcd. for B,CH_3I: I, 33.75; N, 7.45. Found: I, 33.72, 33.63; N, 7.51.

The Zinc Chloride.—Sparteine dissolved in 10% hydrochloric acid (2 moles) treated with excess of saturated zinc chloride solution within a few minutes begins to deposit crystals of the double chloride with zinc.[9] Recrystallized from water and dried in a desiccator these were free from water of crystallization and melted at 316–317°.

Anal. Calcd. for $B2HCl \cdot ZnCl_2$: Cl, 32.09. Found: Cl, 32.01, 31.84. $(\alpha)^{30}\mathrm{D}$ -19.57 in water; $c = 0.9912$, $l = 1$, $a = 0.194°$.

Isolation of a New Lupine Alkaloid, Dilupine.—The highest boiling fraction of the original fraction A distilled at 190–222° and 1 mm. It consisted of a thick reddish oil of strong burnt-wool odor, $(\alpha)^{25}\mathrm{D}$ 69.50°, $n^{24}\mathrm{D}$ 1.5395. It contained some sparteine which was removed by distillation with steam. The non-volatile alkaloid was recovered by shaking the water solution with chloroform and on distilling the chloroform a sirup was obtained that did not react to the modified Grant test for sparteine. On standing the sirup deposited a small quantity of needles which were filtered off and proved to be a third alkaloid which is described in detail below. The sirupy alkaloid was redistilled under reduced pressure several times until it was obtained as light yellow, very thick sirup. It has not been crystallized. The analytical figures agree best with a formula for a C-methyl-lupanine oxide and this is tentatively accepted. Further study of the base is in progress.

Anal. Calcd. for $C_{16}H_{26}O_2N_2$: C, 69.01; H, 9.41; N, 10.07. Found: C, 69.38, 69.31, 69.45; H, 9.81, 9.66, 9.75; N, 10.05, 10.08. $(\alpha)^{26}\mathrm{D}$ 65.59°, in water, $c = 6.5028$, $l = 1$, $a = 4.26°$, $n^{27}\mathrm{D}$ 1.5440.

The Methiodide.—A mixture of equal volumes of the alkaloid and methyl iodide began to deposit crystals within thirty minutes and in twenty hours the mixture had solidified. Recrystallized from boiling alcohol several times the m. p. was 253°. The analytical figures for this compound do not agree with those calculated for a methiodide of a base of the composition assigned to the free alkaloid but require a base with one less oxygen atom. This would indicate that dilupine is an amine oxide.

Anal. Calcd. for $C_{16}H_{26}ON_2 \cdot CH_3I$: C, 50.47; H, 7.17; N, 6.94; I, 31.40. Found: C, 50.47; H, 7.19; N, 6.80, 6.94; I, 31.32, 31.13. $(\alpha)^{32}\mathrm{D}$ 51.10°, in water, $c = 1.409$, $l = 1$, $a = 0.72°$.

The Hydrobromide.—The base, dissolved in alcohol and treated with a slight excess of hydrobromic acid, deposited cubical crystals after several days' standing in an ice box. Recrystallized from alcohol and dried at 115° these crystals melted at 233–234°. As in the case of the methiodide the analytical figures agree better for a less oxygenated base.

Anal. Calcd. for $C_{16}H_{26}ON_2 \cdot HBr$; Br, 23.31. Found: Br, 23.86, 23.83.

Three grams of the hydrobromide was dissolved in water, alkalized with sodium hydroxide, and the liberated base shaken out with chloroform. The solvent was removed and the residual sirup was dissolved in methanol and the solvent boiled off three times to remove chloroform. The base was a reddish sirup.

Anal. Calcd. for $C_{16}H_{26}ON_2$: N, 10.68. Found: N, 10.62. $(\alpha)^{25}\mathrm{D}$ 49.78°, in water, $c = 1.832$, $l = 1$, $a = 0.91$. $n^{25}\mathrm{D}$ 1.5454.

Isolation of a New Lupine Alkaloid, Trilupine.—Fraction B was freed from benzene by warming on the water-bath. An attempt to separate the constituents of this fraction by distillation under reduced pressure resulted in considerable decomposition. On standing several weeks the fraction deposited a mass of prismatic crystals embedded in thick sirup. The crystals were collected by filtering the mass through a porous plate under suction. The sirupy filtrate proved to consist of a small quantity of sparteine, much dilupine, and some of the crystalline alkaloid. The crystals were washed with small quantities of cold acetone in which they were slowly soluble and then were recrystallized from boiling ethyl acetate several times, finally with addition of charcoal. By this means the melting point was raised from 112 to 127° where it was constant. The product was colorless efflorescent needles, soluble in water, alcohol, and chloroform, less soluble in cold acetone and ethyl acetate, and nearly insoluble in ether. They contained 2 moles of crystal water and, when anhydrous, melted at 252°. The aqueous solutions are neutral to litmus.

Anal. Calcd. for $C_{15}H_{24}O_3N_2 \cdot 2H_2O$: C, 56.93; H, 8.92; N, 8.85; $2H_2O$, 11.38. Found: C, 56.71, 56.85, 56.42; H, 9.02, 9.05, 9.15; N, 8.88, 8.79; H_2O 11.07, 11.25. $(\alpha)^{30}\mathrm{D}$ 63.76°, in water, $c = 1.7252$, $l = 1$, $a = 1.10°$.

Certain salts could be prepared from trilupine if the reaction mixtures were not heated for more than a very short time. Heating mixtures of trilupine and acids resulted in salts of *d*-lupanine.

Trilupine Platinum Chloride.—A solution of trilupine (1 g.) and a few drops of dilute hydrochloric acid in 5 cc. of water was treated with platinum chloride solution. No precipitation occurred. The solution was evaporated to dryness in a desiccator over concentrated sulfuric acid. The dried mass was freed from excess platinum chloride by extraction with alcohol and the residue was dried. It melted at 224° (dec.).

Anal. Calcd. for $C_{15}H_{26}O_3N_2 \cdot H_2PtCl_6 \cdot 4H_2O$: Pt, 25.61; Cl, 27.95. Found: Pt, 25.66, 25.66; Cl, 27.78, 27.86.

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(9) E. J. Mills, *J. Chem. Soc.*, **15**, 1–8 (1862).

Trilupine Gold Chloride.—A solution of the alkaloid in dilute hydrochloric acid treated with gold chloride solution yielded a yellow flocculent precipitate which was redissolved in the mother liquor by gentle warming and set aside. Golden needles were deposited on standing which were collected, washed and dried. The melting point was 188–189° (dec.). The mother liquors on standing deposited much metallic gold.

Anal. Calcd for $C_{15}H_{24}O_3N_2{\cdot}2HAuCl_4{\cdot}4H_2O$: Au, 38.19; H_2O, 6.97. Found: Au, 38.18; H_2O, 6.91.

Trilupine Methiodide.—To a cold solution of trilupine (1 g.) in ethyl acetate (5 cc.) was added 2 cc. of methyl iodide. On standing octahedral crystals slowly separated. These were collected and dried, m. p. 127°. Analysis indicated that this substance contains one atom of iodine and that one oxide oxygen had been replaced by methyl iodide. The substance is, therefore, the methiodide of the mono-N-oxide of *d*-lupanine.

Anal. Calcd. for $C_{15}H_{24}O_2N_2.CH_3I$: I, 31.25. Found: I, 31.47, 31.50.

Conversion of Trilupine into *d*-Lupanine.—Five grams of trilupine dissolved in acetone (100 cc.) and treated with 4 cc. of hydrochloric acid in 4 cc. of alcohol evolved heat. On cooling there was a scanty deposition of colorless crystals. These were collected, washed with acetone and dried. They melted at 163–164°. When mixed with *d*-lupanine dihydrochloride there was no depression of the melting point. This substance lost 16.32% in weight when dried at 120° corresponding to one mole each of hydrochloric acid and water of crystallization. The anhydrous monohydrochloride melted at 252–254° as does anhydrous *d*-lupanine hydrochloride.

Anal. Calcd. for $C_{15}H_{24}ON_2{\cdot}2HCl{\cdot}H_2O$: 2Cl, 20.95; 1 HCl and 1 H_2O, 16.06, 1 Cl, 10.47. Found: Cl_2, 20.46; "moisture" 16.30, 16.34; Cl_1, 10.43.

Recovery of *d*-Lupanine from (Trilupine) Dihydrochloride.—Four grams of dihydrochloride prepared from trilupine was dissolved in 25 cc. of water and alkalized with sodium hydroxide. The precipitated oil was shaken out with chloroform which was separated, evaporated off and the residue was three times treated with methanol and evaporated to remove traces of chloroform. The alkaloid so obtained was a light brown oil with the characters of *d*-lupanine.

Anal. Calcd. for $C_{15}H_{24}ON_2$: N, 11.28. Found: N, 11.27. $(\alpha)^{25}D$ 79.20°, in alcohol, $c = 5.404$, $l = 1$, $a = 4.28°$; $n^{23}D$ 1.5470. Dextro-lupanine prepared from *L. albus* had $(\alpha)^{25}D$ 84.35 in alcohol and $n^{24}D$ 1.5444.

***d*-Lupanine Gold Chloride.**—Trilupine in dilute hydrochloric acid treated with excess of gold chloride solution gave a heavy flocculent precipitate which was redissolved in boiling dilute hydrochloric acid and crystallized on cooling; yellow needles, m. p. 206°. *Anal.* Calcd. for $C_{15}H_{24}ON_2{\cdot}HAuCl_4$: Au, 33.52. Found: Au, 33.33, 33.25.

***d*-Lupanine Perchlorate.**—The dihydrochloride prepared from trilupine (1 g.) dissolved in 5 cc. of water, was treated with 0.5 cc. of perchloric acid and 2 cc. of saturated sodium acetate solution. An immediate crystalline precipitate fell which was recrystallized twice from water, dried, and then melted at 207–209° and did not depress the melting point of *d*-lupanine perchlorate.

***d*-Lupanine Dihydrochloride.**—Since this compound had not been reported it was necessary to prepare it from authentic *d*-lupanine for comparison with the salt derived from trilupine. Seven grams of *d*-lupanine hydrochloride from *L. albus* was dissolved in 30 cc. of alcohol, 3 cc. of hydrochloric acid was added and then enough acetone to produce a slight cloud. The mixture was filtered and set in an ice box. Crystallization began within an hour. After twenty-four hours the crystals were collected, washed, redissolved in 10 cc. of alcohol and treated with 30 cc. of acetone. On standing the substance crystallized. Washed and dried the crystals melted at 161–162° and did not depress the melting point of the dihydrochloride obtained from trilupine. On drying at 120° their behavior was similar to the trilupine derivative.

Anal. Calcd. for $C_{15}H_{24}ON_2{\cdot}2HCl{\cdot}H_2O$: 2Cl, 20.95; 1 HCl and 1 H_2O, 16.06; 1 Cl, 10.47. Found: Cl_2, 20.72; "moisture" 16.05, 16.12; Cl_1, 10.50, 10.44.

Conversion of *d*-Lupanine into Trilupine.—To 10 g. of *d*-lupanine dihydrochloride dissolved in 50 cc. of water was added in small portions 4 moles of calcium dioxide (8.4 g.) with frequent shaking. When the calcium dioxide had all been added hydrochloric acid was added a few drops at a time until the calcium dioxide was nearly all dissolved. The solution was then alkaline to litmus. It was warmed for four hours on the water-bath, let cool and shaken out with chloroform. On distilling off the chloroform after separating it from the aqueous layer there remained a light brown sirup that soon crystallized to a mass of needles embedded in a dark sirup. The mixture was treated with ether, which dissolved the sirup, and the crystals were recrystallized from hot ethyl acetate with a little charcoal; colorless needles, m. p. 125–126°. Mixed with trilupine, m. p. 127°, the mixture melted at 126–127°.

Examination of Fraction C.—The portion of the original crude alkaloid that was not dissolved in ether or benzene proved to contain small amounts of sparteine, some dilupine which was recovered and added to fraction B, trilupine worked up with that alkaloid, much resinous matter, and a quantity of basic matter from which nothing definite has yet been obtained.

Summary

Lupinus barbiger S. Wats. from Arizona and Utah contains three alkaloids, sparteine, dilupine and trilupine, the last two of which were previously undescribed. Dilupine, provisionally $C_{16}H_{26}O_2N_2$, appears to be the amine oxide of a C-methyl-lupanine. Trilupine, $C_{15}H_{24}O_3N_2$, is the di-amine oxide of *d*-lupanine into which it may be converted by the action of acids and heat. It may be prepared by oxidizing *d*-lupanine with calcium dioxide.

WASHINGTON, D. C.

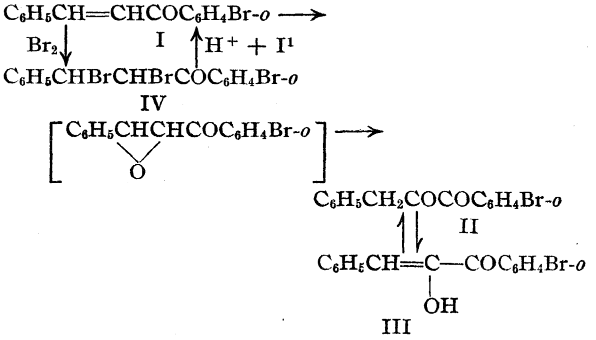
RECEIVED MAY 1, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

Preparation and Properties of *o*-Bromophenylbenzylglyoxal—Methylation of Alpha Diketones

BY R. P. BARNES AND NOBLE F. PAYTON[1]

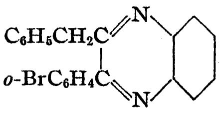
In continuation of the study of the properties of alpha diketones,[2,3,4] it was thought wise to prepare a substituted phenylbenzylglyoxal and study its reactions, since we believe that the glyoxylic acid residue present in the enolic modification of every alpha diketone is intimately related to the methylation reaction. Thus *o*-bromophenylbenzylglyoxal (III) was obtained by the following series of reactions



o-Bromoacetophenone was prepared according to the method given by Thorp and Brunskill[5] for *o*-chloroacetophenone. The *o*-bromoacetophenone was condensed with benzaldehyde to benzal-*o*-bromoacetophenone (I), whose constitution was established by converting it into the dibromide (IV) with subsequent reduction to (I). This α,β-unsaturated ketone was in turn oxidized and isomerized to *o*-bromophenylbenzylglyoxal (II). By means of alkali the diketone (II) was converted into the enolic modification (III).

As is the case with the other diketones of this series, *o*-bromophenylbenzylglyoxal differs very markedly from the isomeric series of beta diketones with reference to the extent of O- and C-compound formation.

o-Bromophenylbenzylglyoxal gives a cherry red color with alcoholic ferric chloride, and is 100% enolic in the solid state. It yields a quinoxaline (V) with *o*-phenylenediamine and is quantitatively cleaved to phenylacetic and *o*-bromobenzoic acids by alkaline hydrogen peroxide. Methylation with dimethyl sulfate gives 84.1% of the O-methyl compound (VI), and sufficient unchanged material to indicate that the O-compound is formed exclusively.



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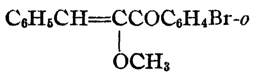


$$\underset{\displaystyle OCH_3}{C_6H_5CH{=}\overset{|}{C}COC_6H_4Br\text{-}o}$$

VI

Since there was no available information in the literature on the physical constants of *o*-bromophenylglyoxylic acid, it was prepared after the manner described by Russanow,[6] and its ionization constant determined by conductivity measurements. The concentration at which these measurements were made is approximately the same as the upper limit of the range of concentrations on the basis of which the ionization constant for *o*-bromobenzoic acid was determined. Therefore the two ionization constants are excellent criteria for judging the relative strength of the two acids.

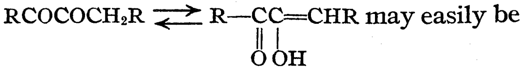
The activating effect of carbonyl groups upon alpha hydrogen atoms is common knowledge. A similar effect is observed when one compares the ionization constants[7] of two series of organic acids such as the following.

Acid	*K* (25°)	Acid	*K* (25°)
$C_6H_5CO_2H$	5.86×10^{-4}	$C_6H_5COCOOH$	6.00×10^{-2}
$o\text{-}BrC_6H_4CO_2H$	1.42×10^{-3}	$o\text{-}BrC_6H_4COCOOH$	8.60×10^{-2}[a]
$(CH_3)_3C_6H_2CO_2H$	3.70×10^{-4}	$(CH_3)_3C_6H_2COCOOH$	5.27×10^{-2}[b]

[a] Experimentally determined value reported in this paper.

[b] Breed, Bryn Mawr College Monographs, Vol. I, No. 1, p. 15.

Thus the introduction of the carbonyl tends to increase the extent of ionization.

It is the opinion of the writer that the amount of O-compound formed upon methylation of an alpha diketone in alkaline solution depends very directly upon the acidity of the enol. Every enolic modification of an alpha diketone of the type  $RCOCOCH_2R \rightleftarrows R{-}\underset{\displaystyle O}{\overset{}{C}}\underset{\displaystyle OH}{C}{=}CHR$ may easily be considered as a glyoxylic acid in which the double

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[1] In part this paper represents a summary of the dissertation presented by Noble F. Payton in partial fulfilment of the requirements for the degree of Master of Arts in 1934.

[2] Kohler and Barnes, THIS JOURNAL, **56**, 211 (1934).

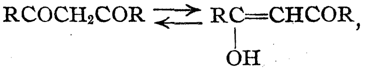
[3] Kohler and Weiner, *ibid.*, **56**, 434 (1934).

[4] R. P. Barnes, *ibid.*, **57**, 937 (1935).

[5] Thorp and Brunskill, *ibid.*, **37**, 1258 (1915).

[6] Russanow, *Ber.*, **25**, 3298 (1892).

[7] "International Critical Tables," Vol. VI, pp. 278, 279, 284.

bonded oxygen has been substituted by a radical. If on the other hand one considers the enolic modification of the isomeric beta diketone of the type  $RCOCH_2COR \rightleftarrows \underset{OH}{RC}{=}CHCOR$, it is obvious that the acid of which the enol may well be considered a derivative is not a glyoxylic acid. With few exceptions[8] the beta diketones, as well as the beta ketonic esters, yield largely C-methylation products with either methyl iodide or dimethyl sulfate.

Obviously, there are two competing reactions which take place, the relative rates of which determine the extent of O- and C-methylation. One of these reactions is a direct metathesis between the alkali salt of the enol and the alkylating agent, which gives rise to the O-compound—the stronger the acid of which the enol is a conceivable derivative, the greater the amount of O-compound. Whatever the other reaction may involve, it seems to be hindered by substitution on the alpha carbon atom.

The methylation of phenylbenzylglyoxal[2] yields a mixture of O- and C-compounds. Benzhydrylphenyl diketone[3] yields 100% O-compound. Thus it seems that the phenyl group substituted for a hydrogen of phenylbenzylglyoxal offers hindrance to one of the competing reactions with the result that the other reaction preponderates. Mesitylbenzylglyoxal[4] and *o*-bromophenylbenzylglyoxal each yields exclusively the O-compound. As further support of this idea, the alpha ketonic esters of which oxalacetic ester is a good example produce mixtures of O- and C-methylation products.

Experimental Part

Preparation of Benzal-*o*-bromoacetophenone (I).—A solution of 8.4 g. of sodium hydroxide in 65 cc. of water, together with 50 cc. of alcohol, was placed in a 500-cc. wide-mouthed bottle equipped with a stirrer and cooled by an ice-bath. To the reaction chamber was added 30.5 g. of *o*-bromoacetophenone after which stirring was begun. The calculated quantity (17 g.) of benzaldehyde was then introduced. The temperature was maintained between 15 and 20° during three hours of constant stirring. The product was 12.5 g. of a yellow oil distilling at 183–185° (2 mm.).

Anal. Calcd. for $C_{15}H_{11}OBr$: C, 62.7; H, 3.9. Found: C, 62.9; H, 4.0.

Bromination: Dibromobenzal-*o*-bromoacetophenone (IV).—An ethereal solution of 2.0 g. of the α,β-unsaturated ketone was brominated in the usual way, resulting in a quantitative yield of the dibromo product which after crystallization from methyl alcohol melted at 86°.

Anal. Calcd. for $C_{15}H_{11}OBr_3$: C, 40.3; H, 2.5. Found: C, 40.6; H, 2.6.

Reduction: Benzal-*o*-bromoacetophenone (I).—When 1 g. of the dibromoketone was dissolved in 20 cc. of acetone and treated with 10% potassium iodide, a pale yellow color developed. Upon acidification a deep reddish-brown color was produced. Upon dilution a yellow oil separated out. Distillation and analysis of this oil proved that it was identical with the α,β-unsaturated ketone.

Preparation of *o*-Bromophenylbenzylglyoxal (II).—A solution of 7.5 g. of benzal-*o*-bromoacetophenone in 100 cc. of alcohol was treated with 3.5 cc. of 6 *N* sodium hydroxide with stirring. To this mixture was added 7 cc. of 30% hydrogen peroxide. A colorless oil separated out. This oil could not be crystallized. On distilling at 155° (2 mm.) a pale yellow oil was obtained which gave a deep cherry-red color with alcoholic ferric chloride.

Anal. Calcd. for $C_{15}H_{11}O_2Br$: C, 59.4; H, 3.7. Found: C, 59.8; H, 3.6.

Preparation of the Enol of *o*-Bromophenylbenzylglyoxal (III).—To 25 g. of the diketone (II) dissolved in 90 cc. of alcohol, there was added a solution of 14.4 g. of sodium hydroxide dissolved in 30 cc. of water. The mixture generated much heat and boiled on the addition of the sodium hydroxide. The mixture separated into a red upper layer and a colorless alkaline botton layer. The two layers were separated and the red solution was acidified with hydrochloric acid. The solution was largely diluted with water and extracted with ether. The ethereal solution was washed with water, dried over anhydrous sodium sulfate and concentrated. There was obtained a yield of 8 g. of colorless needle-like crystals melting at 107°.

Anal. Calcd. for $C_{15}H_{11}O_2Br$: C, 59.4; H, 3.7. Found: C, 59.2; H, 3.8.

Oxidation.—When 1.0 g. of the alpha diketone was dissolved in 50 cc. of methyl alcohol and treated with an excess of alkaline hydrogen peroxide, cleavage resulted in the production of phenylacetic and *o*-bromobenzoic acids. These products were identified by their melting points and mixed melting points with known pure samples.

Reaction with *o*-Phenylenediamine (V).—A solution of 1.0 g. of the diketone and 1.0 g. of *o*-phenylenediamine in 25 cc. of methyl alcohol was boiled for one hour and allowed to cool. The solution was poured into water, extracted with ether, washed with dilute hydrochloric acid, dried and concentrated. A practically quantitative yield of colorless needles melting sharply at 110° was obtained.

Anal. Calcd. for $C_{21}H_{15}N_2Br$: C, 67.2; H, 4.0. Found: C, 67.5; H, 4.2.

Methylation: Methyl Ether of α-Hydroxybenzal-*o*-bromoacetophenone (VI).—A suspension of 5.0 g. of the powdered enol in 20 cc. of water was treated with 4.2 g. of dimethyl sulfate. To this mixture a 20% solution of potassium hydroxide was added dropwise with vigorous shaking until permanent alkalinity was effected. After extraction with ether, an equal volume of petroleum ether was added to the ethereal layer. This solution was then shaken with successive small portions of 10% potassium hydroxide until the alkaline layer was colorless. The alkaline washings upon acidification gave 0.5 g. of unchanged material. The ethereal solution was dried, filtered

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(8) Von Auwers, *Ber.*, **45**, 996 (1912).

and concentrated. There resulted a viscous yellow oil boiling at 280–285° (2 mm.). The yield was 4.4 g. or 84.1%.

Anal. Calcd. for $C_{16}H_{13}O_2Br$: C, 60.5; H, 4.1; —OCH_3, 9.8. Found: C, 60.8; H, 4.0; —OCH_3, 10.0.

***o*-Bromophenylglyoxylic Acid.**—This acid was purified by several crystallizations from methyl alcohol and water. The thin colorless needles melted over a range with decomposition as reported by Russanow. For a concentration of 0.03449, molecular conductivity 266.21, and conductivity at infinite dilution 348, the ionization constant at 25° was calculated to be 8.6×10^{-2}.

Summary

The preparation and properties of a new diketone are herein reported in connection with a discussion of the methylation of alpha diketones.

WASHINGTON, D. C. RECEIVED APRIL 24, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 140]

The Hydroxylation of the Double Bond[1]

BY NICHOLAS A. MILAS AND SIDNEY SUSSMAN

The use of osmium tetroxide and chlorates for the addition of hydroxyl groups to the double bond[2] is limited to aqueous solutions, and, at times, to specialized conditions. Similarly, organic peracids which have been used for this purpose are not of general applicability.[3] During the past year and a half we have been engaged in the preparation of tertiary alkyl peroxides and hydroperoxides, and found that anhydrous solutions of hydrogen peroxide and tertiary butyl alcohol are stable at room temperature for long periods of time. Such solutions, however, are perfectly inert toward olefinic double bonds, but in the presence of a small amount of osmium tetroxide, likewise dissolved in anhydrous tertiary butyl alcohol, a reaction proceeds smoothly to yield almost invariably a glycol. For example, from ethylene we obtained ethylene glycol; from tetramethylethylene, pinacol; from cyclohexene, adipic acid; from the ethyl esters of crotonic, maleic and fumaric acids, the corresponding dihydroxy esters. Table I shows some of the quantitative results obtained.

TABLE I

Olefinic substance	Main product	% yield
Isobutylene	Isobutylene glycol	37.6
Trimethylethylene	Trimethylethylene glycol	37.8
Allyl alcohol	Glycerol	60.2
Cinnamic acid	Phenylglyceric acid	56.2
Crotonic acid	Dihydroxybutyric acid	53.8
Maleic acid	Mesotartaric acid	30.3
Fumaric acid	Racemic acid	48.3

While our work was under way Criegee[4] published recently some preliminary results using osmium tetroxide and hydrogen peroxide in ethyl ether, and obtained aldehydes as his main products. In the present research, however, all of the unsaturated substances tried yielded glycols, although in certain cases the latter oxidized further to yield small amounts of by-products. We are now actively engaged in this field and hope to publish in the near future a more extended investigation.

Experimental

Preparation of the Reagent.—To 100 cc. of 30% hydrogen peroxide (Albone C) was added 400 cc. of pure tertiary butyl alcohol and the solution treated with small portions of anhydrous sodium sulfate whereby two layers separated out. The alcohol layer, which contained most of the hydrogen peroxide, was removed and dried with anhydrous sodium sulfate and finally with anhydrous calcium sulfate (Drierite). A solution of 6.32% hydrogen peroxide in tertiary butyl alcohol was obtained, giving a recovery of 93.8%. This solution can easily be concentrated by vacuum distillation of the alcohol at room temperature to any desired concentration without any loss of the peroxide provided an all-glass apparatus is employed. When hydrogen peroxide solutions of this sort were allowed to stand at room temperature for over six months, only a small decrease in hydrogen peroxide concentration was noticed.

The Catalyst.—Osmium tetroxide (Merck osmic acid) dissolves readily in tertiary butyl alcohol and the solution is perfectly stable provided no isobutylene is present, otherwise most of the osmium tetroxide is readily reduced into an insoluble black colloidal oxide which is a very active catalyst for the decomposition of hydrogen peroxide. In aqueous solutions osmium tetroxide destroys hydrogen peroxide in a very short time, whereas in anhydrous tertiary butyl alcohol it decomposes the latter to the extent of 20% in one month's time.

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[1] A preliminary report of this work was presented before the research conference, M. I. T., December 13, 1935.

[2] (a) Milas and Terry, THIS JOURNAL, **47**, 1412 (1925); (b) Terry and Milas, *ibid.*, **48**, 2647 (1926); (c) Milas, *ibid.*, **49**, 2005 (1927).

[3] (a) Milas and Cliff, *ibid.*, **55**, 352 (1933); (b) Milas and McAlevy, *ibid.*, **56**, 1219 (1934).

[4] Criegee, *Ann.*, **522**, 75 (1936).

Isobutylene Glycol from Isobutylene.—The isobutylene was prepared by the dehydration of tertiary butyl alcohol with oxalic acid. To 4.3 g. (0.0768 mole) of isobutylene dissolved in 36.3 g. of tertiary butyl alcohol was added 39.3 cc. (0.0768 mole) of 6.62% hydrogen peroxide reagent. The mixture was cooled in an ice-bath and to it added 0.75 cc. of a 0.5% solution of osmium tetroxide in tertiary butyl alcohol, and allowed to stand overnight at 0°. The reaction was complete on the following day when the mixture was fractionated and the fraction boiling at 176–178° collected; yield, 2.6 g. or 37.6% of the theoretical. This had a density of 0.999 at 25°. The boiling point and density of isobutylene glycol are recorded in the literature[5] as 176–178° and 1.003 at 20°, respectively.

Trimethylethylene Glycol from Trimethylethylene.—To 7 g. (0.1 mole) of trimethylethylene[6] (b. p. 38.3–38.4°) were added 48.4 cc. (0.1 mole) of 7.03% hydrogen peroxide reagent and 1 cc. of the osmium tetroxide solution catalyst, and the mixture allowed to stand at room temperature for twenty-four hours. At the end of this time the reaction was complete; the mixture was then fractionated whereby 2.9 g. of trimethylethylene was recovered and a fraction boiling at 175° collected; yield, 2.3 g. or 37.8% of the theoretical. This had a density of 0.992 at 25°. The boiling point and density of trimethylethylene glycol are recorded in the literature[7] as 176–178° and 0.989 at 25°, respectively.

Glycerol from Allyl Alcohol.—To 6.1 g. (0.105 mole) of allyl alcohol (Eastman Kodak Company) were added 54.6 cc. (0.1 mole) of 6.3% hydrogen peroxide reagent and 1 cc. of the osmium tetroxide solution catalyst. The reaction mixture warmed up considerably and had to be cooled under running water. At the end of three hours the peroxide was completely consumed and the reaction mixture subjected to fractionation to remove the solvent, the catalyst and the unreacted allyl alcohol (1.7 g.). The glycerol obtained amounted to 4.2 g. or 60.2% of the theoretical. The glycerol was definitely identified as the tribenzoyl ester which was prepared in pyridine from benzoyl chloride and the product obtained. It had a m. p. of 69°. Balbiano[8] gives the m. p. of this derivative as 71–72°.

Phenylglyceric Acid from Cinnamic Acid.—To 3.7 g. (0.025 mole) of cinnamic acid (Eastman Kodak Company) were added 13.6 cc. (0.025 mole) of 6.3% hydrogen peroxide reagent and an equal volume of tertiary butyl alcohol. The mixture was cooled in an ice-bath, to it added 2 cc. of the osmium tetroxide solution catalyst, and allowed to stand overnight at 0°. The reaction was complete on the following day when the solvent was removed by vacuum distillation and the residue taken up with water. The unchanged cinnamic acid (2.4 g.) was removed by filtration and the filtrate distilled under reduced pressure when a semi-solid residue separated out; yield 0.9 g. or 56.2% of the amount of cinnamic acid consumed. The semi-solid phenylglyceric acid was not crystallized, but was found to have a neutralization equivalent of 190 which is in close agreement with the theoretical value of 182 for phenylglyceric acid.

Dihydroxybutyric Acid from Crotonic Acid.—To 4.3 g. (0.05 mole) of crotonic acid (Eastman Kodak Company) was added 27.2 cc. (0.05 mole) of 6.3% hydrogen peroxide reagent. The mixture was cooled in an ice-bath and to it added 1 cc. of the osmium tetroxide solution catalyst, and allowed to stand overnight at 0°. The reaction was complete on the following day when the solvent was removed by distillation under reduced pressure, and the residue taken up with water. The unchanged crotonic acid was then extracted with chloroform following the method of Braun.[9] When the chloroform was evaporated 2.7 g. of unchanged crotonic acid was recovered. The aqueous portion was evaporated under reduced pressure and yielded 1.2 g. of a thick sirup; yield, 53.8% of the amount of crotonic acid consumed. This had a neutralization equivalent of 122, which is in close agreement with the calculated value of 120 for dihydroxybutyric acid.

Mesotartaric Acid from Maleic Acid.—To 2.9 g. (0.025 mole) of maleic acid (Eastman Kodak Company) were added 27.2 cc. (0.05 mole) of 6.3% hydrogen peroxide reagent, 2 cc. of the osmium tetroxide solution catalyst, and the mixture was allowed to stand overnight at room temperature. The reaction was complete on the following day when the solvent was removed under reduced pressure and the residue dissolved in water. The solution was then made ammoniacal, heated to boiling and treated with excess 10% calcium chloride solution, whereby the calcium oxalate and mesotartrate precipitated out. This precipitate was removed, dried and weighed; yield, 1.9 g. To remove the calcium mesotartrate, the precipitate was extracted with 20% sodium hydroxide solution. This separation yielded 1.2 g. of calcium mesotartrate and 0.7 g. of calcium oxalate. The calcium mesotartrate was further purified by reprecipitation and analyzed.

Anal. Calcd. for $C_4H_4O_6Ca{\cdot}3H_2O$: Ca, 16.53. Found: Ca, 16.28.

The filtrate from the calcium precipitation was treated with three volumes of 95% alcohol, and the calcium maleate, which precipitated out, collected, dried and weighed; 2.1 g., equivalent to 1 g. of unreacted maleic acid. From these results the yield of mesotartaric acid was calculated to be 30.3% and that of oxalic acid 14.6% of the maleic acid consumed in the reaction. Obviously the mesotartaric acid formed from maleic acid oxidizes further to oxalic acid.

Racemic Acid from Fumaric Acid.—To 2.9 g. (0.025 mole) of fumaric acid prepared from furfural[2c] were added 27.2 cc. (0.05 mole) of 6.3% hydrogen peroxide reagent, 2 cc. of the osmium tetroxide solution catalyst, and the mixture was allowed to stand for two days at 0°. The solvent was then removed under reduced pressure, the residue taken up with a small volume of water and the unreacted fumaric acid (1.7 g.) removed by filtration. The filtrate yielded 0.3 g. of calcium oxalate precipitated in acetic acid solution, and 1.3 g. of calcium racemate precipitated in ammoniacal solution. These correspond to 9.9% yield of oxalic acid and 48.3% yield of racemic acid. The calcium racemate was then analyzed for calcium.

Anal. Calcd. for $C_4H_4O_6Ca{\cdot}4H_2O$: Ca, 15.38. Found: Ca, 15.26.

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(5) Nevole, *Bull. soc. chim.*, [2] **27**, 63 (1877).

(6) Furnished through the courtesy of Dr. George Thomson.

(7) Krassuski, *Chem. Centr.*, **73**, I, 628 (1902).

(8) Balbiano, *Ber.*, **36**, 1573 (1903).

(9) Braun, THIS JOURNAL, **51**, 228 (1929).

Summary

1. It has been found that hydrogen peroxide in anhydrous tertiary butyl alcohol and in the presence of osmium tetroxide reacts with olefinic substances to yield glycols as the main products.

2. Ethylene glycol, isobutylene glycol, trimethylethylene glycol, pinacol, glycerol, phenylglyceric acid, dihydroxybutyric acid, mesotartaric acid and racemic acids have been obtained from their corresponding olefinic substances.

CAMBRIDGE, MASSACHUSETTS RECEIVED MAY 27, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

Conversion of Aldoximes to Carboxylic Acids by Means of Hot Alkali. The Elimination of Water from Aldoximes

BY EARL JORDAN[1] AND CHARLES R. HAUSER

The common statement that a β-aldoxime loses water to form a nitrile more readily than its α-isomer has been based presumably on the well-known fact that, in the presence of certain reagents, as for example acetic anhydride followed by alkali, the β-aldoxime forms nitrile, whereas the α-isomer usually gives only negligible amounts of this product. Under these conditions, however, the nitrile is *not* formed by the elimination of water from the β-aldoxime; the latter is first converted to its acetyl derivative which eliminates acetic acid to form nitrile.[2] Apparently there has been no direct evidence that in general, a β-aldoxime loses water more easily than its α-isomer.[3]

In this paper it is shown that certain β-aldoximes in 2 *N* sodium hydroxide solution[4] at 97–100° are slowly converted into mixtures of the corresponding carboxylic acids, ammonia and the α-aldoximes;[5] the latter are more slowly converted into carboxylic acids. The yields of acid and oxime isolated after certain periods of time are given in Table I. It can be seen that after the same periods of time the yields of acid obtained from β-aldoximes are higher than those from the α-isomers. Since these carboxylic acids[6] are probably formed by the hydrolysis of intermediate nitriles produced from the aldoximes by elimination of water, β-aldoximes apparently *do* lose water more readily than their α-isomers; however, this reaction is not recommended for distinguishing a pair of geometrically isomeric aldoximes[7] because, under the conditions used to effect the elimination of water, a considerable portion of the β-aldoxime is converted into the α-isomer.[5]

The rate of conversion[5] of β-3,4-methylenedioxybenzaldoxime into the α-isomer under these conditions is roughly indicated by the melting points of the products recovered after various periods of time. Evidently, complete conversion of the β-aldoxime to the α-isomer requires from sixty to ninety minutes. Likewise, β-4-methoxybenzaldoxime apparently is converted into the α-isomer within four hours. Since practically pure α-benzaldoxime is often obtained as an oil, the products recovered after four hours from both α- and β-benzaldoximes are probably almost pure α-aldoxime. On the other hand, both α- and β-furfuraldoxime apparently are converted into a mixture of the two isomers.[8]

The changes occurring when benzaldoximes in

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[1] This paper is from a portion of a thesis presented by Earl Jordan in partial fulfilment of the requirements for the Ph.D. degree at Duke University.

[2] For a recent discussion of this reaction see Hauser and Jordan, THIS JOURNAL, **57**, 2450 (1935); Hauser and Sullivan, *ibid.*, **55**, 4611 (1933).

[3] This has been pointed out by Brady, *Science Progress*, **29**, 485 (1935). In this connection it should be mentioned that Hantzsch and Lucus [*Ber.*, **28**, 748 (1895)] have reported that β-mesitylaldoxime with hot alkali gives nitrile whereas the α-isomer is stable under similar conditions; also, Hantzsch [*ibid.*, **24**, 47 (1891)] has reported that β-thiophenaldoxime with hot sodium carbonate gives nitrile. For references to the thermal decomposition of aldoximes see Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., N. Y., 1929, p. 659.

[4] Aldoximes in alkaline solutions are quite stable at room temperatures. See Freudenberg, "Stereochemie," Vol. VII, 1933, p. 987. In this Laboratory β-3,4-methylenedioxybenzaldoxime (m. p., 146°), after being kept in 2 *N* sodium hydroxide solution at 30° for thirty-six hours was recovered in a yield of 93% melting at 133–135°; the α-isomer melts at 110°.

[5] It is well known that there is a tendency for the β-benzaldoximes to revert to the α-isomers. See Freudenberg, "Stereochemie," Vol. VII, 1935, p. 988.

[6] It does not seem possible that the carboxylic acids could have been produced by a Cannizzaro reaction since no benzyl alcohol has been found; moreover, in certain cases, the total yields of carboxylic acid and aldoxime recovered amounts to over 90% of the theoretical quantitatives.

[7] These isomers are more readily distinguished by the reactions of their acetyl derivatives with bases; see references 2 and 3.

[8] This is in agreement with the results reported by Brady and Goldstein, *J. Chem. Soc.*, 1959 (1927).

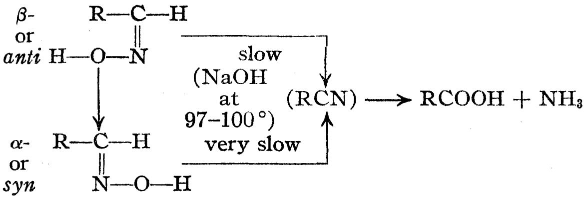
TABLE I

PERCENTAGE YIELDS OF PRODUCTS FROM BENZALDOXIMES AND 2 *N* SODIUM HYDROXIDE AT 97–100°

			Recovered oxime		Acid			Total yield, %
Oxime	M. p., °C.	Time	%, yield	M. p., °C. crude prod.	%, yield	M. p., °C. crude prod.	Authentic m. p., °C.	
α-3,4-Methylenedioxy-	110	15 min.	84	110	Trace			84
α-3,4-Methylenedioxy-	110	90 min.	90	108–110	3	224	228	93
α-3,4-Methylenedioxy-	110	4 hrs.	78	109–110	5	225	228	83
α-3,4-Methylenedioxy-	110	12 hrs.	74	110	21	220–222	228	95
β-3,4-Methylenedioxy-	146	15 min.	87	124–127	5	224–225	228	92
β-3,4-Methylenedioxy-	146	60 min.	68	100–102	16	227–228	228	84
β-3,4-Methylenedioxy-	146	90 min.	62	110[a]	31	225	228	93
β-3,4-Methylenedioxy-	146	4 hrs.	53	110[a]	37	225	228	90
β-3,4-Methylenedioxy-	146	12 hrs.	41	110[a]	58	224–226	228	99
α-Benzal-	35	4 hrs.	87	Oil	10	121	121	97
β-Benzal-	132	4 hrs.	52	Oil	38	121	121	90
α-4-Methoxy-	64	4 hrs.	89	64	8	179–180	184	97
β-4-Methoxy-	133	4 hrs.	59	64[a]	39	182	184	98
α-3-Nitro-	123	90 min.	96	123	Trace			96
β-3-Nitro-	123	90 min.	26	116	62	137–139	140	88
α-Furfuraldoxime	75–76	90 min.	67	47–50	18	115–118	132–134	85
β-Furfuraldoxime	89–91	90 min.	38	48–50	49	132–133	132–134	87

[a] Melting point of α-isomer.

2 *N* sodium hydroxide solution are heated at 97–100° may be represented by the scheme[9]



In order to show that the formation of carboxylic acid is brought about by the presence of alkali, β-3,4-methylenedioxybenzaldoxime was heated at 97–100° with water alone for four hours, and in a solution of dioxane and water for ninety minutes. No nitrile or carboxylic acid could be isolated in either case; the only change observed was the conversion of a portion of the β-aldoxime to the α-isomer.

Experimental

Approximately 2 g. of aldoxime was dissolved in 50 cc. of 2 *N* sodium hydroxide and heated on a boiling water-bath (97–100°). In cases in which considerable acid was produced, ammonia was readily detected in the vapors. After a designated time the solution was cooled and saturated with carbon dioxide. The oxime which precipitated was filtered through a sintered glass crucible. The filtrate was extracted with ether to remove the oxime in solution. The filtrate was then acidified with hydrochloric acid and the precipitated carboxylic acid filtered off; the filtrate was extracted with ether. The products were dried and weighed; they were identified by the mixed melting point method. No other products were found.

Blanks were run with β-3,4-methylenedioxybenzaldoxime at 97–100°: (a), after four hours with water, 99% oxime (m. p. 138–140°) was recovered; (b), after ninety minutes in water–dioxane solution, 95% oxime (m. p. 99–101°) was recovered.

Summary

1. Certain β-aldoximes with 2 *N* sodium hydroxide at 97–100° are slowly converted into mixtures of carboxylic acids and the corresponding α-aldoximes. The latter are more slowly changed to carboxylic acids.

2. These results indicate that a β-aldoxime eliminates water to form nitrile more readily than its α-isomer; presumably, the nitrile undergoes hydrolysis in the presence of hot alkali to form the corresponding carboxylic acid and ammonia.

DURHAM, N. C.

RECEIVED MAY 1, 1936

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(9) For references to the evidence supporting these configurations of aldoximes, see note 2.

[CONTRIBUTION FROM THE NATIONAL RESEARCH INSTITUTE OF CHEMISTRY, ACADEMIA SINICA]

The Alkaloids of Fritillaria Roylei. I. Isolation of Peimine[1]

BY YUOH-FONG CHI, YEE SHENG KAO AND KOU JEN CHANG

Previous contributions on the alkaloidal content of the plant *Fritillaria Roylei* (Pei-Mu) by Fukuda[2] and Chou[3,4] have shown that it contains the following alkaloids: (A) verticin, $C_{18}H_{33}O_2N$ or $C_{19}H_{30}O_2N$; (B) verticilin, $C_{19}H_{33}O_2N$; (C) peimine, $C_{19}H_{30}O_2N$; (D) peiminine, $C_{18}H_{28}O_2N$; (E) fritimine, $C_{38}H_{62}O_3N_2$; and (F) fritillarin, $C_{19}H_{33}O_2N$. The properties of these alkaloids are recorded in Table I.

TABLE I

Name	Formula	M. p., °C.	Rotation	Pei-Mu source
Peimine	$C_{19}H_{30}O_2N$	223	0°	Chekiang
Peiminine	$C_{18}H_{28}O_2N$	135	−62.5°	Chekiang
Fritimine	$C_{38}H_{62}O_3N$	167	−50°	Szechuen
Verticin	$C_{18}H_{33}O_2N$ $C_{19}H_{35}O_2N$	224–224.5	−10.66°	Japanese
Verticillin	$C_{19}H_{33}O_2N$	Sinters at 130, melts at 148–150, resolidifies at 157–159, decomposes at 212–213		Japanese
Fritillarin	$C_{19}H_{33}O_2N$	130–131		Japanese

This interesting drug (Pei-Mu) finds wide application in medicine and is prescribed in fevers, coughs, dysuria, hemorrhages, deficiency of milk, threatened mammary abscess, lingering labor, rheumatism and diseases of the eye. This plant was identified as *Fritillaria Roylei* by Stuart[5] or *Fritillaria verticillata* by Read and Liu.[6] The part of the plant used in medicine is the starchy corm of this liliaceous plant growing in different parts of China, especially in Chekiang and Szechuen. The material used for this investigation was a Chekiang variety known by the commercial name "Ta Pei," and was obtained from a local drug store or pharmacy. The pharmacological properties of peimine, peiminine and fritimine have been described by Chen.

The alkaloid A, (verticin) recently isolated by us, had the same melting point as C (peimine); but the results of our analyses of the free bases and its salts proved it to have the formula $C_{26}H_{43}O_3N$, instead of $C_{19}H_{30}O_2N$ assigned to peimine by Chou. Judging from the analytical data already known, we conclude this was probably the same alkaloid as peimine, to which the present authors have assigned a different formula.

Experimental Part

Ninety-eight kilograms of the starch corms of *Fritillaria Roylei*, known under the commercial name "Ta Pei" was powdered, and percolated with 95% alcohol. When the solvent had been removed from the alcoholic extract under diminished pressure at 40–45°, the residue was dissolved in 2% hydrochloric acid, and the solution filtered. The crude alkaloid was then liberated from the acid extract with sodium carbonate, and extracted with ether and then with chloroform. After distilling the solvent from the ethereal solution, the ether-soluble alkaloid weighed 48 g., which represented about 0.05% of the total quantity of the crude drug. This crude alkaloid dissolved in benzene, to which some petroleum ether was added just to turbidity, whereupon peimine separated as an amorphous powder. It was then purified by recrystallization from an alcohol–petroleum ether mixture, from which peimine separated in needles, melting at 223–224°.

In some cases, it was better to convert the ether-soluble alkaloids, after solution in dry ether, into their hydrochlorides by passing in dry hydrogen chloride. The mixed hydrochlorides were then separated into peimine hydrochloride and peiminine hydrochloride (to be described in our next paper) by fractional crystallization from an alcohol–ether mixture.

Pure peimine was recovered from its hydrochloride by action of sodium carbonate. It was recrystallized from a mixture of alcohol–petroleum ether, and separated in needles melting at 224°. The yield of pure peimine was 3 g. For analysis, the alkaloid was dried over phosphorus pentoxide at 80° in a vacuum, $[\alpha]^{13}_{D}$ 0°.

The hydrochloride and hydrobromide of peimine were prepared by dissolving in each case 100 mg. of the pure alkaloid in ether, passing in hydrogen chloride or bromide and recrystallizing from an alcohol–ether mixture. The acid sulfate was prepared in similar fashion except that dilute sulfuric acid was employed. The different products were dried for analysis over phosphorus pentoxide at 80° in a vacuum.

The platinichloride and aurichloride were prepared by precipitation in aqueous solution. The former salt was recrystallized from water and the latter from dilute hydrochloric acid. The products were dried for analysis over phosphorus pentoxide at 110° in a vacuum. The results of analyses of the alkaloid and its different salts are recorded in Table II.

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(1) The authors wish to express their sincere thanks to Mr. Yao Tseng Huang for his assistance in running the microanalyses recorded in this paper, and to Professor Treat B. Johnson of the Sterling Chemistry Laboratory of Yale University for his aid in the arrangement of this paper for publication.

(2) Fukuda, *Science Reports, Tôhoku Imp. Univ., Japan*, **1**, 18, 323 (1929). Also *Chem. Zentr.*, **1**, 988 (1930).

(3) Chou and Chen, *Chinese J. Physiol.*, **6**, 265 (1932).

(4) Chou and Chen, *ibid.*, **7**, 41 (1933).

(5) Stuart, Chinese Materia Medica, 178 (1911).

(6) Read and Liu, "Plantae Medicinalis Sinensis," No. 630, 1927, pp. A-1, 51.

TABLE II

Compound		Peimine (P)	Hydrochloride	Hydrobromide	Acid sulfate	Platinchloride	Aurichloride
M. p., °C.		224	295, dec.	293.5–294	278–280	233–235, dec.	164–165
Formula		$C_{26}H_{43}O_3N$	P·HCl	P·HBr	$P \cdot H_2SO_4$	$P_2 \cdot H_2PtCl_6$	$P \cdot HAuCl_4$
Carbon, %	Calcd.	74.75	68.74	62.61	60.53		
	Found[a,b]	74.65[c]	69.07, 68.77	62.92, 62.88, 63.13[a]	60.28, 60.27		
Hydrogen, %	Calcd.	10.38	9.77	8.90	8.80		
	Found[a,b]	10.42[d]	9.84, 9.85	9.04, 8.86, 8.77[a]	8.81, 8.64		
Nitrogen, %	Calcd.	3.35		2.81			
	Found[a,b]	3.56[e]		2.72[a]			
%	Calcd.			Br 16.04		Pt 15.68	Au 26.03
	Found			Br 15.55[a]		Pt 15.45 15.36	Au 24.9 25.09

Molecular weight determination (Rast); 0.288 mg. in 3.520 mg. camphor. ΔT, 9.2°. 0.268 mg. in 3.810 mg. camphor; ΔT, 7.7°. Calcd. for $C_{26}H_{43}O_3N$, 417.3. Found: 336,[a] 365.[2]

[a] Analyses made by Dr. Ing. A. Schoeller, Toelzestrasse 19, Berlin-Schmargendorf, Germany. [b] Analyses made by Dr. Carl Tiedcke, Bismarckstrasse, Hamburg 19, Germany. [c] Average: 74.75, 74.85,[a] 74.67,[a] 74.76, 74.58,[b] 74.39,[b] 74.53.[b] [d] Average: 10.30, 10.15, 10.49,[a] 10.54,[a] 10.43,[b] 10.53,[b] 10.51.[b] [e] Average: 3.52, 3.60, 3.77, 3.38,[a] 3.36,[a] 3.72.[b]

Summary

Peimine, melting at 224°, has been obtained in a more pure condition. Its formula is $C_{26}H_{43}O_3N$, instead of $C_{19}H_{30}O_2N$, which was assigned to it by Chou. The present formula is substantiated by the results of analysis of several salts; namely, the hydrochloride, bromide, acid sulfate, platinichloride and aurichloride.

SHANGHAI, CHINA

RECEIVED MAY 7, 1936

NOTES

An Apparatus for the Determination of the Absorption of Small Quantities of Gas by Solutions

BY H. E. BENT, W. F. GRESHAM AND N. B. KEEVIL

The apparatus illustrated in the figure is designed to measure the absorption of small amounts of gas by solutions contained in sealed glass capsules. The apparatus allows one to break and empty the capsule, measure the amount of oxygen absorbed and make a correction for the amount of oxygen dissolved in the solvent. The sample is contained in a capsule "G" and the oxygen to be introduced is measured in a capillary by means of the scale "B," a small slug of mercury in the capillary serving to confine the gas.

The particular problem which necessitated the construction of this apparatus was the determination of the purity of small quantities of organic free radicals by measuring the quantity of oxygen absorbed. Samples of a half gram or larger may conveniently be studied in the apparatus developed for measuring the heat of the reaction.[1] Frequently, however, it is desirable to analyze with a precision of about 1% a dilute solution of a free radical which will not absorb more than about 1 cc. of oxygen. The details of breaking the capsule and measuring the absorption of oxygen together with typical experimental results are given in the following paragraphs.

The manipulation of the apparatus will be evident from the figure and the following description. "A" is a stopcock through which the apparatus may be evacuated after the capsule containing the solution of the free radical has been placed in the apparatus. "B" is a scale placed behind the capillary (diameter 4 mm.) in order that the volume of oxygen introduced into the absorption bulb may be accurately measured. "C" is a three-way stopcock which connects the capillary tube to the supply of oxygen and to the

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(1) Bent, Cuthbertson, Dorfman and Leary, THIS JOURNAL, **58**, 165 (1936); Bent and Cuthbertson, *ibid.*, **58**, 170 (1936).

absorption bulb. "D" leads to the oxygen supply and has a blow-off tube below it to permit better control of the pressure. By properly adjusting the pressure a small volume of mercury is introduced into the capillary through "C" before it is filled with oxygen. This slug is blown by oxygen to the top of the capillary. When the cock "C" is carefully turned to introduce oxygen into the absorption bulb which is at a slightly lower pressure the slug of mercury descends and gives a measure of the amount of gas which has been introduced. Provided the tube is clean no difficulty is encountered from the slug's dropping in the capillary. "E" is a thermometer which measures the temperature in the jacket around the absorption bulb. The absorption bulb is just above "F" and at "F" is a reference mark to which the bulb is calibrated. "G" is the capsule which is of rather peculiar design. At the top the capsule is sufficiently blunt to prevent its wedging in the constriction. At the bottom there is a little bulge which permits the glass rod "H" to hold the capsule submerged after it has been emptied. The capsule below the lower bulge is constricted for a short length before drawing down to a capillary. The reason for this is that the capsule cannot easily be emptied unless there is sufficient volume between the lower part of the capsule and the outside tube to hold all of the solution. The contents of the capsule are expelled below the surface of the mercury by warming. If the capsule had not been constricted at the bottom the solution would have come out of the capsule and surrounded the latter, thus making it difficult to expel the contents, as the solution around the outside would have warmed up first and been pushed back into the capsule. The glass rod "H" is connected by a fresh piece of gum rubber tubing. The rubber is connected to a glass tube at such an angle that it is always covered by mercury and does not come in contact with the solution. At the beginning of a run the mercury is lowered and the capsule held by the rod "H." After evacuation the mercury is raised around the capsule and the tip of capsule broken by means of this rod. After emptying the capsule the rod holds the glass down out of the way of the solution while it is absorbing oxygen. "I" is a rubber stopper which is held up by a steel washer which in turn is held securely in place by wires which are not shown. "J" is a pinchcock which permits the mercury to be held at a fixed height in the absorption bulb. "K" is a reservoir of mercury which can be evacuated for removal of mercury from the absorption bulb or may be open to the atmosphere or maintained at any desired intermediate pressure. The pressure in the absorption bulb is measured by means of the mercury column in the tube which is open at the top, a small cathetometer and steel scale, not shown.

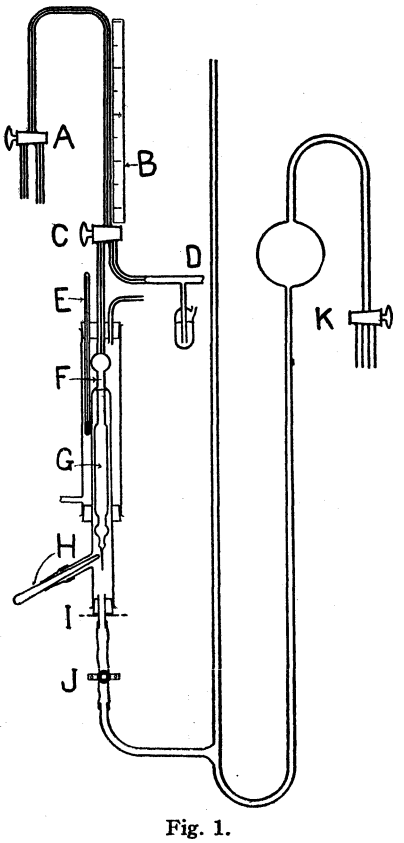

Fig. 1.

In carrying out a run the capsule is first introduced by removing the rubber stopper "I." The pinchcock is closed and the space surrounding the capsule evacuated. Mercury is then allowed to rise, floating the capsule above the rod "H." A correction is made for any trace of residual gas by measuring it before adding the oxygen. The quantity amounted usually to one or two tenths of a cubic centimeter. The pressure is then adjusted, the tip broken and the contents expelled by gentle warming, the broken tip being kept slightly below the surface of the mercury. The pressure is then adjusted to a little less than one atmosphere and an excess of oxygen introduced. The volume of the gas phase is increased to three times that of the calibrated bulb (9.9 cc.), an auxiliary calibration fixing this point, and the solution allowed to stand with occasional shaking in order to come to equilibrium. The ether meniscus is then raised to the graduation on the constriction at "F" and the amount of residual oxygen computed from the total pressure and the vapor pressure of the solvent. A correction is applied for the amount of oxygen dissolved in the solvent at the partial pressure of the oxygen existing at the time equilibrium is being established. The compression of the oxygen, as the solution is raised, increases its solubility. However, the surface of contact is so small at the constriction that the new equilibrium is approached very slowly. Since this is a correction to a correction it is not of importance. When ether is used as a solvent the largest error is due to the changing vapor pressure of ether with slight change in temperature. The table illustrates the accuracy which may be obtained without thermostating the water jacket. Doubtless a more accurate control of the temperature by circulating water at constant temperature through the jacket would still further improve the results. The apparatus was checked by determining the solubility of oxygen in ether using a sample of ether about three times as large as that required in the determination of the purity of a free radical. An error of 10% in determining the solubility of oxygen in ether amounts to about 0.5% in the correction to be applied to a run on a free radical. The data on diphenyl α-naphthylmethyl in the table give an idea of the accuracy of the method.

ABSORPTION OF OXYGEN BY DIPHENYL α-NAPHTHYLMETHYL

Concn. of cpd. from soly., wt. %	1.427	1.427
Ether soln., g.	3.074	3.279
O_2 (N. T. P.) added, cc.	2.535	3.065
Inert gas in capsule, cc.	0.165	0.119
Gas after run, cc.	.982	1.275
O_2 abs. by cpd. $\times 10^3$, g.	2.34	2.55
Concn. cpd. in wt. %	1.395	1.426
Purity, %	98.7	100.0

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RECEIVED APRIL 28, 1936

The Catalytic Oxidation of Carbon

BY HANS M. CASSEL

The activating effect of sodium chloride on the combustion of soot in contact with it, described by R. K. Taylor,[1] has recently been the object of further interesting experiments by Day, Robey and Dauben,[2] using other salts as activating substances. In explaining their observations these authors refer to a theory proposed by H. S. Taylor and H. A. Neville[3] for the heterogeneous reaction of steam with carbon.

It should be taken into consideration, however, that the topochemical relations in the two cases are distinctly different: in the steam experiments the salt particles are imbedded in the carbon surface; in the combustion experiments, on the other hand, the oxygen molecules have to penetrate the soot layer before they can possibly reach the salt surface.[4] It is difficult to see how the contact of the soot with the salt is maintained and continues to be effective once the reaction has started in the interface.

On the basis of the earlier work of Eucken[5] two observations made by me may offer a more satisfactory explanation. Eucken, studying the combustion of graphite under low pressures, observed a rather low rate on smooth surfaces. But after a longer attack by oxygen the carbon surface takes on a velvet-like appearance, accompanied by an acceleration of the reaction. The condition of the surface may, however, be "ironed out" again by a process which Eucken calls "healing." Probably this is due to the reaction $2CO = C + CO_2$ which takes place in the range of not too high temperatures, the formation of CO being the first step of oxidation. According to R. K. Taylor, this process of regeneration seems to occur also in the case of burning soot, for he observed a slowing down of the reaction "presumably because of the more rapid oxidation at first of smaller particles or more active patches on the carbon surface."

I deposited a layer of soot on Pyrex glass by cracking CH_2Cl_2 at about 450°. In burning this by exposing it to a current of oxygen at about 600° the reaction once started generally spreads parallel to the surface, the soot being removed as if swept out by a piston. The fact that the reaction does not visibly proceed perpendicularly to the surface indicates that the carbon deposit is more easily attacked from the sides than from the

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(1) R. K. Taylor, THIS JOURNAL, **52**, 3025 (1930).

(2) J. E. Day, R. F. Robey and H. J. Dauben, *ibid.*, **57**, 2725 (1935).

(3) H. S. Taylor and H. A. Neville, *ibid.*, **43**, 2055 (1921).

(4) The impermeability of thin layers of soot is evident in the case where it acts as an emulsifier.

(5) A. Eucken, *Z. angew. Chem.*, **43**, 986 (1930).

surface. This should be expected if the soot particles, as hexagonal crystals,[6] have grown orientated with their cleavage planes lying parallel to the glass surface.[7]

This view is in agreement with the theory of Eucken, which assumes that the adsorption of gas molecules or atoms by graphite takes place preferentially in the planes perpendicular to the cleavage planes of the crystal lattice.[8] The reaction, therefore, should be facilitated wherever two adjacent crystals touch each other or project into the gas phase.

If this is true, and if the soot deposits are always orientated, the combustion of soot deposits should be accelerated when the underlying glass surface is etched or ground. In order to check this the externally ground part of a Jena glass ground joint and the adjacent smooth surface were coated with soot from a natural gas flame and exposed to oxygen at about 600° for a few seconds. This treatment cleaned the ground part perfectly of carbon, while no visible attack took place on the smooth glass surface, a sharp line dividing the two.

Considering that the deposits in the salt experiments naturally have a very coarse structure, it may be concluded that the function of the salts in the case of soot combustion is quite the same as that of the ground glass, in the above described experiment, namely, interrupting the primary growth of large crystals and preventing a secondary regeneration.

From the same point of view the theory of the mechanism of the steam–carbon reaction should be revised. It is known from the experiments of Frankenburger[9] that sodium chloride inserted into iron deposits causes a highly dispersed structure by inhibiting the growth of coherent crystals. Such iron appears remarkably activated. Accordingly the increased activity of the impregnated graphite seems to be due to the opening of the prismatic planes[6] of the crystal lattice combined with the hygroscopic action of the salt ions.

CONTRIBUTION FROM THE
GREAT WESTERN ELECTRO-CHEMICAL COMPANY
PITTSBURG, CALIF. RECEIVED APRIL 13, 1936

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[6] U. Hofmann, *Z. angew. Chem.*, **44**, 841 (1931).

[7] The orientation of soot particles is also very probable in its operation as emulsifying agent.

[8] The findings of L. Meyer [*Z. physik. Chem.*, **B17**, 385 (1932)] and U. Hofmann [*Ber.*, **65**, 1821 (1932)] who describe the basal planes of graphite as being attacked preferentially are related to temperatures above 750°.

[9] W. Frankenburger, *Z. Elektrochem.*, **37**, 473 (1931).

Resin Studies. IV. Sublimed *l*-Abietic Acid

BY DAVID LIPKIN AND W. A. LA LANDE, JR.

l-Abietic acid (and rosin) have been observed to give a "sublimate" when heated under a variety of conditions at a temperature below the distillation point of the acid.[1] We have studied this sublimate carefully and find that it shows certain marked differences from the products obtained by Shaw and Sebrell and by Labatut and Duffour. Dupont[2] considered the sublimate obtained by the latter investigators to be identical with *l*-abietic acid.

To obtain a sufficient quantity of the sublimate the previously described procedure of La Lande[1] was used, except that stirring was eliminated and a large glass tube substituted for the reaction vessel. The yield of dry and colorless product was highest in the range 175–275°; at 330–385° the yield was negligible and the product quite impure due to the rapid decomposition. About 0.5 g. of sublimate was collected during an eight-hour period from a 14-g. charge; none was obtained from various rosins, and air or oxygen could not be substituted for the pure nitrogen.

Fig. 1.—"Sublimed" *l*-abietic acid (× 100).

The product, which is illustrated in the accompanying figure, showed the following properties as compared with a sample of *l*-abietic acid prepared according to Steele.[3]

The rotary power of the sublimate was practically constant regardless of the temperature and its rate of formation. It underwent no change on exposure to the light (including occasional sunlight) and air of the laboratory for a few months,

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[1] Labatut and Duffour, *Soc. des Sc. de Bordeaux*, 31 (1919); Shaw and Sebrell, *Ind. Eng. Chem.*, **18**, 612 (1926); La Lande, *ibid.*, **26**, 678 (1934).

[2] Dupont, *Bull. soc. chim.*, [4] **35**, 1209 (1924).

[3] Steele, THIS JOURNAL, **44**, 1333 (1922).

TABLE I

PROPERTIES OF STEELE'S *l*-ABIETIC ACID AND "SUBLIMED" *l*-ABIETIC ACID

	Steel's *l*-abietic acid	"Sublimed" *l*-abietic acid
M. p., °C.	158	150
M. p. after 1 recrystn. from EtOH, °C.	158	150
$[\alpha]^{25}D$ (5% in EtOH)	−75.5	−35.1
Acid no.	185.4	185.3
Sapn. no.	185.4	185.3
Calcd. acid no.	185.5	......
% C	79.24	79.32
% H	9.86	9.90
Calcd. % C	79.40	......
Calcd. % H	10.00	......
C_6H_5COCl color reaction	Indigo-blue	Indigo-blue

in marked contrast to the original acid which turned brown and opaque under these conditions. In xylene solutions, however, this difference was not apparent. Using the technique of Dupont and Lévy[4] it was found that both acids absorbed oxygen at practically the same rate and to the same degree.

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[4] Dupont and Lévy, *Bull. soc. chim.*, **47**, 60 (1930).

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RECEIVED APRIL 15, 1936

Studies in the Phenanthrene Series. X. Naphthoquinolines[1]

BY ERICH MOSETTIG AND JOHN W. KRUEGER

The skeleton of morphine consists of a phenanthrene nucleus and a nitrogen-containing ring. Neither in natural nor synthetic products is any other example known of such a condensed ring system as is found in the morphine group. As an approach to the preparation of compounds containing similar ring systems, which might exhibit morphine-like action, we have considered it advisable to include the synthesis of several naphthoquinolines and naphthoisoquinolines.[2]

This communication deals with the synthesis of a naphthoquinoline derived from 3-aminophenanthrene. Since the latter compound has been hitherto prepared practically only through a very tedious detour (phenanthrene sulfonic acid to hydroxyphenanthrene to aminophenanthrene),[3] we sought for a more feasible preparative method. Very recently Bachmann and Boatner[4] described in a preliminary form the preparation of 1-, 2-, and 3-aminophenanthrenes by the Beckmann rearrangement of the oximes of 1-, 2-, and 3-acetylphenanthrenes, emphasizing the practical usefulness of this procedure. We have, independently of these authors, prepared 2- and 3-aminophenanthrenes in the same way. We are withholding the preparative details until comparison with Bachmann and Boatner's procedure can be made.

By application of Skraup's synthesis to 3-aminophenanthrene, a naphthoquinoline of m. p. 106–107° was obtained. In spite of careful search, no other isomer could be found, which indicates that ring closure took place in only one direction. A tetrahydro derivative, obviously hydrogenated in the nitrogen-containing ring, was readily obtained by high pressure reduction, employing Chromite catalyst. By catalytic reduction under ordinary conditions, using platinum oxide catalyst, the same py-tetrahydronaphthoquinoline was formed together with a more highly hydrogenated compound which is most probably an octahydronaphthoquinoline. Since there is still some uncertainty in our minds as to the nature of the substance obtained by the Emde degradation of the methochloride of N-methyltetrahydronaphthoquinoline, the comparison of the degradation product with 2-[3-(dimethylamino)-*n*-propyl]-phenanthrene does not permit any conclusions as to whether the nitrogen-containing ring is attached in the 3,4- or 3,2-positions of the phenanthrene nucleus.

We intend to present this final structural proof together with analogous experiments on the 2- and 9-aminophenanthrenes respectively, in a following communication.

Experimental

Naphtho-(1,2-f)-quinoline or Naphtho-(2,1-g)-quinoline.—For the sake of simplicity we shall refer to this compound as "naphthoquinoline." It was prepared by Cohn's modified method of Skraup.[5] Thirty grams of 3-aminophenanthrene was added to a suspension of 4.5 g. of ferrous sulfate in 30 cc. of nitrobenzene, which was subsequently mixed with a solution of 9.1 g. of boric acid in 46 cc. of glycerol. Finally, 25 cc. of concentrated sulfuric acid was introduced in small portions to the thoroughly stirred mixture. The gray pasty mass was then transferred to an Erlenmeyer flask, kept in a water-bath for three hours, and finally heated on a hot-plate until it turned to

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[1] The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: the Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

[2] See also Benzofuroquinolines, Mosettig and Robinson, THIS JOURNAL, **57**, 902 (1935).

[3] Werner and co-workers, *Ann.*, **321**, 248 (1902).

[4] Bachmann and Boatner, THIS JOURNAL, **58**, 857 (1936).

[5] Cohn, *ibid.*, **52**, 3685 (1930).

PROPERTIES AND ANALYTICAL DATA

Compound	Solvent	M. p., (corr.) °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found		% Calcd.	% Found
Oxime of 2-acetylphenanthrene[a]	EtOH	196–198	$C_{16}H_{13}ON$					N	5.95	5.93
3-(Methylamino)-phenanthrene[b]	Pet. ether (70–90°)	69–70	$C_{15}H_{13}N$	86.91	86.97	6.32	6.33			
Hydrochloride	EtOH-ether	190–200 dec.	$C_{15}H_{14}NCl$					Cl	14.55	14.63
3-(Dimethylamino)-phenanthrene[b]	Pet. ether (70–90°)	75–76	$C_{16}H_{15}N$	86.84	86.80	6.83	7.04			
Hydrochloride	EtOH	210–213 dec.	$C_{16}H_{16}NCl$					Cl	13.76	13.96
3-(1-Aminoethyl)-phenanthrene-HCl[c]	EtOH	265–266	$C_{16}H_{16}NCl$	74.52	74.45	6.25	6.40	Cl	13.76	13.59
"Naphthoquinoline"	Bz pet. ether	106–107	$C_{17}H_{11}N$	89.04	89.11	4.84	4.95	N	6.11	6.09
Hydrochloride	EtOH	239–243	$C_{17}H_{12}NCl$					N	5.27	5.17
Tetrahydro-"naphthoquinoline"[d]	EtOH	72–74	$C_{17}H_{15}N$	87.51	87.78	6.49	6.63	N	6.01	6.16
Hydrochloride	EtOH	255–260	$C_{17}H_{16}NCl$					N	5.19	5.19
Octahydro-"naphthoquinoline"[d]	Pet. ether	111–112	$C_{17}H_{19}N$	86.02	86.04 86.14	8.07	8.16 8.20	N	5.91	5.95
Hydrochloride	EtOH	305–307	$C_{17}H_{20}NCl$					N	5.12	5.15
2-(3-(Dimethylamino)-1-chloro-*n*-propyl)-phenanthrene hydrochloride[e]	EtOH	248–252 dec.	$C_{19}H_{21}NCl_2$					Cl	21.22	20.57
2-(3-(Dimethylamino)-*n*-propyl)-phenanthrene hydrochloride[f]	EtOH	222–227	$C_{19}H_{22}NCl$	76.07	76.01	7.41	7.25	Cl N	11.83 4.67	11.79 4.59

[a] Five grams of finely divided 2-acetylphenanthrene (m. p. 143–144°), 4 g. of hydroxylamine hydrochloride, 80 cc. of alcohol and 2 cc. of pyridine were heated in a pressure bottle for three and one-half hours at 100°. Practically pure oxime crystallized from the cooled reaction mixture; yield, 90%.

[b] The methylation of 3-aminophenanthrene was carried out in 10-g. batches using dimethyl sulfate and potassium hydroxide. The separation of the tertiary and secondary bases was effected by Hinsberg's method with benzene sulfonyl chloride. The quaternary compound was isolated as the methiodide. This, on thermal decomposition, yielded another batch of tertiary amine. The average yield of tertiary amine was 40–50%, of secondary amine, 10%.

[c] Obtained in yields of 60–70% by reduction of the oxime with 2.5% sodium amalgam in alcohol–acetic acid solution.

[d] Ten grams of "naphthoquinoline" suspended in 15 cc. of absolute alcohol with 1 g. of Chromite catalyst was heated to 135° during one hour, and kept at this temperature for one and one-half hours under a hydrogen pressure of 133–144 atm. (apparatus, Adkins and Cramer, THIS JOURNAL, **52**, 4349 (1930), catalyst, 37 KAF, *ibid.*, **54**, 1138 (1932)). The catalyst, together with the crystallized reduction product was filtered, the base (7.5 g., m. p. 70–74°) was separated from the catalyst by extraction with ether in a Soxhlet apparatus. From the alcoholic filtrate 1.5 g. of tetrahydronaphthoquinoline hydrochloride was obtained. No other substances could be obtained. Five grams of naphthoquinoline, dissolved in 125 cc. of glacial acetic acid, was reduced catalytically under ordinary conditions, using 0.25 g. of platinum oxide. Within ten days 1700 cc. of hydrogen was taken up (calcd. for 2 moles, 1100). Three and one-half grams of the octahydro compound was obtained by the aid of its difficultly soluble hydrochloride. When the hydrogenation was interrupted after about two and a quarter moles of hydrogen had been taken up, octahydro- and tetrahydronaphthoquinoline and a considerable amount of oily, undefined products were obtained. The octahydronaphthoquinoline may be prepared more conveniently by catalytic reduction (platinum oxide and glacial acetic acid) of the tetrahydro compound. The tetrahydronaphthoquinoline is rather unstable and becomes dark in solution.

[e] To a suspension of 1 g. of phosphorus pentachloride in 2 cc. of chloroform, 1 g. of finely powdered 2-(3-(dimethylamino)-1-hydroxy-*n*-propyl)-phenanthrene hydrochloride (Mosettig and van de Kamp, unpublished results) was added in small portions, and the mixture was shaken for several minutes. The hydrochloride was precipitated with ether and recrystallized from alcohol; yield, 0.7 g. Its m. p. depends greatly on the speed of heating.

[f] A suspension of 0.075 g. of palladous hydroxide–calcium carbonate catalyst (Pd content 1%), and 0.5 g. of 2-(3-(dimethylamino)-1-chloro-*n*-propyl)-phenanthrene hydrochloride in 10 cc. of alcohol was shaken in a hydrogen atmosphere. The hydrogen absorption was completed in two hours. The catalyst was filtered off, the alcohol was evaporated *in vacuo*, and the residue treated with ether and 10% potassium hydroxide. The brown oily base obtained from the ether layer was distilled in an oil pump vacuum, and converted into the hydrochloride: yield, 30–50%; mol. wt. of free base by micro Rast, calcd. 263; found, 278. In this reduction a white amorphous solid, insoluble in ether and water, was formed, probably according to the equation: $2C_{19}H_{20}NCl \longrightarrow C_{38}H_{40}N_2 + 2HCl$.

a homogeneous liquid which was kept at a gentle boil for nineteen hours. The reaction mixture was steam distilled.

On addition of saturated sodium chloride solution, the naphthoquinoline hydrochloride precipitated in the form of light brown needles. For further purification the base was liberated and taken up in ether. If necessary, a separation from unchanged aminophenanthrene can be effected through the difficultly soluble sulfate of the latter compound. The naphthoquinoline can be purified by high vacuum distillation or by crystallization, and is obtained in the form of long, flat, nearly colorless needles or pale yellow prisms; average yield, 45% of the amount calculated from the aminophenanthrene. The hydrochloride crystallizes in lemon-yellow felt-like needles.

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RECEIVED JUNE 1, 1936

An Improvement on the Quantitative Determination of Radioactivity

BY A. R. OLSON, W. F. LIBBY, F. A. LONG AND R. S. HALFORD

In an investigation of the mechanism by which acetylchloroaminobenzene rearranges into *p*-chloroacetanilide, which is to be published soon, Olson, Porter, Long and Halford used radioactive chloride ion in order to get one datum in addition to the usual kinetic data. It was necessary to determine the radioactivity of the chloride ion remaining in solution at various times as the reaction progressed. The methods which previously have been used for this purpose have utilized solid materials and because of this have had the following defects in common: (a) lack of reproducibility of the sample due to variations in particle size, crystal structure, thickness of the layer, etc., (b) the activity of the sample is at an optimum for a Geiger counter for a time approximately equal to the half-life of the active material.

By dissolving the solid material and introducing the solution into a counter of the type shown in Fig. 1, the errors mentioned in (a) can be eliminated. Then, if the original material is sufficiently radioactive, the time during which the counting can be done in the optimum range can be increased many-fold by utilizing a method of dilution of the original solution.

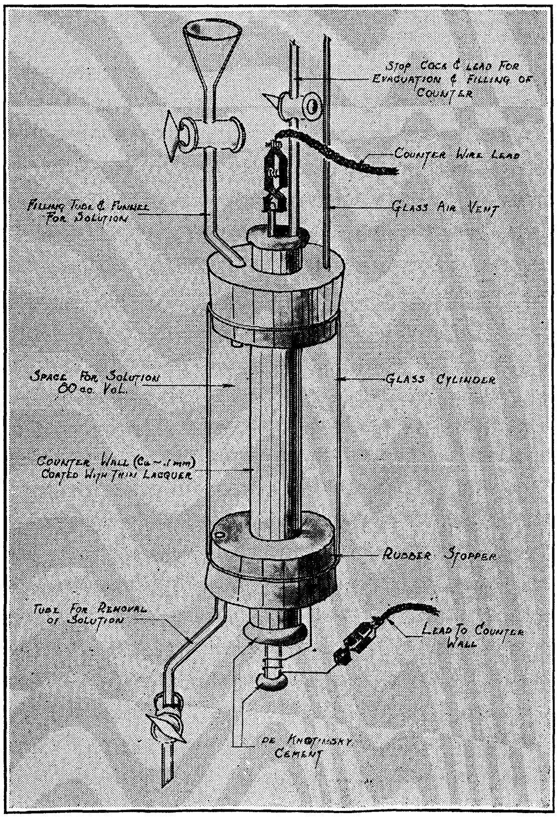

Fig. 1.—Counter assembly for dilution method.

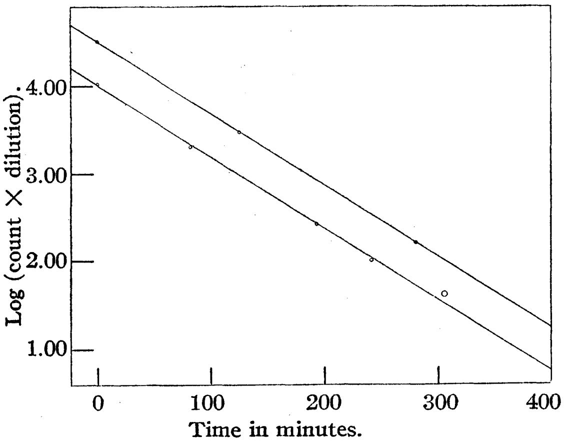

Fig. 2.—Logarithms of the last column of Table I plotted against the time of counting. The circles are these experimental results. The straight lines are calculated under the assumption that the half-life of radioactive chlorine is 37.0 minutes.

Thus in the investigation referred to above, the chloride ion was precipitated as silver chloride, washed and dried. Four-tenth gram of this was dissolved in 15 cc. of five molar ammonium hydroxide and made up to 150 cc. in a volumetric flask with distilled water. This original solution, however, was much too active to be accommodated by the counting apparatus and so 5 cc. of it was used to determine what dilution was necessary to give the optimum counting. The diluent was an ammoniacal solution of silver chloride that differed from the original solution only in that the silver chloride was non-radioactive. From this preliminary experiment and the half-life of radioactive chlorine, it was possible to calculate the most advantageous dilution for any subsequent time. With the strength of the sample of radioactive chlorine that was available to us, it was possible to remain in the optimum counting range for six hours even though the first count was not made until two hours after irradiation of the sample.

In Table I and Fig. 2 we show the data for typical determinations.

TABLE I

Results from two experiments. For both, the solutions were 0.0187 molar silver chloride and 0.5 molar ammonium hydroxide. Each count is the result of a ten minute period of counting.

Sample	Time, min.	Dil.	Net count per minute	Net count times the dil.
1a	0	200	158.8 ± 4.5	31760 ± 900
1b	125	20	147.2 ± 4.4	2944 ± 88
1c	280.5	2	81.2 ± 3.6	162.4 ± 7.2
2a	0	80	134.0 ± 4.0	10520 ± 320
2b	82	20	101.3 ± 3.7	2026 ± 74
2c	193	2	134.0 ± 4.0	268.0 ± 8
2	241	1	102.5 ± 3.7	102.5 ± 3.7
2	305.5	1	41.9 ± 2.8	41.9 ± 2.8

The use of this method for any material that can be brought into solution is obvious. It may be worthwhile to point out that the diluent should be chemically identical with the stock radioactive solution in order to eliminate any errors due to differential absorption.

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BERKELEY, CALIF.
RECEIVED MAY 18, 1936

5,7-Diiodo-8-hydroxyquinoline

BY VIKTOR PAPESCH AND ROBERT R. BURTNER

5,7-Diiodo-8-hydroxyquinoline, which is of therapeutic interest, has been prepared previously by the interaction of iodine and sodium iodide with 8-hydroxyquinoline in alkaline solution.[1] Although the yield is satisfactory, the procedure requires working in rather dilute solution, thus involving the use of large-scale equipment even for semi-commercial production. A different procedure was therefore developed which is distinctly more economical with respect to ease of manipulation and materials required.

A solution of 2105 g. (14.5 moles) of 8-hydroxyquinoline in 5800 cc. of 15% (by weight) hydrochloric acid is added in a slow stream with stirring at laboratory temperature to 4872 g. (30.0 moles) of iodine monochloride dissolved in 6000 cc. of 15% hydrochloric acid. Stirring is continued for four hours longer and the mixture then allowed to stand for twelve hours. The product is washed by decantation with 5% hydrochloric acid to remove excess iodine monochloride, followed by a washing with water and finally with a 2% solution of sodium hydrosulfite to reduce traces of free iodine. An additional amount of product may be recovered by combining the liquors of the first two washings and allowing them to stand for several days. The total yield of product melting at 198–200° is 4900–5300 g. or 83.5–92.5% of the theoretical, the purity of which is approximately 98.5% as determined by iodine analysis.

RESEARCH LABORATORY
G. D. SEARLE & CO.
CHICAGO, ILLINOIS
RECEIVED APRIL 23, 1936

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[1] British Patent 351,605.

On a Relation between the Dissociation Constants of Substituted Aliphatic Acids and the Distance between the Dissociating and the Substituted Groups

BY JESSE P. GREENSTEIN

A relationship between the dissociation of a substituted acid and the distance between the carboxyl and substituted groups was suggested by MacInnes[1] in 1928 in which pK_∞ represents the

$$pK = pK_\infty + S(1/d) \qquad (1)$$

value of the dissociation constant for an acid whose substituent is removed an infinite length along the chain, and d has the value 1 for an α-, 2 for a β- and 3 for a γ-substitution. This inverse linear relationship held for the hydroxy and the chloro substituted acids, and was extended by subsequent authors[2–4] to the variously substituted amino acids, diamines, dicarboxylic acids and amino acid esters.

In the endeavor to introduce physical quantities into equation (1), an interesting relation developed. If in place of d in the equation there is substituted the square of the distance, l^2, in Ångströms, from the center of the group dipole to the carboxyl center on the assumption of an extended chain, there is found for the substituted aliphatic acids an inverse linear relationship between pK and l^2.

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[1] MacInnes, THIS JOURNAL, **50**, 2587 (1928).
[2] Edsall and Blanchard, *ibid.*, **55**, 2337 (1933).
[3] Greenstein, *J. Biol. Chem.*, **96**, 499 (1932).
[4] Schmidt, Appleman and Kirk, *ibid.*, **81**, 723 (1929).

In applying this consideration to substituted aliphatic acids, we may assume tetrahedral symmetry for the carbon atoms, and the estimates of Pauling and Sherman[5] that the interatomic distance from the carboxyl carbon to the two oxygens is 1.29 Å. and the bond angle 124°. The linear component of the carboxyl group will be, therefore, 0.6 Å. In the case of the amino and hydroxyl substituents the mid-point of the dipole may be located in the center of the nitrogen and oxygen atoms, respectively. On the other hand, for the halogen substituents the dipole will lie somewhere along the halogen–carbon bond and we may for all purposes designate its center as midway along this bond. Using the value of the half tetrahedral angle and Pauling's single bond distances,[6] and expressing the straight line distance l from the dipole center to the carboxyl center in terms of Ångströms, there is found for the variously substituted molecules the following data for l^2:

TABLE I

Position	Substituted groups					
	OH l^2	NH_2 l^2	Cl l^2	Br l^2	I l^2	COOH l^2
α	9.18	9.36	6.66	6.97	7.34	13.84
β	18.40	18.66	14.75	15.21	15.76	24.80
γ	30.80	31.14	26.01	26.63	27.35	38.94
δ		46.79	40.45	41.22	42.12	56.25
ϵ		65.61				76.74
ζ						100.4
η						127.2
θ						157.8

Substitution of the above values in the formulation

$$pK = pK_\infty + S(1/l^2) \qquad (2)$$

leads to an excellent linear agreement between pK and $1/l^2$ (Fig. 1), where the values of pK have been derived from Cohn[7] and from Simms.[8]

Examination of the values in Table I suggests the linear integer relation of MacInnes, l^2 for a β-substitution appears to be about twice that for the α-substitution, for a γ-substitution l^2 is about three times that for the α-value, etc. Similar to MacInnes' findings, the lines for the chloro, bromo and iodo acids are identical. Furthermore, within the limits of accuracy of this type of calculation the pK_∞ values derived from either equation (1) or (2) are identical. For the dicarboxylic acids only the value for malonic acid, where both carboxyls are attached to the α-carbon falls widely off the curve and has been omitted from the graph. The inability to fit this acid into any relation involving its higher isomers has been discussed by Gane and Ingold.[9]

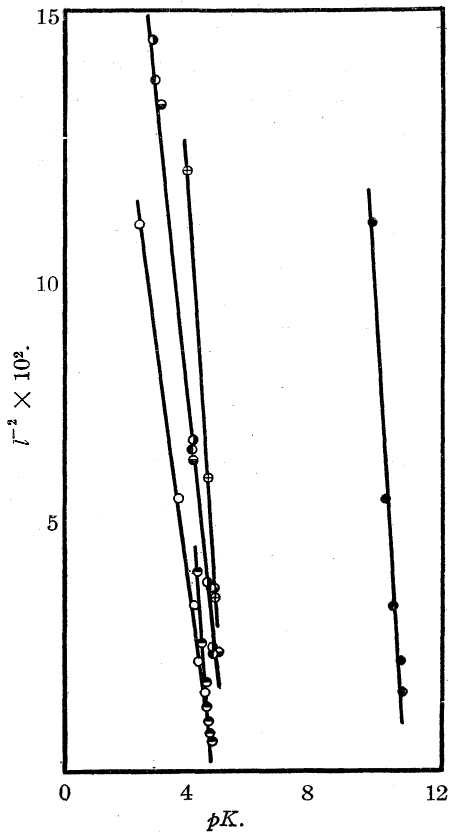

Fig. 1.—Amino acids, pK_1 ○, pK_2 ●; hydroxy acids, ⊕; chloro acids, ◑; bromo acids, ◐; iodo acids, ◒; dicarboxylic acids, ◓.

The constants in equation (2) for the variously substituted acids are gathered in Table II.[10]

TABLE II

Substituent	Ionizing group	pK_∞	$-S$
OH	COOH	5.2	0.085
COOH	COOH	4.7	.081
COOH	NH_2	10.9	.089
Halogens	COOH	5.1	.067
NH_2	COOH	4.8	.040

Equation (2) recalls the formulation of the field due to a dipole at a distance from its center large in comparison to the distance of separation of the two charges: $V = (\mu/d_0^2) \cos \theta$, where μ is the

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[5] Pauling and Sherman, *Proc. Nat. Acad. Sci.*, **20**, 340 (1934).

[6] Pauling, *ibid.*, **18**, 293 (1932).

[7] Cohn, *Ergebnisse Physiol.*, **33**, 781 (1931).

[8] Simms, THIS JOURNAL, **48**, 1251 (1926).

[9] Gane and Ingold, *J. Chem. Soc.*, 1594 (1928).

[10] If the interatomic zigzag distance in Ångströms through the chain from the center of the substituent to the center of one of the oxygens of the carboxyl group be considered, an analogous inverse square relation between dissociation constant and distance is revealed in all the cases discussed above. Only malonic acid again provides an exception.

electric moment and θ the angle between d_0 and the dipole axis. It would be difficult, in view of the changes in orientation of the dipole along the chain to derive at present any closer basis of relation other than analogy between the two formulations. It is interesting to note, however, that the value for the slope constant S in equation (2) is practically identical for the three halogen acids. The electric moments of the C–halogen bond for the three halogens are likewise very nearly equal. The relative magnitude of the slope constants, however, bears no obvious relation to that of the electric moments of the substituents.

DEPARTMENT OF PHYSICAL CHEMISTRY
HARVARD MEDICAL SCHOOL,
BOSTON, MASS.
RECEIVED MARCH 16, 1936

The Mechanism of the Diene Synthesis

BY EDWIN R. LITTMANN

The observation of Diels and Alder[1] that a yellow color appears during the synthesis of the colorless α-phellandrene-maleic anhydride suggests that the reaction mechanism involves a colored intermediate compound. Such a mechanism would imply a second order followed by a first order process, and in the absence of side reactions the observed reaction rate constants should approach those for a first order reaction as the concentration increases.

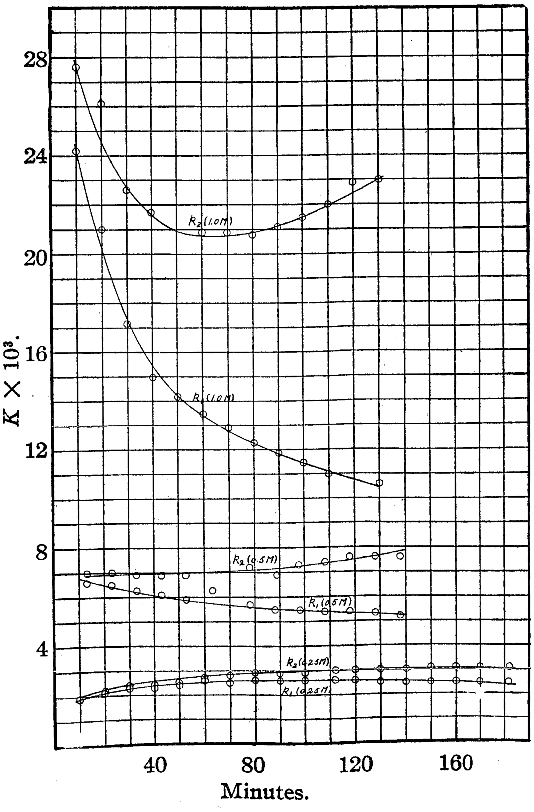

Fig. 1.—Reaction rate constants of α-phellandrene–maleic anhydride.

To test this matter measurements of the rate of reaction between α-phellandrene and maleic anhydride in acetone solutions have now been carried out at 0.25, 0.50 and 1.0 molality.

The α-phellandrene (Schimmel and Company) had the following properties: specific rotation (sodium light), −110.7°; refractive index (white light), 1.4775, and density, both at 20°, 0.856. The maleic anhydride (Eastman Kodak Company) was completely soluble in benzene and was used without further purification. The solutions, cooled to 25°, after thoroughly mixing were transferred to 2-dm. polarimeter tubes and observations of the rotation taken at definite intervals. The temperature of the polarimeter tube was maintained at 25 ± 0.5° by means of an air jet directed on the tube.

The results obtained are given in Fig. 1 in which the rate constants were calculated from the integrated forms of the standard rate equations. The values of the computed constants indicate that the reaction is more nearly unimolecular in the dilute than in the concentrated solutions and therefore it appears either that some other reaction mechanism is involved or that side reactions take place.

In order if possible to isolate the hypothetical polymer formed in the reaction, 6.8 g. of α-phellandrene and 4.9 g. of maleic anhydride were mixed without the use of any solvent and heated to 55–65° whereupon a violent reaction ensued which subsided in a few minutes. After standing for fifteen minutes the mixture was distilled at 3–5 mm. from an oil-bath at 250° until no more distillate was formed. The non-volatile residue was extracted repeatedly with ether, but only a small portion dissolved. The residual white powder when washed with methanol and dried gave, on analysis, 68.7% carbon and 7.27% hydrogen. Its molecular weight by the Rast method was found to be approximately 1220. These data agree with an empirical formula approximating either $C_{46}H_{56}O_{12}$ or $C_{60}H_{74}O_{15}$, giving 69.0 or 69.6% carbon, 7.00 or 7.17% hydrogen, and a molecular weight of 800 or 1034, respectively.

Since α-phellandrene and maleic anhydride were the only substances present, and since the

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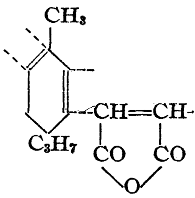
[1] Diels and Alder, *Ann.*, **460**, 98 (1927).

analysis precluded either terpene or maleic anhydride polymers, it seemed highly probable that a polymeric addition product had been obtained in which the average ratio of maleic anhydride to terpene was 4:3 or 5:4. Polymers of probable similar type have been reported by Wagner-Jauregg.[2]

The size of the polymeric α-phellandrene-maleic anhydride molecule and probable excess of anhydride over terpene would seem to exclude any but linear type polymers and would indicate a bifunctional character of the intermediate. An intermediate of the type



would satisfy the requirements of both polyfunctionality and color and would explain the formation of a polymeric material of the type $C_4H_2O_3$ $(C_{10}H_{16}-C_4H_2O_3-)$ $C_4H_2O_3$ in which there is an alternation of terpene and maleic anhydride molecules.

HERCULES POWDER CO.
WILMINGTON, DELAWARE
RECEIVED DECEMBER 10, 1935

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[2] Wagner-Jauregg, *Ber.*, **63**, 3213 (1930).

COMMUNICATION TO THE EDITOR

THE DECOMPOSITION OF GASEOUS PARAFFINS INDUCED BY ETHYLENE OXIDE

Sir:

Heckert and Mack [THIS JOURNAL, **51**, 2706 (1929)] obtained evidence that *n*-butane and *n*-pentane were "cracked" in presence of decomposing ethylene oxide at temperatures (—400°) at which the normal rate of decomposition of these paraffins is negligible. We have confirmed this observation in the case of *n*-butane, and have in addition shown that isobutane and propane, but not ethane, also undergo appreciable decomposition under like conditions.

Our method consisted in analyzing the gases, pumped from the reaction vessel, for carbon monoxide (acid Cu_2Cl_2) and for total olefins (bromine water). At a total pressure of about 500 mm. and a temperature of 425°, the following results were obtained.

It will be noted that the relative amount of olefin increases with the complexity of the paraffin; and also (in the case of *n*-butane at least) with the relative amount of paraffin initially present. Since the C_nH_{2n}/CO ratio can exceed unity, it is evident that reaction chains may be set off in the paraffin.

HC.	Initial ratio HC./C_2H_4O	Ratio C_nH_{2n}/CO by anal.
C_2H_6	1.6	<0.05
C_3H_8	1.6	.55
i-C_4H_{10}	1.7	.75
n-C_4H_{10}	1.6	1.2
n-C_4H_{10}	4.1	4.5
n-C_4H_{10}	8.0	12.

The rate of pressure increase falls off rapidly as reaction proceeds, which may indicate that the products of the paraffin decomposition are inhibiting reaction. A similar result is obtained in the uninduced decomposition of paraffins [*e. g.*, Pease and Durgan, *ibid.*, **52**, 1262 (1930)].

The effect of temperature on the C_nH_{2n}:CO ratio is not great.

The accelerated decomposition of acetaldehyde in presence of ethylene oxide noted by Fletcher [*ibid.*, **58**, 534 (1936)] has been confirmed.

This work is being continued.

PRINCETON UNIVERSITY
PRINCETON, N. J.
L. S. ECHOLS, JR.
R. N. PEASE

RECEIVED JUNE 24, 1936

NEW BOOKS

Grundlagen der Quantenmechanik. (Fundamentals of Quantum Mechanics.) By Dr. H. Dänzer, Assistant at the Physics Institute of the University of Frankfort A.M. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1935. xi + 163 pp. 11 figs. 15.5 × 22.5 cm. Price, RM. 12; bound, RM. 13.

The author aims to present compactly and logically the fundamental content of quantum-mechanical theory, in the forms which may now be regarded as standard. Emphasis is placed upon clear exposition of principles, rather than exhaustive rigor or completeness, so that the book may be useful to those whose specialties lie in other directions, but who require a working knowledge of the subject. The statistical interpretation of wave-mechanics is stressed, and frequent analogies from optics are adduced. The purpose of the book does not include applications to concrete problems, which are discussed only sparingly and by way of illustration.

In the reviewer's opinion, the author has succeeded in accomplishing his aim.

A. S. Coolidge

Molekülspektren und ihre Anwendung auf Chemische Probleme. II. Text. (Molecular Spectra and Their Application to Chemical Problems.) By H. Sponer. Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1936. xii + 506 pp. 87 figs. 14.5 × 22 cm. Price, RM. 36; bound, RM. 37.80.

The first volume of this work has already been reviewed in This Journal, **58**, 861 (1936). The present and final volume contains the theory of molecular spectra with many excursions into allied fields and also additional tables of molecular constants, bringing these up to date.

After a brief introduction into atomic spectra and the structure of atoms, the author takes up the theory of quantization of diatomic molecules, with many examples taken from analyzed spectra. Chapters on polyatomic molecules and on the determination from spectroscopic data of such chemically important molecular properties as internuclear distances, heats of dissociation, heat capacities, entropies, etc., follow. Some seventy pages are devoted to the problems of chemical binding and valence, the theories of the homopolar and the ionic bond being discussed in detail. The next chapter deals with different types of inelastic collisions, while the last sixty pages contain remarks on a variety of problems of interest to many chemists, such as photochemical processes, chemiluminescence, etc.

The discussion is carried on in a rather elementary manner and, considering the subject, very few equations will be found in the book. Results and conclusions of various theories are stated without attempts to derive them, but with extensive explanations and illustrations which are well chosen and give the reader some idea of the present status of the theoretical development in this field.

Perhaps if the subject matter were more restricted and instead more details were given occasionally, the book would have been even more useful. It can be recommended, however, as a reference source and should thus find extended use in conjunction with the first volume containing numerical data.

G. B. Kistiakowsky

Über katalytische Verursachung im biologischen Geschehen. (On Catalytic Causation in Biological Processes.) By Alwin Mittasch. Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1935. x + 126 pp. 14.5 × 22 cm. Price, RM. 5.70.

This small book represents the reflections of a distinguished chemist, long deeply concerned with catalysis and its industrial applications, on catalytic phenomena in biology. After a brief but penetrating discussion of catalysts in general and of enzymes, the author turns his attention to hormones, vitamines, genes and other constituents of the living organism, and inquires how far their basis of operation may also be catalytic. Finally there is an extensive discussion of the possible relation of such processes to the higher integration of the living organism.

The book bears witness, not only to the author's deep knowledge of his own field, but to a wide acquaintance with many aspects of current philosophical thought. Many of the problems raised lie far beyond the present scope of experimental science, but others have much more immediate application. In the author's words, the book is "a question to the biologist"; it avoids dogmatic pronouncements, and its aim is to stimulate inquiry into regions still unexplored.

John T. Edsall

Collected Scientific Papers of Sir William Bate Hardy. Published under the Auspices of the Colloid Committee of the Faraday Society. Cambridge University Press, The Macmillan Company, 60 Fifth Avenue, New York, N. Y., 1936. 922 pp. 18 × 26 cm. Price, $18.00.

This collection is of value for at least two reasons; it makes readily available the many scattered contributions of an unusually stimulating and suggestive investigator; also, by virtue of the chronological arrangement that has been adopted, it discloses the genetic relationships among Hardy's researches and the progressive development of his ideas.

Hardy's initial researches were concerned chiefly with problems of morphology, particularly the morphology of blood corpuscles and other wandering cells in both vertebrate and invertebrate organisms. These researches led him naturally, at about the beginning of the present century, to the study of colloidal solutions and colloidal phenomena in general, and it was in this field that the largest number and perhaps the most important of his investigations were conducted. Although some of these dealt with such inanimate phenomena as adhesion and lubrication, most of them were fundamentally concerned with the physical and chemical processes taking place in the living cell.

Interspersed among the accounts of his experimental investigations and his theoretical speculations are a number of noteworthy summaries and recapitulations, some of them constituting important occasional lectures, namely, the Croonian, the Guthrie and the Bakerian Lectures.

The collection as a whole and these special lectures in particular afford a veritable mine of information, entertainment and stimulation.

ARTHUR B. LAMB

Poggendorffs biographisch-literarisches Handwörterbuch für Mathematik, Astronomie, Physik mit Geophysik, **Chemie,** Kristallographie und verwandte Wissensgebiete. **(Poggendorff's Biographical and Bibliographic Encyclopedia** for Mathematics, Astronomy, Physics, Geophysics, **Chemistry,** Crystallography and Related Sciences.) Vol. VI, 1923–1931, Part I. A–E. Edited by Dr. HANS STOBBE. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany, 1936. lxxii + 696 pp. 16 × 25.5 cm. Price, RM. 63.75.

This is the first part of the sixth Volume of this very useful and unique Encyclopedia. The first Volume appeared in 1863 and the following Volumes, II to V, contain the scientific biographies of workers in the field of the exact sciences throughout the whole world during the intervening period.

Volume VI when completed will cover the year 1923 to 1931 and will give biographical data for some eight thousand scientists, together with information as to the books, pamphlets and articles which they have published. The second part is already in print and will be published during the current year; Parts III and IV are to be published in the summer of 1937 and the spring of 1938, respectively.

This Encyclopedia is not only of great current utility but it will also be of permanent value as well, and the scientific community certainly owes a debt of gratitude to the several German Academies of Science who are sponsoring its publication. However, it is unfortunate that in this as in similar monumental bibliographic undertakings, more prompt publication cannot be attained. A delay of five years, such as obtains in this instalment, detracts perceptibly from its current usefulness.

ARTHUR B. LAMB

Annual Tables of Constants (A.T.C.) and Numerical Data, Chemical, Physical, Biological and Technological. Published under the Patronage of the International Union of Chemistry. Volume X (1930), Part II. McGraw-Hill Book Co., Inc., 330 West 42d St., New York, N. Y., 1936. Two parts, about 1800 pages. Price (for subscribers), cloth, $20.00.

This instalment completes Volume X and with it the Second Series of the Tables, except for the Index to Volumes VI–X, inclusive, which is soon to appear.

As the years elapse since the appearance of the International Critical Tables, the continued publication of these Annual Tables becomes even more essential. It is devoutly to be hoped that the gallant efforts of Dr. Marie and the Editors of the Annual Tables receive that international support which is absolutely necessary for their existence.

It should be pointed out that all the texts in the Tables are given in both English and French; also that the full Tables of Contents in each Volume make it easy to locate the information desired.

ARTHUR B. LAMB

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth edition. System-Number 55, **Uranium and its Isotopes, with an Appendix on Transurania.** Issued by the Deutsche Chemische Gesellschaft. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany, 1936. 278 pp. 17 × 25 cm. Price, RM. 34.50.

The publication of this instalment of the Gmelin Handbook is opportune particularly in view of the current interest in the radioactive phenomena connected with uranium; for instance, the new radioactive elements recently discovered by Fermi during the bombardment of uranyl salts with neutrons. Although the nature of these truly synthetic elements is still somewhat obscure, it is certain that they are intimately related to uranium, the element of highest atomic number and atomic weight known to occur in Nature. For this reason it is appropriate that the information relative to these elements should be presented in an Appendix to this volume under the caption "Transurania." It is also appropriate and a striking coincidence that this name should be so similar to that assigned to the planet Neptune after its existence had been deduced but before it had actually been discovered.

The literature on uranium has been covered to the end of 1935 and with this instalment the volume on molybdenum, tungsten and uranium is now completed.

ARTHUR B. LAMB

Mikroskopische Methoden in der Mikrochemie. (Microscopic Methods in Microchemistry.) By Prof. Dr. LUDWIG KOFLER and Dr. ADELHEID KOFLER, with the collaboration of Prof. Dr. ADOLF MAYRHOFER. Emil Haim and Co., Maria-Theresien-Strasse 10, Vienna I, Austria, 1936. vi + 134 pp. 21 figs. + 12 plates. 17.5 × 25 cm. Price, RM. 9; bound, RM. 10.80.

One of a series of monographs in the general field of microchemistry by Austrian writers, this book is intended to acquaint chemists with the extraordinary advantages of applying the microscope to everyday work. It is illustrated by examples of the isolation and identification of a number of organic compounds of pharmacological interest. The first two sections, by L. K., describe the use of a hot stage microscope in the determination of melting points, and in the purification by sublimation, of small amounts of material. The third section, by A. K., deals with the more formidable technique of the measurement of optical constants of crystals by the immersion method; it is addressed to readers without special training in crystallography. The concluding brief section by A. M. treats liquids used with the immersion method.

The subject with which this book is concerned deserves consideration by the generality of chemists such as it has not heretofore received here or abroad. In the examination of any sort of transparent solid material the microscope should be as a matter of practice the first, not the last, resort of the chemist. The limitations of the methods are discussed by the present writers; in section 3 they are overstressed. In the same section reference to some useful American work is absent. An obvious error occurs in the description of potassium nitrate on p. 114.

C. D. WEST

BOOKS RECEIVED

May 15, 1936–June 15, 1936

A. BÖMER, A. JUCKENACK AND J. TILLMANS, Editors. "Handbuch der Lebensmittelchemie. Vol. III. Tierische Lebensmittel." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 1049 pp. RM. 129; bound, RM. 132.60.

H. J. BUNKER. "A Review of the Physiology and Biochemistry of the Sulphur Bacteria." Chemistry Research, Special Report No. 3. H. M. Stationery Office, Adastral House, Kingsway, London W. C. 2, England. 48 pp. 9d., net.

ROBIN CHARLES BURRELL. "Organic Chemistry." McGraw-Hill Book Company, Inc., 330 West 42d St., New York, N. Y. 331 pp. $2.75.

K. R. BUTLIN. "The Biochemical Activities of the Acetic Acid Bacteria." Chemistry Research Special Report No. 2. H. M. Stationery Office, Adastral House, Kingsway, London W. C. 2, England. 47 pp. 1s./0d., net.

N. I. CHERNOSCHOUKOV, Editor. "Transactions of the First All-Union Scientific-Technological Conference on Production and Use of Lubricating Oils." (In Russian.) Central Publishing Office for Petroleum Literature, ONTI, NKTL, Leningrad, U. S. S. R. 576 pp.

CARL J. ENGELDER. "Elementary Quantitative Analysis." Second edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 270 pp. $2.75.

E. CH. FRITZMAN. "Nature of Water. Heavy Water." (In Russian.) ONTI—Chimtheoret, Leningrad, U. S. S. R. 314 pp.

GERHARD HERZBERG. "Atomspektren und Atomstruktur. Eine Einführung für Chemiker, Physiker und Physikochemiker." Verlag von Theodor Steinkopff, Residenzstrasse, 32, Dresden-Blasewitz, Germany. 188 pp. RM. 13; bound, RM. 14.

K. IMHOFF. "Taschenbuch der Stadtentwässerung." Seventh edition. Verlag von R. Oldenbourg, Schliessfach 31, München, 1 Germany, 195 pp. RM. 5.40.

ALEXANDER LOWY AND BENJAMIN HARROW. "An Introduction to Organic Chemistry." Fourth edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 429 pp. $3.00.

M. C. NEUBERGER. "Die Allotropie der chemischen Elemente und die Ergebnisse der Röntgenographie." Verlag von Ferdinand Enke, Hasenbergsteige 3, Stuttgart W, Germany. 106 pp. RM. 9.30.

CARL OPPENHEIMER. "Die Fermente und ihre Wirkungen." Supplement. Lieferung 4 (Band I: Specieller Teil: Haupt-Teil IX–XII). W. Jung Verlag, Den Haag, Holland. 160 pp. $6.80.

WILLIAM F. PETERSEN AND MARGARET E. MILLIKEN. "The Patient and the Weather. Vol. I, Part 2. Autonomic Integration." Lithoprinted by Edwards Brothers, Inc., Ann Arbor, Mich. 781 pp. $9.00.

E. JOHN RUSSELL. "Boden und Pflanze." Second edition, edited by K. W. Müller. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 446 pp. RM. 30; bound, RM. 32.

T. J. WEBB. "Elementary Principles in Physical Chemistry." D. Appleton-Century Company, Inc., 35 West 32d St., New York, N. Y. 344 pp. $4.00.

"The New Hilger Wave Length Spectrometer for Visible, Ultra-violet and Infra-red." Adam Hilger, Ltd., 98 Kings Road, Camden Road, London N. W. 1, England. 54 pp.

"Official Directory of the British Chemical Plant Manufacturers' Association." 1936. Distributed by the Association, 166 Piccadilly, London W 1, England. 140 pp.

JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 58 AUGUST 5, 1936 NUMBER 8

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

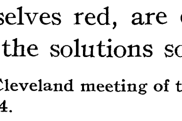
1,2-Diketo-3-phenylhydrindene[1]

BY C. FREDERICK KOELSCH

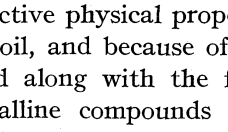
Few α-diketones derived from hydrindene have been studied and some phenomena observed in connection with these compounds have been incorrectly interpreted. These α-diketones may be conveniently divided into three classes corresponding to the number of activated hydrogen atoms they contain: class A having none, B one and C two.

Representatives of class C have been prepared by Perkin and co-workers.[2] No compounds of class A have been described. Since representatives of these two classes do not enolize and since enolization is the main topic investigated in the present research, a discussion of these types will be deferred for later papers.

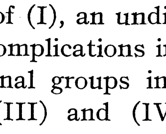
In class B, the compounds represented in the accompanying formulas (I, II, III, IV) have been investigated by v. Braun and co-workers.[3] These substances, themselves red, are easily soluble in aqueous alkalies, the solutions so obtained being deep blue or green. Now 1,3-diketo-2-methylhydrindene, a colorless substance, dissolves in aqueous alkalies to give a deep red solution, and this solution has been shown by Hantzsch[4] to contain a salt of the formula (V). Primarily on the basis of this difference in color between (V) and the enolates of his diketones[5] v. Braun postulated the formula (VI) for the latter.



I, R = CH_3, X = H
II, R = CH_3, X = NO_2
III, R = CH_3, X = $NHCOC_6H_5$
IV, R = CH_2COOH, X = H



V



VI

Since the *o*-quinoid structure is generally unstable,[6] it was decided to investigate this enolate formula more thoroughly. Because of the unattractive physical properties of (I), an undistillable oil, and because of the complications introduced along with the functional groups in the crystalline compounds (II), (III) and (IV), a search was made, ending with 1,2-diketo-3-phenylhydrindene (VII), for a compound not possessing these disadvantages.[7]

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[1] Presented at the Cleveland meeting of the American Chemical Society, September, 1934.

[2] Perkin, Roberts and Robinson, *J. Chem. Soc.*, **101**, 232 (1912); *ibid.*, **105**, 2405 (1914).

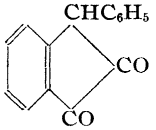
[3] V. Braun and Kirschbaum, *Ber.*, **46**, 304 (1913); v. Braun and Heider, *ibid.*, **49**, 1268 (1916); v. Braun and Fischer, *ibid.*, **64**, 1790 (1931).

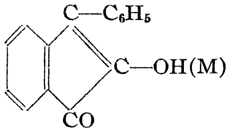
[4] Hantzsch, *Ann.*, **392**, 286 (1912).

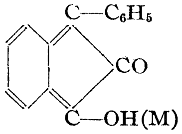
[5] Secondary considerations were the observation that (I) reacted with neither bromine nor ferric chloride. These observations are probably erroneous, the physical character of (I) making visual determination of reaction difficult.

[6] Especially unstable is the *o*-quinomethylene grouping, represented with certainty only by 3,4-benzofuran; *cf.* Koelsch, THIS JOURNAL, **58**, 1331 (1936).

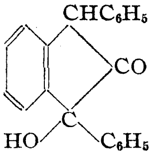
[7] After the present work had been completed, the preparation of diketophenylhydrindene by a different method was carried out by Pfeiffer and de Waal [*Ann.*, **520**, 185 (1935)]. Since a different aspect of the chemistry of the diketone was studied by these investigators, little duplication has taken place. Descriptions of the few similar compounds involved in the two researches check closely.

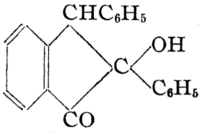

VII


VIII


IX

This substance in the crystalline state closely resembles potassium permanganate; like (I) its solutions in organic solvents are red, those in aqueous alkalies deep blue. However, it enolizes to give (VIII) and not (IX). This is clearly shown by the following evidence: the diketone in carbon tetrachloride combines instantly with the calculated amount of bromine; it is mono-phenylated by phenylmagnesium bromide, and the product of this reaction must be (X) and not (XI) since it yields *o*-dibenzoylbenzene on oxidation. To be noted also is the fact that the blue enolate gives a red O-methyl derivative with dimethyl sulfate.[8]

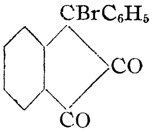

X

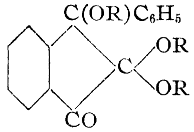

XI

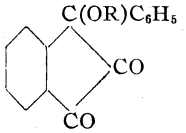
The diketone apparently exists completely in the enolic form: on quantitative treatment with methylmagnesium iodide it reacts with two equivalents of the reagent, liberating one equivalent of gas; and furthermore, as stated above, it combines instantly with the calculated amount of bromine. Also the color of the substance, solid or in solution, indicates that its chromophore is not the α-diketone group (orange) but is the indone nucleus (red). Although the compound gives no color reaction with ferric chloride, this is not evidence against its enolic nature, since it is oxidized immediately by this reagent.

Comparison of 1,2-diketo-3-phenylhydrindene, more properly 2-hydroxy-3-phenylindone, with its β-diketonic isomer and of these with their open chained analogs (Table I) indicates that in the cases of both α and β-diketones of class B, a greater tendency toward enolization is found in the cyclic compounds. That the reverse is true for diketones of class C will be shown in a later paper.

Certain derivatives of 1,2-diketo-3-phenylhydrindene obtained through the replacement of the enolizable hydrogen indicate a considerable reactivity of one of the carbonyl groups. The bromo compound (XII) reacts readily with alcohols giving colorless ether–acetals of the probable structures (XIII).


XII


XIII


XIV

By appropriate treatment, these compounds can be converted into the alkoxy diketones (XIV), whose colors are strikingly different from those of open chain diketones and also from that of the enol (VIII).

Experimental

2-Isonitroso-3-phenylhydrindone.—To a solution of 75 g. of 3-phenylhydrindone in 450 ml. of 95% alcohol is added 75 ml. of butyl nitrite and 10 ml. of concd. hydrochloric acid. The mixture is warmed to 55° for one hour, and after twelve hours at room temperature, the isonitroso compound is removed. The product so obtained (55 g.) is quite pure; crystallization from ethyl acetate–petroleum ether yields faintly yellow prisms that melt at 198–203° with decomposition. The compound gives a yellow-orange solution in aqueous sodium hydroxide.

Anal. Calcd. for $C_{15}H_{11}O_2N$: C, 76.0; H, 4.64. Found: C, 75.8; H, 4.73.

In alkaline solution with methyl sulfate the above oxime yields its methyl ether, which forms pale tan plates that melt at 148–149° after crystallization from alcohol.

Anal. Calcd. for $C_{16}H_{13}O_2N$: C, 76.4; H, 5.18. Found: C, 76.4; H, 5.26.

1,2-Diketo-3-phenylhydrindene (VII).—The maximum yield of the diketone if its monoxime is hydrolyzed in the presence of the usual formaldehyde is 20%, and the product so obtained is difficult to purify. (Optimum conditions developed from many experiments: a mixture of 1 g. of oxime, 10 ml. of 40% formaldehyde, 5 ml. of acetic acid, 5 ml. of water, and 1 ml. of concd. hydrochloric acid is heated at 80–85° for ten minutes.)

The use of pyruvic acid as a hydroxylamine acceptor[9] is very advantageous. A mixture of 50 g. of the oxime, 50 ml. of pyruvic acid, 300 ml. of water, 300 ml. of acetic acid and 50 ml. of concd. hydrochloric acid is boiled for thirty minutes. On standing the solution deposits 29 g. of diketone, and an additional 2.5 g. may be obtained from the mother liquors. In larger runs one-half the proportional amount of pyruvic acid may be used with only a slight reduction in yield. Crystallized from benzene–petroleum

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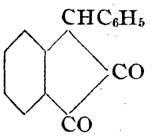
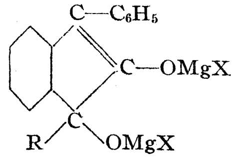
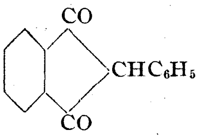
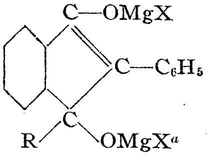
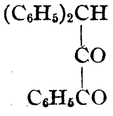
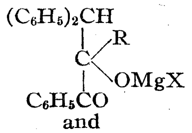
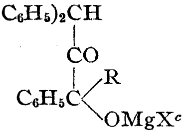
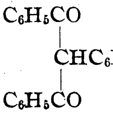
[8] It is also of interest in this connection that the red 2-*p*-hydroxyphenyl-3-phenylindone forms a deep purple sodium salt. Postulation of *o*-quinoidation in this case necessitates the assumption of a considerable, and therefore improbable, shifting of the aromatic double bonds.

[9] Suggested by Dr. P. D. Bartlett.

TABLE I

Compound	Action with Br$_2$	FeCl$_3$	NaOH aq.	Grignard prod.	Color (solid)	Structure
	Reacts rapidly	Oxidized	Stable salt formed		Red-violet	Enolic
	Reacts slowly	No color	Stable salt		White	Ketonic; some enol in polar solvents[b]
 $(C_6H_5)_2CH\text{—}CO\text{—}C_6H_5CO$	Reacts[c]	Transient color; oxidized[c]	Unstable salt formed; benzilic rearrangement[c]	 $(C_6H_5)_2CH\text{—}C(R)(OMgX)\text{—}C_6H_5CO$ and  $(C_6H_5)_2CH\text{—}CO\text{—}C_6H_5C(R)(OMgX)$[c]	Yellow[c]	16% enol in CH_3OH[c]
 $C_6H_5CO\text{—}CHC_6H_5\text{—}C_6H_5CO$	Reacts (?)[d]	No color (?) forms no Cu derivative[e]	Unstable salt formed; cleavage[c]	Cleavage or addition:[e] no gas with CH_3MgI[f]	Colorless[d] yellow[g]	Ketonic[e]

[a] Unpublished data. Compare ref. 7. [b] Ref. 5. [c] Kohler and Weiner, THIS JOURNAL, **56**, 434 (1934); corrected in accordance with a private communication from Professor Kohler. [d] Marshall, *J. Chem. Soc.*, **107**, 520 (1915). [e] Kohler and Erickson, THIS JOURNAL, **53**, 2301 (1931). [f] Kohler, Stone and Fuson, *ibid.*, **49**, 3181 (1927). [g] De Neufville and v. Pechmann, *Ber.*, **23**, 3377 (1890).

ether, the diketone forms violet black needles; from dilute acetic acid, red violet plates. Both forms melt at 140–147°. The diketone decomposes and liquefies on standing in air; the decomposition is complete after about three months.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.0; H, 4.51. Found: C, 81.0; H, 4.58.

Solutions of the compound in organic solvents, polar or non-polar, are dark red. It is readily soluble in cold aqueous sodium hydroxide or in warm carbonate, giving deep blue solutions from which the diketone is precipitated by acids. The solutions in alkali lose their color on long (*ca.* ten minutes) boiling, acidification then giving a small amount of diphenylmethane-*o*,α-dicarboxylic acid together with unworkable oils.

Oxidation.—To a solution of 0.5 g. of the diketone in 10 ml. of 0.5 *N* sodium hydroxide is added 5 ml. of 3% hydrogen peroxide. After the mixture has become colorless (two minutes) it is acidified. The product, diphenylmethane-*o*,α-dicarboxylic acid, forms fine white needles from ethyl acetate–benzene that melt at 171–172° with gas evolution.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.3; H, 4.7. Found: C, 70.1; H, 4.8.

Quinoxaline Formation.—The diketone is condensed with *o*-phenylenediamine in alcohol in the usual way. The product forms colorless needles that melt to a blue liquid at 169–172°.

Anal. Calcd. for $C_{21}H_{14}N_2$: C, 85.6; H, 4.76. Found: C, 85.3; H, 4.82.

Reaction with Ferric Chloride.—The color of an alcoholic solution of the diketone (0.5 g.) rapidly fades when ferric chloride (0.8 g. of $FeCl_3 + 6H_2O$) in alcohol is added. The orange-pink crystalline precipitate (0.45 g.) contains only a trace of iron, and is insoluble in all solvents other than hot nitrobenzene, by which it is altered. It darkens at 180° and melts at 200–205° with gas evolution.

Anal. Calcd. for $C_{30}H_{18}O_4$: C, 81.4; H, 4.1. Found: C, 80.9; H, 4.36.

Bromination.—The diketone (5 g.) in chloroform (30 ml.) is treated with 3.75 g. of bromine in carbon tetrachloride. The halogen is absorbed immediately and hydrogen bromide is given off. The solvents are removed under reduced pressure, and the residue is crystallized from ether–petroleum ether. There is obtained 4.9 g. of 1,2-diketo-3-bromo-3-phenylhydrindone (XII) which forms orange-brown prisms that melt at 77–79°.

Anal. Calcd. for $C_{15}H_9O_2Br$: C, 59.9; H, 3.0. Found: C, 60.1; H, 3.0.

Methylation.—A solution of 28 g. of the diketone in 150 ml. of *N* sodium hydroxide is treated with 15 ml. of methyl sulfate, and the mixture is stirred vigorously for thirty minutes. The solid is filtered and crystallized from methanol, when it is obtained in the form of red prisms and needles (18 g.) that melt at 67–68°. Although it can be distilled without decomposition at 20 mm., the 2-methoxy-

3-phenylindone rapidly (three days) decomposes on standing in air, giving off an odor of formaldehyde and leaving a red resin.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.2; H, 5.1. Found: C, 80.6; H, 5.1.

The oxime of the methyl ether, obtained with hydroxylamine hydrochloride and sodium acetate in alcohol, forms orange prisms that melt to a red liquid at 184–186° and are stable in air.

Anal. Calcd. for $C_{16}H_{13}O_2N$: C, 76.4; H, 5.2. Found: C, 76.0; H, 5.2.

With phenylmagnesium bromide, the methyl ether gives a colorless carbinol which could not be obtained crystalline and could not be converted into a solid methyl ether, but whose solution in acetic acid is colored red-violet by a trace of sulfuric acid.

2-Methoxy-3-phenylindone (15 g.) is reduced when its solution in acetic acid (150 ml.) is treated with zinc dust (15 g.). The solution becomes warm and its color rapidly disappears. The product, 2-methoxy-3-phenylhydrindone, is precipitated by water, distilled at 20 mm. and crystallized from methanol, when it forms colorless prisms that melt at 96–98°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9. Found: C, 80.7; H, 6.0.

Reaction with Grignard Reagents.—Quantitative examination of its behavior in the Grignard machine[10] shows that 1,2-diketo-3-phenylhydrindene reacts with two equivalents of methylmagnesium iodide, liberating one equivalent of gas.

With an excess of phenylmagnesium bromide, the diketone yields 1,3-diphenyl-1-hydroxy-2-ketohydrindene (X), which from ethanol forms white plates that melt at 195–200° with decomposition.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.9; H, 5.3. Found: C, 83.1; H, 5.3.

Oxidized with chromic acid in acetic acid, this hydroxy ketone yields *o*-dibenzoylbenzene (mixed m. p.) nearly quantitatively.

Reduced with hydriodic acid in acetic acid, the hydroxy ketone is converted into 1,3-diphenyl-2-ketohydrindene, which, from acetic acid, forms white needles that melt with decomposition at 169°.

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.6; H, 5.6. Found: C, 88.0; H, 5.7.

With benzylmagnesium chloride, diketophenylhydrindene yields 1-benzyl-1-hydroxy-2-keto-3-phenylhydrindene, white needles that melt at 155–157°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.1; H, 5.7. Found: C, 84.1; H, 6.1.

Reactions of the Bromo Compound (XII) with Alcohols.—A solution of the crude bromo compound from 5 g. of diketophenylhydrindene in methanol is distilled to a small volume, the methanol is replaced, and the resulting solution is cooled. There is deposited 5 g. of 2,2,3-trimethoxy-3-phenylhydrindone (XIII, R = CH_3), which forms colorless prisms that melt at 102–103°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.4; H, 6.0. Found: C, 71.9; H, 6.0.

The trimethoxy compound does not react with *o*-phenylenediamine in alcohol even on warming, but the addition of a trace of hydrochloric acid to the mixture causes the immediate precipitation of the quinoxaline of 1,2-diketo-3-methoxy-3-phenylhydrindene.

Anal. Calcd. for $C_{22}H_{16}ON_2$: C, 81.4; H, 4.94; OCH_3, 9.6. Found: C, 81.3; H, 4.96; OCH_3, 9.3.

The trimethoxy compound (0.5 g.) forms a faintly pink solution in acetic acid (8 ml.) which becomes deep crimson on the addition of a drop of sulfuric acid. Dilution with water causes the separation of a crystalline precipitate which can be separated by extraction with cold benzene into a soluble orange compound and a colorless insoluble substance. The orange compound melts at 86–87° and is the methoxy diketone (XIV, R = CH_3).

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8. Found: C, 76.3; H, 4.8.

The colorless substance is a hydrate of the methoxy diketone, since at its melting point (115–120°, gas evolution) it is converted into the latter.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.2; H, 5.2. Found: C, 71.2; H, 5.3.

With ethanol, the bromo compound (XII) yields 2,2,3-tri-ethoxy-3-phenylhydrindone (XIII, R = C_2H_5), which forms white plates that melt at 89–90°. This compound is much more easily soluble than its trimethoxy analog, and its quantitative isolation is more difficult.

Anal. Calcd. for $C_{21}H_{24}O_4$: C, 74.0; H, 7.06. Found: C, 74.0; H, 7.09.

Treatment of the triethoxy compound with acetic acid–sulfuric acid converts it into the ethoxy diketone (XIV, R = C_2H_5), which from benzene forms cerise plates that melt at 102–103°. No benzene insoluble substance (hydrate) is formed.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.6; H, 5.26. Found: C, 76.4; H, 5.28.

Summary

It is shown that 1,2-diketo-3-phenylhydrindene exists in the enolic form, and that this enolization does not involve *o*-quinoidation. When enolization is prevented by the replacement of the enolizable hydrogen by alkoxyl, one of the diketonic carbonyl groups becomes active enough to form an acetal.

MINNEAPOLIS, MINN. RECEIVED MAY 19, 1936

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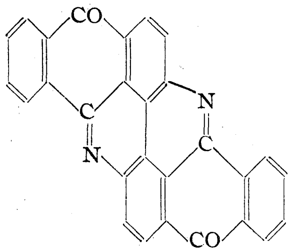
[10] Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

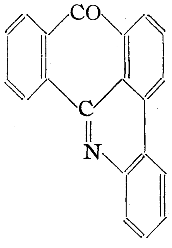
Benzo-semiflavanthrene. I. Reduction

BY C. FREDERICK KOELSCH

The researches of Scholl and his collaborators[1] have cleared up to a large extent the constitutions of the vat dye flavanthrene (I) and of its reduction products. The chemistry of these substances is, however, quite involved. For example Scholl has obtained from flavanthrene nine different reduction products, of which six exist in two forms: one form non-hydrated, the other containing a molecule of water "in a very firm atomically bound condition."



I

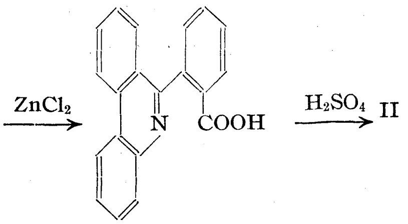


II

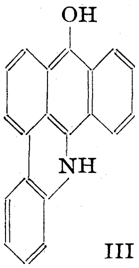
Doubtless still more can be learned about this type of quinone imine by a study of related substances whose structures are less complex. To this end, the substance (II) has been prepared; the name benzo-semiflavanthrene is proposed for this compound to indicate its relation to flavanthrene. Incidentally, benzo-semiflavanthrene appears to hold little promise as a dye, since the color it imparts to fabrics is a very pale yellow.

The preparation of benzo-semiflavanthrene, illustrated by the accompanying formulas, is easily carried out. Each reaction gives a single product in a good yield.

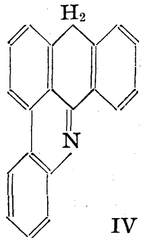
$$o\text{-}C_6H_5C_6H_4NH_2 + C_6H_4(CO)_2O \longrightarrow o\text{-}C_6H_5C_6H_4N(CO)_2C_6H_4$$



Two reduction products have been obtained from benzo-semiflavanthrene: the dihydro compound (III), and a desoxy compound, probably (IV).



III



IV

The reduction product (III), a violet-black substance, separates directly in a crystalline condition when benzo-semiflavanthrene is boiled with alkaline hydrosulfite. It is only weakly acidic and is little soluble in aqueous sodium hydroxide. In such a solution, or dissolved in organic solvents, it is readily oxidized to benzo-semiflavanthrene by air; however, it is quite stable in the solid state. It cannot be acylated, for when it is boiled with acetic anhydride or treated with benzoyl chloride in pyridine, or even when it is boiled with aqueous hydrochloric acid it undergoes disproportionation to benzo-semiflavanthrene and the desoxy compound (IV).

This desoxy compound, a deep red-brown substance, is most readily obtained by the acid reduction of benzo-semiflavanthrene. It, too, is sensitive to air even when dissolved in dilute aqueous hydrochloric acid. Nitrous acid also reconverts it into benzo-semiflavanthrene.

None of the reduction products so far isolated has shown any tendency to form a stable hydrate.

The investigation is being continued.

Experimental

***o*-Xenylphthalimide.**—A mixture of 100 g. of *o*-aminobiphenyl with 88 g. of phthalic anhydride is heated at 200° for ten minutes. The product (175 g.), crystallized from acetic acid, forms colorless prisms that melt at 165–166°.

Anal. Calcd. for $C_{20}H_{15}O_2N$: C, 80.3; H, 4.35. Found: C, 80.3; H, 4.41.

***o*-(9-Phenanthridyl)-benzoic Acid.**—An intimate mixture of 175 g. of *o*-xenylphthalimide with 350 g. of zinc chloride is heated rapidly to 275° and kept at this temperature for one minute; no reaction takes place at lower temperatures and longer heating results in considerable decomposition. The melt is stirred into much water, and the insoluble product is purified by dissolving in 5% aqueous soda and treatment with charcoal. The acid is precipitated by dilute hydrochloric acid as a fine powder which is pure enough for most purposes; yield, 135 g. Recrystal-

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(1) Scholl and Mansfield, *Ber.*, **43**, 1734 (1910), and previous papers.

lized from ethyl acetate, in which it is very difficultly soluble, it forms colorless prisms that melt at 268–270° with decomposition.

Anal. Calcd. for $C_{20}H_{13}O_2N$: C, 80.3; H, 4.35. Found: C, 80.3; H, 4.38.

The methyl ester obtained from the acid with methanol and sulfuric acid forms prisms from benzene that melt at 150–151°.

Anal. Calcd. for $C_{21}H_{15}O_2N$: C, 80.5; H, 4.8. Found: C, 80.0; H, 4.77.

Distilled with copper acetate (1 g.) *o*-(9-phenanthridyl)-benzoic acid (5 g.) gives 9-phenylphenanthridene (3.5 g.) which melts at 104–106° alone or mixed with a sample of the substance prepared according to the method of Pictet and Hubert.[2]

Benzo-semiflavanthrene.—Ninety grams of *o*-(9-phenanthridyl)-benzoic acid is stirred into 450 ml. of concd. sulfuric acid and the solution is heated for two hours at 160°. The product is isolated by pouring into water. After drying and crystallizing from xylene there is obtained 45 g. of pure benzo-semiflavanthrene which melts at 221–223°.

Anal. Calcd. for $C_{20}H_{11}ON$: C, 85.4; H, 3.96. Found: C, 85.3; H, 3.96.

The Reduction Product (III).—A suspension of 2 g. of benzo-semiflavanthrene in 50 ml. of *N* sodium hydroxide is treated with 4 g. of sodium hydrosulfite, and the mixture is boiled in an inert atmosphere for thirty minutes. Fifteen ml. of acetic acid is added, the precipitate is filtered, washed well with water and dried for a short time at 100°. The product forms black-violet needles that melt at 197°.

Anal. Calcd. for $C_{20}H_{13}ON$: C, 84.7; H, 4.6. Found: C, 84.8; H, 4.46.

The hydroxyamine is little soluble in boiling *N* sodium hydroxide and is completely extracted from the violet solution thus formed by toluene. This solution and the deep red solution in alcohol rapidly become yellow on exposure to air, and deposit yellow needles of benzo-semiflavanthrene. With an excess of acetic anhydride, the reduction product dissolves to give a red solution which becomes deep brown on boiling and deposits benzo-semiflavanthrene, even when air is excluded. From the brown solution, the desoxy compound can be precipitated by dilution with water. A similar result is obtained when the deep red solution of the hydroxyamine in pyridine is treated with benzoyl chloride.

The Desoxy Compound (IV).—A mixture of 1.5 g. of benzo-semiflavanthrene, 5 ml. of hydrochloric acid and 35 ml. of acetic acid is boiled until all of the solid is dissolved. A solution of 3.5 g. of stannous chloride in 5 ml. of hydrochloric acid and 10 ml. of acetic acid is added in one portion, and the boiling is continued until the yellow-green precipitate has become black (thirty minutes to one hour). This black tin double salt is filtered, washed well with acetic acid and water, and boiled for five minutes with 50 ml. of 0.5 *N* sodium hydroxide, excluding air. The red-brown desoxy compound is quite readily attacked by air, even when dry, and in a capillary tube has the same melting point as benzo-semiflavanthrene. Freshly prepared, it is completely soluble in 10% hydrochloric acid; on keeping, even in an evacuated desiccator, it is oxidized, becoming yellow and insoluble in dilute acid. Concordant analytical results could not be obtained. Found: C, 87.5 to 88.2; H, 4.5 to 4.7. $C_{20}H_{13}N$ requires: C, 89.8; H, 4.87.

Summary

This paper reports the preparation of benzo-semiflavanthrene, a quinone imine related in structure to the vat dye flavanthrene. Some experiments on the reduction of the substance are described.

MINNEAPOLIS, MINN. RECEIVED MAY 19, 1936

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[2] Pictet and Hubert, *Ber.*, **29**, 1183 (1896).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies in the *peri*-Naphthindene Series. I. The Condensation of β-Naphthol with Cinnamic Acid

BY C. FREDERICK KOELSCH

Comparatively few derivatives of *peri*-naphthindene have been investigated, but the reactions of these few indicate that the chemistry of this system is quite different from that of the at first sight related indene system.[1] In the present series of papers, the syntheses and reactions of *peri*-naphthindene derivatives will be examined with special reference to the analogous procedures in the indene series.

Phenol reacts with cinnamic acid in the presence of sulfuric acid to give 3,4-dihydro-4-phenylcoumarin.[2] It is now shown that β-naphthol and cinnamic acid behave similarly forming 3,4-dihydro-4-phenyl-5,6-benzocoumarin (I).[3] This lactone is easily hydrolyzed and methylated to give

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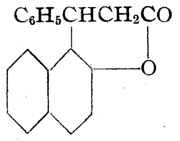
[1] Compare, *e. g.*, the ease of formation, stability and basicity of *peri*-naphthindone [Cook and Hewett, *J. Chem. Soc.*, 368 (1934)] with the unknown, presumably easily polymerizable indone, whose derivatives are not basic; the tendency to enolize of 8-phenyl-*peri*-naphthindandione-7,9 [Cesaris, *Gazz. chim. ital.*, **42**, II, 453 (1912)] with the tendency to ketonize of 2-phenylindandione-1,3 [Hantzsch, *Ann.*, **392**, 286 (1912)]; the action of phenylmagnesium bromide on benzanthrone [Allen and Overbaugh, THIS JOURNAL, **57**, 740 (1935)] with its action on fluorenone [Ullmann and v. Wurstemberger, *Ber.*, **37**, 73 (1904)].

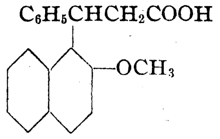
[2] Liebermann and Hartmann, *Ber.*, **24**, 2586 (1891).

[3] The present paper is published in its incomplete form to avoid duplication, a recent article by Miller and Robinson [*J. Chem. Soc.*, 1535 (1934)] having announced a projected investigation of the condensation of α,β-unsaturated carbonyl compounds with phenols.

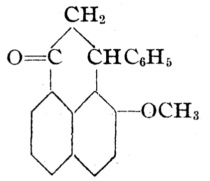
β-phenyl-β-(2-methoxynaphthyl-1)-propionic acid (II), whose chloride, treated with aluminum chloride, is cyclized to 6-methoxy-7-phenyl-7,8-dihydro-9-keto-*peri*-naphthindene (III).



I



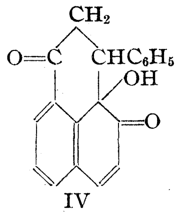
II



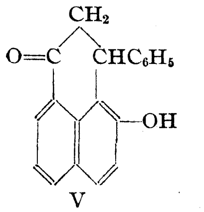
III

In view of the results of Cook and Hewett,[1] who obtained 9-keto-*peri*-naphthindene and not the corresponding 7,8-dihydro compound by the cyclization of β-(naphthyl-1)-propionic acid, it was at first believed that in the present cyclization also hydrogen had been lost. This belief was strengthened by: (a) the yellow color of the product (III), (b) the non-reactivity of it toward phenylmagnesium bromide[4] and (c) the non-formation of a benzal derivative. However, analyses of the ketone (III), its oxime, its demethylation product and its oxidation product indicate that these substances are all dihydro compounds.[5]

The most remarkable reaction of the ketone III is its behavior on oxidation with chromic acid. It is thus converted into a compound which must be 6,9-diketo-7-phenyl-6a-hydroxy-6,6a,7,8-tetrahydro-*peri*-naphthindene (IV) since this oxidation product is easily reduced by alkaline hydrosulfite to (V), the demethylation product of (III).[6]



IV



V

Experimental

3,4-Dihydro-4-phenyl-5,6-benzocoumarin.—A mixture of 250 g. of β-naphthol, 250 g. of cinnamic acid, 700 ml. of acetic acid and 300 ml. of sulfuric acid is boiled for one hour and then poured into water. The resinous precipitate is washed with hot water and boiled with dilute sodium carbonate, enough of the salt being added to cause the red substance to become green. The insoluble material is washed, distilled under reduced pressure and crystallized from alcohol. There is obtained 125–130 g. of the lactone which forms colorless prisms that melt at 115–116°.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.1; H, 5.1. Found: C, 83.2; H, 5.3.

β-Phenyl-β-(2-methoxynaphthyl-1-)-propionic Acid (II).—The lactone (120 g.) is dissolved in 400 ml. of 10% sodium hydroxide by boiling. The solution is cooled and 40 ml. of methyl sulfate is added slowly with stirring. The methylation is completed by boiling for two minutes, cooling, adding more sodium hydroxide (20 g.) and methyl sulfate (20 ml.). The solution is boiled a short time and cooled; the difficultly soluble sodium salt is filtered and decomposed with hydrochloric acid. The precipitate is crystallized from acetic acid, giving 95–100 g. of the methoxylated acid which forms colorless prisms that melt at 168–170°.

Anal. Calcd. for $C_{20}H_{18}O_3$: C, 78.4; H, 5.9. Found: C, 77.9; H, 6.0.

6-Methoxy-7-phenyl-7,8-dihydro-9-keto-*peri*-naphthindene (III).—The methoxylated acid (80 g.) and phosphorus pentachloride (60 g.) are added to 280 ml. of benzene and boiled for five minutes. The solution is cooled and 45 g. of aluminum chloride is added in portions. After boiling a few minutes, the mixture is hydrolyzed and the benzene is removed with steam. The residue is crystallized from acetic acid, giving 66 g. of pale yellow needles that melt at 144–145°. The compound is insoluble in hot sodium hydroxide, and gives a bright red color with sulfuric acid.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.3; H, 5.55. Found: C, 83.1; H, 5.65.

The oxime, obtained by boiling the ketone with hydroxylamine hydrochloride in alcohol for two hours, melts at 207–211°.

Anal. Calcd. for $C_{20}H_{17}O_2N$: C, 79.2; H, 5.6. Found: C, 79.4; H, 5.7.

6-Hydroxy-7-phenyl-7,8-dihydro-9-keto-*peri*-naphthindene (V).—A mixture of 2 g. of the methoxy ketone, 15 ml. of acetic acid and 5 ml. of 40% hydrobromic acid is boiled for three hours. Ether and water are added, the phenol is extracted from the ether with dilute sodium hydroxide, distilled at 20 mm. and crystallized from dilute acetic acid. The compound forms bright yellow needles that sinter at 185° and melt at 191–193°. Its solution in dilute caustic soda is orange-brown.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.2; H, 5.1. Found: C, 83.3; H, 5.1.

6,9-Diketo-7-phenyl-6a-hydroxy-6,6a,7,8-tetrahydro-*peri*-naphthindene (IV).—The methoxy ketone (10 g.) in acetic acid (75 ml.) is treated with 20 g. of chromic acid in dilute acetic acid. When the vigorous reaction is over, the mixture is poured into water and extracted with ether. Sodium carbonate removes very little acidic product; the neutral product is crystallized from dilute ethanol, when it forms bright yellow needles (3.6 g.) that melt with gas evolution at 105–110°.

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[4] The forced reaction will be described in a later paper.

[5] Compare the cyclization of β-(2-methoxynaphthyl-1)-propionic acid, Barger and Starling, *J. Chem. Soc.*, **99**, 2033 (1911).

[6] Compare the oxidation of 1-methylnaphthol-2. Bargellini and Silvestri, *Gazz. chim. ital.*, **37**, II, 412 (1907).

Anal. Calcd. for $C_{19}H_{14}O_3 + H_2O$: C, 74.0; H, 5.2. Found: C, 73.7; H, 5.4.

The quinol also separates from dilute methanol or dilute acetic acid in needles that contain water. From toluene it is obtained in the form of pale tan prisms which are solvent free and melt at 160–163° with darkening.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.6; H, 4.8. Found: C, 78.4; H, 4.7.

Boiling with sodium hydroxide transforms the quinol into an amorphous brown substance. On boiling with alkaline sodium hydrosulfite it gives a clear orange-brown solution from which acids precipitate the hydroxy compound (V), identified by mixed melting point and by its conversion to the methoxy ketone (III) on methylation with methyl sulfate and alkali.

Summary

The condensation of β-naphthol with cinnamic acid yields a dihydrocoumarin which has been converted into a *peri*-naphthindene derivative. Some reactions of this latter substance are described.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

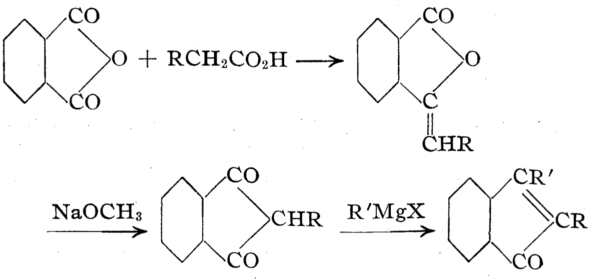
Some Applications of the Rosenmund-v. Braun Nitrile Synthesis

BY C. FREDERICK KOELSCH

When an aromatic bromide is heated in a sealed tube with water, sodium cyanide and cuprous cyanide, the halogen is replaced by carboxyl.[1] Hydrolysis of the intermediate nitrile may be avoided by omitting the water and sodium cyanide, this procedure making the use of a sealed tube or an autoclave unnecessary.[2] The importance of this reaction has been demonstrated in a recent synthesis of phenanthrene-9-carboxylic acid.[3]

In the present research the reaction has been applied to the preparation of some derivatives of 2,3-diphenylindone, and the cyano group has been introduced into each of the three benzenoid rings of this compound. Likewise it has been found that β,γ,γ-triphenylacrylonitrile and β-phenyl-γ-diphenyleneacrylonitrile are readily obtainable from the corresponding vinyl bromides. However, when α-*p*-bromophenyl-β,β-diphenylvinyl bromide is heated with cuprous cyanide under the usual conditions, it is completely resinified; at lower temperatures it is recovered unchanged.

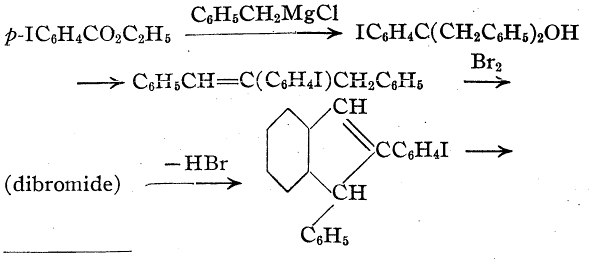
The halogenated indones were prepared by the following series of reactions, the last step of the series constituting a hitherto undescribed diarylindone synthesis.



When 4-bromophthalic anhydride was used, a mixture of benzalbromophthalides was obtained which was converted quantitatively into 1,3-diketo-2-phenyl-5-bromoindane. This with phenylmagnesium bromide gave an easily separable mixture of the isomeric 5- and 6-bromodiphenylindones; thus enolization of this unsymmetrical β-diketone involves either of the carbonyl groups.

It is noteworthy that although solid 2-phenylindandione is obtainable in only the white keto form,[4] the halogenated derivatives of this substance prepared in this research were each easily obtainable in two forms: by crystallization from non-polar solvents in a white modification (keto), and from polar solvents in a violet-black modification (enol).

The structure of 5-bromo-2,3-diphenylindone was proved by oxidation to the known 4-bromo-2-benzoylbenzoic acid, and that of 2-*p*-iodophenyl-3-phenylindone by a separate synthesis according to the scheme[5]



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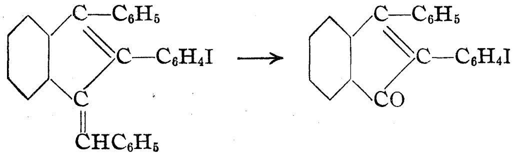
[1] Rosenmund and Struck, *Ber.*, **52**, 1749 (1919).

[2] Von Braun and Manz, *Ann.*, **488**, 111 (1931).

[3] Mosettig and van de Kamp, THIS JOURNAL, **54**, 3334 (1932).

[4] Hantzsch, *Ann.*, **392**, 286 (1912).

[5] Compare Orechoff, *Ber.*, **47**, 89 (1914); Ruggli, *Ann.*, **414**, 125 (1917).



Experimental

Substitution in the 2-Phenyl of 2,3-Diphenylindone

_p_-Iodobenzalphthalide.—_p_-Iodophenylacetic acid was prepared from phenylacetic acid by direct iodination,[6] from _p_-aminophenylacetic acid by diazotization, and from _p_-iodotoluene through _p_-iodobenzyl bromide and cyanide.[7] The last method is much the better.

A mixture of 80 g. of _p_-iodophenylacetic acid, 46 g. of phthalic anhydride and 1 g. of sodium acetate is heated for two hours at 225–235°. The melt is dissolved in hot acetic acid and cooled. The product (70 g.) is deposited in the form of yellow needles. Recrystallized from acetic acid, the compound melts at 172–173°.

Anal. Calcd. for $C_{15}H_9O_2I$: C, 51.7; H, 2.62. Found: C, 51.7; H, 2.58.

2-_p_-Iodophenylindandione-1,3.—A solution of 4.7 g. of sodium in 100 ml. of methanol is added to a suspension of 68 g. of _p_-iodobenzalphthalide in 300 ml. of methanol. After the mixture has been boiled for five minutes, water is added, the diketone is precipitated with hydrochloric acid, dried and recrystallized (64 g.). From acetic acid it separates in red-violet prisms, and from non-polar solvents in colorless needles. Both of these forms melt at 145–146° to a red liquid.

Anal. Calcd. for $C_{15}H_9O_2I$: C, 51.7; H, 2.62. Found: C, 51.9; H, 2.61.

2-_p_-Iodophenyl-3-phenylindone.—A solution of 100 g. of iodophenylindandione in hot benzene is added to a phenylmagnesium bromide solution containing 17 g. of magnesium. The mixture is boiled for one hour and decomposed with iced sulfuric acid. Washing the organic solution with dilute sodium carbonate removes unchanged diketone (17 g.). The neutral product is distilled under reduced pressure and crystallized from acetic acid. There is obtained 61 g. of bright orange-red needles that melt at 141–143°.

Anal. Calcd. for $C_{22}H_{13}ON$: C, 86.0; H, 4.23. Found: C, 86.1; H, 4.35.

2-_p_-Cyanophenyl-3-phenylindone.—Iododiphenylindone (20 g.) and cuprous cyanide (10 g.) are mixed and heated for three hours at 240°. The melt is pulverized and extracted in a Soxhlet with acetone. The product, obtained in a nearly quantitative yield, is distilled at 15 mm. and crystallized from acetic acid, when it forms orange plates that melt at 142–144°.

Anal. Calcd. for $C_{22}H_{13}ON$: C, 86.0; H, 4.23. Found: C, 86.1; H, 4.35.

α,γ-Diphenyl-β-_p_-iodophenylpropanol-β.—This carbinol, obtained from ethyl _p_-iodobenzoate and benzylmagnesium chloride in a yield of about 75%, after crystallization from ether–petroleum ether and then from ethanol, forms white needles that melt at 117–117.5°.

Anal. Calcd. for $C_{21}H_{19}OI$: C, 60.9; H, 4.61. Found: C, 60.9; H, 4.54.

α,γ-Diphenyl-β-_p_-iodophenylpropene.—This hydrocarbon is obtained in a good yield by boiling a solution of the above carbinol in acetic acid containing a little sulfuric acid. It forms colorless prisms from a mixture of ethanol and ethyl acetate that melt at 92–92.5°.

Anal. Calcd. for $C_{21}H_{17}I$: C, 63.6; H, 4.32. Found: C, 63.7; H, 4.25.

1-Phenyl-2-_p_-iodophenylindene.—The above iodotriphenylpropene dissolved in 2.5 times its weight of acetic acid is treated with the calculated amount of bromine, and the solution is boiled for twenty minutes. The product can be separated by crystallization from ligroin into nearly equal amounts of a yellow substance that melts at 165–168° with decomposition (probably α-bromo-α,γ-diphenyl-β-_p_-iodophenylpropene; $C_{21}H_{16}BrI$ requires: C, 53.1; H, 3.4. Found: C, 54.2; H, 3.02) and the indene, which forms microscopic white needles that melt at 184–185°.

Anal. Calcd. for $C_{21}H_{15}I$: C, 63.9; H, 3.83. Found: C, 63.5; H, 3.82.

1-Benzal-2-_p_-iodophenyl-3-phenylindene.—To a suspension of 7 g. of 1-phenyl-2-_p_-iodophenylindene in 70 ml. of absolute ethanol is added 3 ml. of benzaldehyde and a solution of 0.3 g. of sodium in 5 ml. of ethanol. The mixture is boiled for five minutes and cooled, giving 6 g. of the benzal compound. The substance separates from acetic acid in the form of yellow needles that melt at 173–174°.

Anal. Calcd. for $C_{28}H_{19}I$: C, 69.7; H, 3.98. Found: C, 69.9; H, 3.91.

This benzal compound is oxidized by the calculated amount of chromic acid in acetic acid to 2-_p_-iodophenyl-3-phenylindone, which melts at 141–143° alone or mixed with the same substance prepared from iodophenylindandione.

Substitution in the 3-Phenyl of 2,3-Diphenylindone

2-Phenyl-3-_p_-bromophenylindone.—A benzene solution of 2-phenylindandione-1,3 is added to a solution of _p_-bromophenylmagnesium bromide containing 7 g. of magnesium. After boiling for one hour, the mixture is hydrolyzed with iced acid, and the unchanged diketone (20 g.) is extracted with sodium carbonate. The neutral product is distilled under reduced pressure and crystallized from acetic acid and then from toluene. There is obtained 9 g. of the bromodiphenylindone which forms orange prisms that melt at 172–174°.

Anal. Calcd. for $C_{21}H_{13}OBr$: C, 69.8; H, 3.6. Found: C, 69.9; H, 3.82.

2-Phenyl-3-_p_-cyanophenylindone.—The preceding bromodiphenylindone is heated with half its weight of cuprous cyanide at 250° for four hours, the melt is powdered and extracted with acetone, and the product is distilled under reduced pressure and crystallized from acetic acid. The cyano compound forms bright red prisms that melt at 184–187°.

Anal. Calcd. for $C_{22}H_{13}ON$: C, 86.0; H, 4.23. Found: C, 85.6; H, 4.34.

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[6] Datta and Chatterjee, THIS JOURNAL, **41**, 292 (1919).

[7] Wheeler and Clapp, _Am. Chem. J._, **40**, 460 (1908).

Substitution in the Indene Nucleus of 2,3-Diphenylindone

2 - Phenyl - 5 - bromoindandione - 1,3.—4 - Bromophthalic anhydride[8] (29 g.) is mixed with phenylacetic acid (17.5 g.) and sodium acetate (1 g.) and heated at 220–240° for three hours. The product (23 g.), a mixture of the two possible benzal bromophthalides, is crystallized from acetic acid, when it melts at 145–170°. This mixture is suspended in methanol and treated with a solution of 2 g. of sodium in the same solvent. The solution is boiled for five minutes, water is added, and the diketone is precipitated with hydrochloric acid. From acetic acid, the product (20 g.) is deposited in the form of violet-black needles, and from benzene in the form of white needles. Both of these forms melt to a red liquid at 166–167°.

Anal. Calcd. for $C_{15}H_9O_2Br$: C, 59.8; H, 2.99. Found: C, 59.4; H, 2.84.

5- and 6-Bromo-2,3-diphenylindones.—The above diketone (19 g.) suspended in benzene is added to a solution of phenylmagnesium bromide containing 4 g. of magnesium. The mixture is boiled for one hour, hydrolyzed, and the unchanged diketone (3 g.) is removed with sodium carbonate. The neutral product is distilled under reduced pressure and fractionally crystallized from ether–petroleum ether. The less soluble part (8.5 g.) is 6-bromo-2,3-diphenylindone, which forms orange-red plates from acetic acid that melt at 192–194°.

Anal. Calcd. for $C_{21}H_{13}OBr$: C, 69.8; H, 3.6. Found: C, 69.7; H, 3.4.

The more soluble part is 5-bromo-2,3-diphenylindone, which forms orange needles from acetic acid that melt at 167–168°.

Anal. Calcd. for $C_{21}H_{13}OBr$: C, 69.8; H, 3.6. Found: C, 69.8; H, 3.4.

The structure of the latter 5-bromodiphenylindone is indicated by its oxidation by chromic acid in acetic acid to 2-benzoyl-4-bromobenzoic acid which melts at 189–191° alone or mixed with a known sample of this same melting point, kindly furnished by Dr. Stephens.

6 - Cyano - 2,3 - diphenylindone.—6 - Bromodiphenylindone is treated with cuprous cyanide and the product is worked up as described for 2-phenyl-3-*p*-cyanophenylindone. The product forms orange red plates that melt at 209–211°.

Anal. Calcd. for $C_{22}H_{13}ON$: C, 86.0; H, 4.23. Found: C, 85.6; H, 4.2.

The Vinyl Compounds

α - *p* - Bromophenyl - β,β - diphenylvinyl Bromide.—An ether solution of benzophenone (28 g.) is added to a solution of *p*-bromobenzylmagnesium bromide containing 7.3 g. of magnesium. The solution is hydrolyzed with iced ammonium chloride, and the product is crystallized from ether–petroleum ether. There is obtained 35 g. of *p*-bromobenzyldiphenylcarbinol, which forms white needles that melt at 124–126°. (Found: C, 68.4; H, 5.0. $C_{20}H_{17}OBr$ requires: C, 68.0; H, 4.7.) This carbinol (7 g.) is dissolved in acetic acid (30 ml.) and treated with bromine (3.2 g.). The bromine is rapidly absorbed, and the solution soon deposits crystals of the vinyl bromide. The product is best purified by distillation under reduced pressure followed by crystallization from acetic acid. It forms colorless needles that melt at 109–110°.

Anal. Calcd. for $C_{20}H_{14}Br_2$: C, 58.0; H, 3.4. Found: C, 57.8; H, 3.4.

Under the usual conditions for the replacement of bromine by cyanogen (240°) this dibromo compound is converted into a black resin. At lower temperatures it is partly resinified and partly recovered unchanged.

Triphenylacrylonitrile.—Triphenylvinyl bromide heated with cuprous cyanide in the usual way gives a quantitative yield of triphenylacrylonitrile which melts at 163–165°.[9]

α - Phenyl - β - diphenyleneacrylonitrile.—α - Phenyl - β-diphenylenevinyl bromide[10] and cuprous cyanide at 240° give a good yield of the corresponding nitrile which forms yellow needles that melt at 188–189°.

Anal. Calcd. for $C_{21}H_{13}N$: C, 90.2; H, 4.66. Found: C, 90.1; H, 4.68.

Summary

The synthesis of some halogenated diphenylindones is described, and it is shown that the Rosenmund–v. Braun method for the replacement of halogen by cyanogen is applicable to these compounds and to certain triarylvinyl bromides.

Minneapolis, Minn. Received May 19, 1936

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(8) Stephens, This Journal, **43**, 1953 (1921).

(9) Hobbe and Feitschel, *Ber.*, **34**, 1967 (1901).

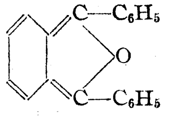
(10) Koelsch, This Journal, **54**, 3387 (1932).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Attempted Synthesis of Some Compounds Containing the *Iso*-indene Nucleus

BY C. FREDERICK KOELSCH

α,α-Diphenyl-β,β-benzofuran (I) is the only compound known definitely to contain an *o*-quinoid structure similar to that formerly postulated for rubrene (II).[1] That this type of structure is formed with difficulty or once formed is not stable is indicated by the relative ease of oxidation of anthracene as compared with phenanthrene, the radical nature of 2,3,6,7-dibenzanthracene, the immediate rearrangement of *o*-quinone-bisdiphenylmethide and other similar phenomena.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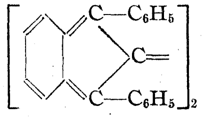
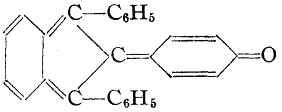
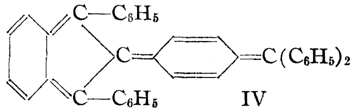

II

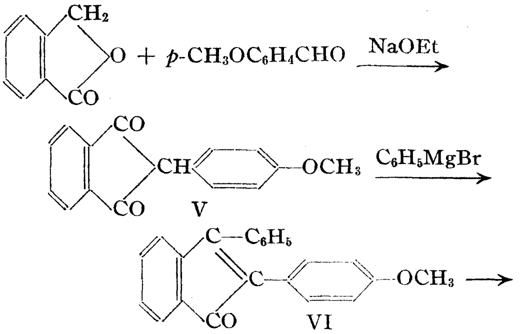
The present investigation was undertaken with the object of throwing some light on the structure and possible tautomeric nature of rubrene through a study of the reactions of the compounds (III) and (IV).

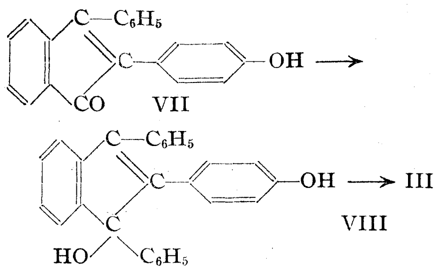

III


IV

Although these substances could not be prepared, it is believed that the syntheses themselves and what few conclusions may be drawn from such negative results warrant publication.

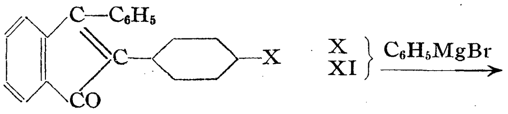
2-(*p*-Quino-)-1,3-diphenyl*iso*indene (III).—The synthesis of this compound was attempted through the following reactions



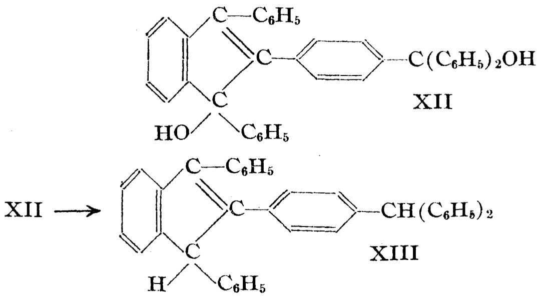


The substance (VIII) could not be dehydrated either by heat alone or by hot acetic acid; when boiled with acetic acid containing a trace of sulfuric acid, it was converted into a white amorphous substance, the reaction being apparently similar to the condensation undergone by 1,2,3-triphenylindenol and 9-phenylfluorenol under like conditions. Similar to Gomberg's easily dehydrated hydroxytriaryl carbinols in that a completely conjugated system connects the phenolic and the alcoholic hydroxyl groups, the compound (VIII) probably owes its resistance to dehydration to the difficulty of forming the necessary *o*-quinoid structure.

2-(*p*-Diphenylmethylenequino)-1,3-diphenyl*iso*indene (IV).—The synthesis of this substance was attempted by the reactions



IX (X = COOH)
X (X = COOR)
XI (X = COC_6H_5)



Neither the glycol (XII), its dimethyl ether, nor its dichloride could be obtained crystalline. The action of metals on the crude dichloride gave intractable orange gums whose solutions were not affected by air.

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[1] Since this work was completed Dufraisse and Velluz [*Compt. rend.*, **201**, 1394 (1935)] have suggested and proved that rubrene has an entirely different structure.

Experimental

2-*p*-Anisylindandione-1,3 (V).—A mixture of 110 g. of phthalide and 110 g. of anisaldehyde is added to a solution of 20.5 g. of sodium in 400 ml. of absolute ethanol. After boiling for fifteen minutes, the deep red solution is poured into water, the alcohol is distilled and the product is precipitated with hydrochloric acid. After crystallization from acetic acid the diketone forms colorless needles that melt at 152–154°; yield 68 g. The remainder of the anisaldehyde is converted into anisyl alcohol and anisic acid.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8. Found: C, 75.52; H, 4.70.

2-*p*-Anisyl-3-phenylindone (VI).—A solution of 65 g. of anisylindandione in hot toluene is added to phenylmagnesium bromide containing 15 g. of magnesium. The mixture is boiled for one hour and decomposed with iced sulfuric acid. After the unchanged diketone (7 g.) has been extracted with sodium carbonate, the product is distilled at 15 mm. and crystallized from acetic acid. There is obtained 43 g. of red needles that melt at 117–118°.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.6; H, 5.1. Found: C, 85.01; H, 5.21.

2-*p*-Hydroxyphenyl-3-phenylindone (VII).—The methoxy ketone (VI) (30 g.) is hydrolyzed by boiling for six hours with a mixture of 120 ml. of acetic acid and 30 ml. of 40% hydrobromic acid. The product, purified by solution in sodium hydroxide and reprecipitation, separates from acetic acid in red plates that contain acetic acid; m. p. 163–165°.

Anal. Calcd. for $C_{21}H_{14}O_2 \cdot 0.5C_2H_4O_2$: C, 80.4; H, 4.9. Found: C, 80.3; H, 4.9.

Dilute aqueous sodium hydroxide dissolves the phenol, giving a purple solution.

The benzoate, prepared with aqueous alkali and benzoyl chloride, forms red prisms that melt at 145°.

Anal. Calcd. for $C_{28}H_{18}O_3$: C, 83.5; H, 4.5. Found: C, 83.5; H, 4.4.

1,3-Diphenyl-2-*p*-hydroxyphenylindenol (VIII).—A benzene solution of the hydroxydiphenylindone is added to an excess of phenylmagnesium bromide. The mixture is worked up in the usual way, and the product, which like all triarylated indenols shows a tendency to supercool, is purified by recrystallization of its sodium salt. The pure phenol-alcohol crystallizes from ether–ligroin as a colorless powder that melts at 196–197°.

Anal. Calcd. for $C_{27}H_{20}O_2$: C, 86.1; H, 5.3. Found: C, 85.9; H, 5.3.

It is readily soluble in acetic acid and can be recovered unchanged after boiling with this solvent. The acetic acid solution becomes red on the addition of a trace of sulfuric acid and now, on boiling, a white amorphous substance is deposited, which is insoluble in the common solvents.

Hydrolysis of Cyanodiphenylindone.—The cyano compound (0.5 g.)[2] is boiled with a mixture of 5 ml. of sulfuric acid and 5 ml. of water until the originally melted substance has resolidified. The mixture is poured into water; the solid is powdered and extracted with hot sodium carbonate solution. The neutral product, **2-*p*-carbamidophenyl-3-phenylindone,** crystallizes from acetic acid in orange needles (0.15 g.) that melt at 248–254° with decomposition.

Anal. Calcd. for $C_{22}H_{15}O_2N$: C, 81.2; H, 4.6. Found: C, 80.5; H, 4.6.

The acidic product (IX) is precipitated with hydrochloric acid and crystallized from acetic acid, when it forms orange plates (0.35 g.) that melt at 212–214° and can be distilled without decomposition at 15 mm. The acid may also be obtained by boiling the amide with 1:1 sulfuric acid and water.

Anal. Calcd. for $C_{22}H_{14}O_3$: C, 80.8; H, 4.3. Found: C, 80.31; H, 4.3.

On boiling with the appropriate alcohol containing a little sulfuric acid, 2-*p*-carboxyphenyl-3-phenylindone is esterified. The esters (X), obtained in yields of about 80%, are best purified by distillation at 15 mm. followed by crystallization.

The methyl ester, from toluene, forms orange plates that melt at 167–168°.

Anal. Calcd. for $C_{23}H_{16}O_3$: C, 81.2; H, 4.7. Found: C, 81.3; H, 4.8.

The ethyl ester, from ethanol, forms orange needles that melt at 120–121°.

Anal. Calcd. for $C_{24}H_{18}O_3$: C, 81.4; H, 5.1. Found: C, 81.4; H, 5.3.

2-*p*-Benzoylphenyl-3-phenylindone (XI).—The acid (IX) dissolved in benzene is treated with a slight excess of phosphorus pentachloride, and after short boiling, with 2.2 equivalents of aluminum chloride. The solution is boiled for fifteen minutes, decomposed with iced acid and washed with sodium carbonate. The product crystallizes from acetic acid in red-orange prisms that melt at 169–171°. This diketone may be distilled at 15 mm. without decomposition.

Anal. Calcd. for $C_{28}H_{18}O_2$: C, 87.0; H, 4.69. Found: C, 86.6; H, 4.55.

2 - (*p* - α - Oxybenzohydrylphenyl) - 1,3 - diphenylindenol-1 (XII).—The methyl ester, the ethyl ester or the phenyl ketone derived from 2-*p*-carboxyphenyl-3-phenylindone dissolve easily in an excess of phenylmagnesium bromide. Decomposition of these solutions with iced acid followed by steam distillation gives in each case a pale orange glassy substance, easily soluble in acetic acid or in methanol. The solution in acetic acid becomes deep green with a trace of sulfuric acid. The methanol solution, on the addition of a little sulfuric acid, deposits an orange gum easily soluble in ether and nearly insoluble in methanol, but this dimethyl ether (?) cannot be crystallized. The chloride (?) obtained from the glycol with hydrogen chloride in benzene or with acetyl chloride also forms an uncrystallizable oil.

2-*p*-Benzohydrylphenyl-1,3-diphenylindene (XIII).—This hydrocarbon can be obtained from the glycol, the dimethyl ether or the chloride as follows. One gram of granulated zinc is added to a solution of one gram of any of the substances mentioned in 20 ml. of acetic acid. The solution is boiled and a drop of concd. hydrochloric acid is added; boiling is continued until the deep green solution is colorless, when more hydrochloric acid is added.

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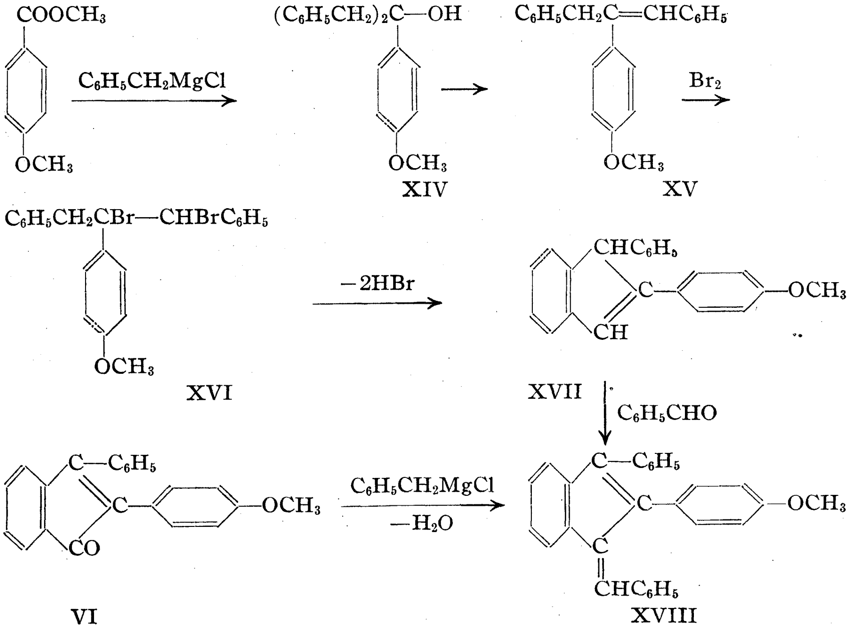
(2) Koelsch, This Journal, **58**, 1328 (1936).

This treatment is continued until the green color is no longer restored by hydrochloric acid. Water and ether are added, the ether solution is freed of acetic acid, dried and evaporated. The product is crystallized from ether–petroleum ether and then from acetic acid, when it forms small colorless flat needles that melt at 173–175°. It may be distilled without decomposition at 15 mm., and this is the most convenient way to purify large quantities (15 g.) of the substance.

Anal. Calcd. for $C_{40}H_{30}$: C, 94.1; H, 5.9. Found: C, 94.4; H, 6.3.

On treating the hydrocarbon in acetic acid with chromic acid, it is oxidized to *o*-dibenzoylbenzene and *p*-carboxytriphenylcarbinol, identified in each case by comparison with an authentic sample.

A Check on the Structure of 2-*p*-Anisyl-3-phenylindone.—In order to make certain of the structure of this compound, the following reactions were carried out



Two products are obtained from the dibromide (XVI), but only the indene (XVII) has been isolated in a pure state.

α,γ-Diphenyl-β-*p*-anisyl-propanol-β (XIV).—This carbinol, obtained in a yield of about 75%, is crystallized from ether–petroleum ether and then from ethanol. It forms white plates that melt at 93–94°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 83.0; H, 6.9. Found: C, 83.4; H, 7.0.

α,γ-Diphenyl-β-*p*-anisylpropene (XV).—This substance is obtained in a quantitative yield by boiling the above carbinol in acetic acid containing a little sulfuric acid.

It forms white plates that melt at 82–83° from ethanol.

Anal. Calcd. for $C_{22}H_{20}O$: C, 88.0; H, 6.7. Found: C, 87.7; H, 6.7.

2-*p*-Anisyl-1-phenylindene (XVII).—The propene dissolved in 2.5 times its weight of acetic acid is treated with the calculated amount of bromine, and the solution is boiled for twenty minutes.

The product is distilled under reduced pressure (decomposition of the bromopropene) and crystallized from acetic acid and then from ligroin, when it forms pale orange plates that melt at 120–122°; yield about 35%.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.5; H, 6.0. Found: C, 87.8; H, 6.0.

1-Benzal-2-*p*-anisyl-3-phenylindene (XVIII).—(a) To a solution of 0.5 ml. of benzaldehyde and 1 g. of the indene (XVII) in 10 ml. of hot *n*-propyl alcohol is added a solution of 0.1 g. of sodium in 2 ml. of ethanol. The benzal compound is rapidly deposited, and on recrystallization from acetic acid forms yellow needles that melt at 188–190° (1.2 g.).

Anal. Calcd. for $C_{29}H_{22}O$: C, 90.1; H, 5.7. Found: C, 90.0; H, 5.6.

(b) A benzene solution of the indone (VI) is added to an excess of benzylmagnesium chloride. Since the resulting carbinol is an oil, it is dehydrated by boiling in acetic acid with a trace of sulfuric acid. The product is identical with that obtained in (a).

Summary

Some unsuccessful attempts to obtain compounds containing the *iso*-indene nucleus are recorded. These failures lend support to the supposition that this nucleus is unstable.

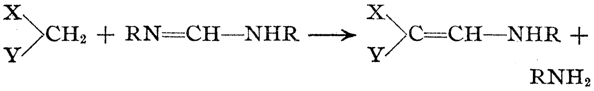
MINNEAPOLIS, MINN. RECEIVED MAY 19, 1936

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF KANSAS]

On the Reactions of Certain Methylene Hydrogen Derivatives Containing Cyanide, Thiocyanate or Sulfinate Radicals

BY CLARENCE E. GROTHAUS AND F. B. DAINS

It has been shown previously in a series of papers[1] that compounds containing the methylene hydrogen grouping exhibit the characteristic property of reacting with disubstituted formamidines, forming a carbon to carbon linking and yielding an aminomethylene derivative which may be represented as follows



$$\overset{X}{\underset{Y}{>}}CH_2 + RN{=}CH{-}NHR \longrightarrow \overset{X}{\underset{Y}{>}}C{=}CH{-}NHR + RNH_2$$

These reactions occur in the case of open-chain compounds as acetoacetic ester, benzoylacetic ester, cyanoacetic ester, malonic ester and desoxybenzoin; also heterocyclic compounds as thiazolidones, pyrazolones, isoxazolones and imidazolones are similarly reactive.

The present investigation was carried out with methylene derivatives in which one group was a benzoyl or substituted benzoyl grouping and the other the CN, SCN or *p*-$CH_3C_6H_4SO_2$ radical, ($XC_6H_4COCH_2Y$), in order to ascertain the effect of the latter groups on the reactivity of the methylene hydrogen with the formamidines and in a few cases with benzaldehyde and *p*-nitrosodimethylaniline.

The aminomethylene derivatives obtained in this study were found usually to react with hydrazine, phenylhydrazine and hydroxylamine yielding pyrazole or isoxazole derivatives. However, *p*-phenylanilinomethylenebenzoylacetonitrile failed to give such pyrazole or isoxazole compounds.

Experimental

I. Derivatives of Phenacyl Cyanide

Anilinomethylenebenzoylacetonitrile (III) $C_6H_5COC(CHNHC_6H_5)CN$.—Phenacyl cyanide (6 g.) and diphenylformamidine (8 g.) were heated in xylene solution at 120° for two hours. Anilinomethylenebenzoylacetonitrile (m. p. 159°) and aniline were formed.

Reactions of Anilinomethylenebenzoylacetonitrile with Hydroxylamine.—The nitrile (III) was refluxed in alcohol solution with hydroxylamine hydrochloride, either by itself, in pyridine solution or after neutralization with sodium carbonate. In all cases the same products were obtained, aniline and a compound (XI) melting at 154°, which was insoluble in hydrochloric acid and was recovered unchanged after solution in alkali. It cannot be the expected 2-phenyl-3-cyanoisoxazole which should in the presence of alkali rearrange to benzoylmalonic dinitrile.[2] The compound failed to react with phenylhydrazine, benzoyl chloride, and ethyl iodide and was hydrolyzed only after long boiling with 40% sodium hydroxide. These properties and its inertness point to the probable structure of 4-benzoyl-5-iminoisoxazole (XI) $\underbracket{ON{=}CHCH(COC_6H_5)C}{=}NH$.

With hydrazine.—When this nitrile (III) was refluxed with hydrazine in alcoholic solution, 3-phenyl-4-cyanopyrazole (XII) (m. p. 134°) and aniline were formed.

With Phenylhydrazine.—The anilinomethylene derivative (III) reacted with phenylhydrazine in an analogous manner and gave aniline and 1,5-diphenyl-4-cyanopyrazole (XIII) (m. p. 182°). This product is soluble in most organic solvents but is practically insoluble in either acid or alkali.

Proof of Structure of 1,5-Diphenyl-4-cyanopyrazole.—This was accomplished by hydrolyzing the cyano group to a carboxylic group. Refluxing with 75% sulfuric acid, concentrated hydrochloric acid or sodium hydroxide failed to effect hydrolysis. Concentrated sulfuric acid at 130° hydrolyzed the compound to benzoic acid. The desired carboxylic acid was obtained by heating the pyrazole in a sealed tube with concentrated alcoholic potassium hydroxide at 160 to 170° for three hours, yielding 1,5-diphenyl-4-pyrazolecarboxylic acid (XIV) (m. p. 173°) and ammonia. This acid was found to be identical with that obtained by hydrolyzing the anilide of 1,5-diphenyl-4-pyrazolecarboxylic acid.

The fact that the phenylhydrazone of the phenacyl cyanide failed to react on heating with diphenylformamidine (two hours at 120°) points to this same structure.

4-Dimethylaminoanilinobenzoylacetonitrile (I) $C_6H_5COC({=}NC_6H_4N(CH_3)_2)CN$.—Nitrosodimethylaniline condensed readily with phenacyl cyanide in boiling alkaline alcoholic solution. The blood-red crystals from dioxane melted at 128°.[3]

II. *p*-Bromophenacyl Cyanide and Derivatives

***p*-Bromophenacyl Cyanide (XV).**—*p*-Bromophenacyl chloride (60 g.) was partially dissolved in alcohol (200 cc.). A solution of sodium cyanide (28 g.) was slowly added with continuous stirring, the mixture being cooled with ice. The mixture was then warmed to 60° and the stirring continued for one hour, the color changing from brown to reddish-violet. The cyanide was precipitated by acidifying and was deposited as slightly colored small thick plates (m. p. 159°).

Anilinomethylene-*p*-bromobenzoylacetonitrile (XVI) *p*-$BrC_6H_4COC({=}CHNHC_6H_5)CN$.—This resulted when

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[1] F. B. Dains, *et al.*, *Ber.*, **35**, 2496 (1902); THIS JOURNAL, **31**, 1148 (1909); **35**, 959, 970 (1913); **38**, 1510, 1841 (1916); **40**, 562 (1918); **43**, 613, 1200 (1921); **44**, 2310 (1922); *K. U. Sc. Bull.*, **15**, 265 (1924); **18**, 627 (1928).

[2] F. B. Dains and E. L. Griffin, THIS JOURNAL, **35**, 959 (1913).

[3] Lippmann, Diss., Berlin, 1905.

TABLE I

Text no.	Compound	Formula	M. p., °C.	Nitrogen, % Calcd.	Found
I	4-Dimethylaminoanilinobenzoylacetonitrile	$C_{17}H_{15}ON_3$	128	15.16	15.05
II	Benzalphenacyl cyanide	$C_{16}H_{11}ON$	85	6.01	5.83
III	Anilinomethylenebenzoylacetonitrile	$C_{16}H_{12}ON_2$	159	11.29	11.23
IV	*p*-Bromoanilinomethylenebenzoylacetonitrile[a]	$C_{16}H_{11}ON_2Br$	205	8.56	8.38
V	*p*-Chloroanilinomethylenebenzoylacetonitrile[b]	$C_{16}H_{11}ON_2Cl$	185	9.91	9.91
VI	*o*-Chloroanilinomethylenebenzoylacetonitrile[c]	$C_{16}H_{11}ON_2Cl$	167	9.91	9.96
VII	*o*-Ethoxyanilinomethylenebenzoylacetonitrile[d]	$C_{18}H_{16}O_2N_2$	138	9.59	9.64
VIII	*p*-Phenoxyanilinomethylenebenzoylacetonitrile[e]	$C_{22}H_{16}O_2N_2$	135	8.24	8.38
IX	*p*-Phenylanilinomethylenebenzoylacetonitrile[f]	$C_{22}H_{16}ON_2$	161	8.64	8.53
X	1,3-Diphenyl-4-(*p*-bromoanilinomethylene-5-pyrazolone[g]	$C_{22}H_{16}ON_3Br$	184	Br, 19.14	19.14
XI	4-Benzoyl-5-iminoisoxazole[h]	$C_{10}H_8O_2N_2$	154	14.89	14.87
XII	3-Phenyl-4-cyanopyrazole[i]	$C_{10}H_7N_3$	134	24.84	24.41
XIII	1,5-Diphenyl-4-cyanopyrazole[j]	$C_{16}H_{11}N_3$	182	17.14	16.78
XIV	1,5-Diphenyl-4-pyrazolecarboxylic acid	$C_{16}H_{12}O_2N_2$	173	10.60	10.39
XV	*p*-Bromophenacyl cyanide	C_9H_6ONBr	159	6.25	6.27
				Br, 35.71	35.85
XVI	Anilinomethylene-*p*-bromobenzoylacetonitrile	$C_{16}H_{11}ON_2Br$	143	Br, 24.54	24.58
XVII	*p*-Bromoanilinomethylene-*p*-bromobenzoylacetonitrile	$C_{16}H_{10}ON_2Br$	209	Br, 39.41	39.26
XVIII	4-(4-Bromobenzoyl)-5-iminoisoxazole	$C_{10}H_7O_2N_2Br$	195	10.48	10.12
XIX	3-(4-Bromobenzoyl)-4-cyanopyrazole	$C_{10}H_6N_3Br$	195	Br, 32.26	32.11
XX	1-Phenyl-5-(4-bromophenyl)-4-cyanopyrazole	$C_{16}H_{10}N_3Br$	212	Br, 24.69	24.40
XXI	2-Imino-3-phenyl-5-benzoylthiazole	$C_{16}H_{12}ON_2S$	257	10.00	10.07
XXII	2-Imino-3-(4-bromophenyl)-5-benzoylthiazole[k]	$C_{16}H_{11}ON_2SBr$	214	7.80	7.97
				Br, 22.28	22.19
XXIII	2-Imino-3-(4-chlorophenyl)-5-benzoylthiazole[l]	$C_{16}H_{11}ON_2SCl$	204	8.90	8.89
XXIV	ω-Benzalphenacyl-*p*-tolyl sulfinate	$C_{22}H_{18}O_3S$	142	S, 8.86	9.18
XXV	Phenylhydrazone of phenacyl-*p*-tolyl sulfinate	$C_{21}H_{20}O_2N_2S$	188	7.69	8.06
				S, 8.81	8.66
XXVI	Anilinomethylenephenacyl-*p*-tolyl sulfinate	$C_{22}H_{19}O_3NS$	208	3.71	3.75
XXVII	*p*-Bromoanilinomethylenephenacyl-*p*-tolyl sulfinate[m]	$C_{22}H_{18}O_3NSBr$	210	3.07	3.05
				Br, 17.55	17.65
XXVIII	1,5-Diphenyl-4-(*p*-tolylsulfonyl)-pyrazole	$C_{22}H_{18}O_2N_2S$	164	7.49	7.93
XXIX	*p*-Chloroanilinomethylenephenacyl-*p*-tolyl sulfinate[n]	$C_{22}H_{18}O_3NSCl$	217	3.40	3.53
XXX	*o*-Chloroanilinomethylenephenacyl-*p*-tolyl sulfinate[o]	$C_{22}H_{18}O_3NSCl$	187	3.40	3.40
XXXI	Anilinomethylene-*p*-nitrobenzyl cyanide	$C_{15}H_{11}O_2N_3$	Above 260	15.85	15.63
XXXII	Anilinomethylene-*p*-nitrophenylacetic ethyl ester	$C_{17}H_{16}O_4N_2$	114–115	8.97	8.82

[a] Fusion of phenacyl cyanide with di-*p*-bromophenylformamidine.

[b] Fusion of phenacyl cyanide with di-*p*-chlorophenylformamidine.

[c] Fusion of phenacyl cyanide with di-*o*-chlorophenylformamidine.

[d] Fusion of phenacyl cyanide with di-*o*-ethoxyphenylformamidine.

[e] Fusion of phenacyl cyanide with di-*p*-phenoxyphenylformamidine.

[f] Fusion of phenacyl cyanide with di-*p*-xenylphenylformamidine.

[g] Fusion of 1,3-diphenyl-5-pyrazolone with di-*p*-bromophenylformamidine.

[h] From action of hydroxylamine on III, IV, V, VI, VII, VIII.

[i] From action of hydrazine on III, IV, V, VI, VII.

[j] From action of phenylhydrazine on III, IV, V, VI, VII, VIII.

[k] Fusion of phenacyl thiocyanate and di-*p*-bromophenylformamidine.

[l] Fusion of phenacyl thiocyanate and di-*p*-chlorophenylformamidine.

[m] Fusion of phenacyl-*p*-tolyl sulfinate and di-*p*-bromophenylformamidine.

[n] Fusion of phenacyl-*p*-tolyl sulfinate and di-*p*-chlorophenylformamidine.

[o] Fusion of phenacyl-*p*-tolyl sulfinate and di-*o*-chlorophenylformamidine.

(XV) and diphenylformamidine were fused at 150° and crystallized from benzene in white needles (m. p. 143°).

Reactions of Anilinomethylene-*p*-bromobenzoylacetonitrile.—This compound (and also *p*-bromoanilinomethylenebenzoylacetonitrile) reacted with hydroxylamine to give an isoxazole (XVIII) (m. p. 195°); with hydrazine to give a phenyl pyrazole (XIX) (m. p. 195°); and with phenylhydrazine to give a diphenyl pyrazole (XX) (m. p. 212°). Aniline (*p*-bromoaniline in the case of the bromine derivative) was the other product of these reactions.

III. Derivatives of Phenacyl Thiocyanate

2-Imino-3-phenyl-5-benzoylthiazole (XXI) $SC(NH)-NC_6H_5CHCCOC_6H_5$.—Phenacyl thiocyanate (3.5 g.) and diphenylformamidine (4 g.) were heated at 160° in xylene for one hour. The product was washed with dilute acid and was crystallized from dioxane in fine light yellow crystals (m. p. 257°). Aniline was formed also in the reaction. Anilinomethylenephenacyl thiocyanate was doubtless formed first, but this evidently rearranged to a thiazole. It was not hydrolyzed with concentrated hydrochloric acid, sulfuric acid or alcoholic potassium hydroxide. No hydrolyzable sulfur was indicated by tests with lead plumbite. This derivative gave negative results for the presence of a free thiocyanate grouping in tests using alkaline lead tartrate.[4] It was unreactive to phenylhydrazine. These properties and the work of Kaufmann on thiocyanate derivatives[5] indicate such rearrangement.

Phenacyl thiocyanate was found to react also with di-*p*-bromophenylformamidine and di-*p*-chlorophenylformamidine to give analogous derivatives (XXII and XXIII).

IV. Derivatives of Phenacyl-*p*-tolyl Sulfinate

ω-Benzalphenacyl-*p*-tolyl Sulfinate (XXIV) $C_6H_5COC(CHC_6H_5)SO_2C_7H_7$.—Phenacyl-*p*-tolyl sulfinate and benzaldehyde (excess) were boiled in alcoholic solution to which had been added a few drops of piperidine. On cooling, small white crystals were deposited (m. p. 142°).

Phenacyl-*p*-tolyl sulfinate failed to react with *p*-nitrosodimethylaniline in an analogous manner.

Phenylhydrazone of Phenacyl-*p*-tolyl Sulfinate (XXV) $C_6H_5C(NNHC_6H_5)CH_2SO_2C_7H_7$.—Phenylhydrazine readily reacted with phenacyl-*p*-tolyl sulfinate to form the phenylhydrazone crystallizing in pale yellow short thick plates (m. p. 188°) from dioxane.

Anilinomethylenephenacyl-*p*-tolyl Sulfinate (XXVI) $C_6H_5COC(CHNHC_6H_5)SO_2C_7H_7$.—Phenacyl-*p*-tolylsulfinate (5 g.) and diphenylformamidine (5 g.) were heated together at 180 to 190° for one hour in xylene. The reaction product was washed with dilute acid to remove the aniline formed, and crystallized from dioxane in fine needles (m. p. 208°).

Di-*p*-bromophenylformamidine, di-*p*-chlorophenylformamidine and di-*o*-chlorophenylformamidine were found to react similarly with the sulfinate (derivatives XXVII, XXIX and XXX).

Reaction with Phenylhydrazine.—The anilinomethylene (XXVI) derivative reacted with phenylhydrazine when refluxed in alcoholic solution to give in small yield 1,5-diphenyl-4-(*p*-tolylsulfonyl)-pyrazole (XXVIII) (m. p. 164° from a mixture of alcohol and dioxane). This same pyrazole was obtained from *p*-bromoanilinomethylenephenacyl-*p*-tolyl sulfinate (XXVII) and phenylhydrazine.

Attempted Reactions with Hydrazine and Hydroxylamine.—The anilinomethylene (XXVI) and the *p*-bromoanilinomethylene (XXVII) derivatives failed to react with hydrazine or with hydroxylamine on refluxing in alcoholic solution.

V. Derivatives of *p*-Nitrobenzyl Cyanide and *p*-Nitrophenylacetic Ester

Anilinomethylene-*p*-nitrobenzyl Cyanide (XXXI) *p*-$NO_2C_6H_4C(CHNHC_6H_5)CN$.—This was prepared by fusing *p*-nitrobenzyl cyanide and diphenylformamidine. It formed fine orange-red needles from dioxane (m. p. above 260°). Aniline was split off in the reaction.

p-Nitrobenzyl cyanide was compared with benzyl cyanide in the ease of reaction with formamidines. The former derivative is much more reactive than benzyl cyanide, reacting readily and approaching phenacyl cyanide in reactivity.

The anilinomethylene derivative (XXXI) failed to react with hydroxylamine.

Anilinomethylene-*p*-nitrophenylacetic Ethyl Ester (XXXII) *p*-$NO_2C_6H_4C(CHNHC_6H_5)COOC_2H_5$.—*p*-Nitrophenylacetic ethyl ester and diphenylformamidine were fused together to yield this derivative. It was deposited from alcohol in long yellow needles (m. p. 114–115°). Aniline was split off in this reaction.

p-Nitrophenylacetic ethyl ester failed to react with *p*-nitrosodimethylaniline.

Summary

The methylene hydrogen reactions of phenacyl cyanide, *p*-bromophenacyl cyanide, *p*-nitrobenzyl cyanide, *p*-nitrophenylacetic ester, phenacyl thiocyanate and phenacyl-*p*-tolyl sulfinate with certain disubstituted formamidines have been studied and a number of new derivatives have been synthesized.

Phenacyl cyanide approaches benzoylacetic ester in methylene hydrogen reactivity as does also *p*-bromophenacyl cyanide and *p*-nitrobenzyl cyanide, while phenacyl thiocyanate is less reactive and phenacyl-*p*-tolyl sulfinate reacts with still more difficulty.

The anilinomethylene derivatives studied condense in nearly all the instances tried with hydroxylamine and the hydrazines to form isoxazoles and pyrazoles, respectively. Failures noted: *p*-phenylanilinomethylenebenzoylacetonitrile (no reaction with phenylhydrazine, hydrazine or hydroxylamine); anilinomethylenephenacyl-*p*-tolyl sulfinate (reacted with phenylhydrazine but not with hydrazine or hydroxylamine); *p*-bromoanilinomethylenephenacyl-*p*-tolyl sulfinate (reacted with phenylhydrazine but not with hydrazine or hydroxylamine); anilinomethylene-*p*-nitrobenzyl cyanide (no reaction with hydroxylamine).

LAWRENCE, KANSAS RECEIVED MAY 28, 1936

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[4] See Söderbäck, *Ann.*, **443**, 156 (1925).

[5] Kaufmann, *Arch. Pharm.*, **266**, 197 (1928).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, NORTHWESTERN UNIVERSITY]

Physical Studies of Non-Aqueous Solvates. I. The Solubility of Magnesium Bromide in Ethyl Ether[1]

BY H. H. ROWLEY

The figures on the solubility of magnesium bromide in ethyl ether as given in the "International Critical Tables"[2] are based on the work of Menschutkin.[3] Recently, Evans and Rowley[4] studying the vapor pressures of the ethyl etherates of magnesium bromide demonstrated the existence of a trietherate, stable below +12–13°, that was unknown to Menschutkin. In view of this fact, it was decided to repeat the work of Menschutkin over a temperature range from −20 to +30° and see if the solubility curve also gave indications of a change of phase. At the same time, the preparation of magnesium bromide in ethyl ether solution was studied.

Experimental

Method of Preparation.—The magnesium bromide was prepared according to Zelinsky[5] by treating pure magnesium turnings in ethyl ether with liquid bromine and agitating until the solution was colorless, cooling the flask when necessary to avoid too violent a reaction. As was previously known,[3–5] when the concentration of magnesium bromide reached a value of about 3.5%, an oily, immiscible liquid separated out and, as the reaction proceeded, increased in amount. This immiscible layer was often brown in color, but when properly prepared was almost colorless. When precipitated from a solution of magnesium bromide, saturated at a higher temperature, by cooling, this oily liquid was absolutely colorless. When pure, it crystallized under ether at about +22–23° but was capable of being supercooled 20 to 30° for several hours. However, agitation or seeding with a crystal of magnesium bromide etherate caused it to solidify into a white crystalline mass, which melted under ether above +23° re-forming the heavy layer.

The magnesium turnings were of reagent quality used in the preparation of Grignard reagents. The bromine was taken from a freshly opened bottle of C. P. grade, transferred to a dropping bottle and kept in a desiccator over phosphorus pentoxide. The ethyl ether was kept over calcium chloride for several days, filtered onto freshly cut sodium and kept in a subdued light for at least three or four days. It was then filtered onto fresh sodium and if no reaction occurred was distilled and kept over sodium in subdued light. The first and last fractions of the distillate were discarded and the freshly distilled middle portion used in less than a week. In this way the amount of degradation products present was kept at a minimum.

Determination of Solubility.—The samples were prepared in 150–250-cc. Erlenmeyer flasks as described above and either used directly or recrystallized, depending upon the purity as shown by the first analysis. The flasks, protected with calcium chloride tubes throughout the preparation and analysis, were immersed in a thermostat at the proper temperature held to less than 0.1°. For the determination at 0°, the melting point of ice was used, while at −10 and −20° an acetone-bath cooled with solid carbon dioxide was maintained at the proper temperature with the aid of an iron–constantan thermo element. In most cases, whenever feasible, the solutions were saturated a few degrees above the bath temperature in order that the equilibrium might be reached from supersaturation rather than unsaturation. After placing the samples in the bath, the flasks were agitated at intervals for at least an hour to ensure equilibrium. When the solid phase was crystalline, the oily immiscible layer was first solidified in ice and then melted before placing in the thermostat. After the immiscible layer had once been solidified and then remelted, the amount of supercooling, so characteristic of this substance, was greatly decreased and crystallization occurred rather quickly at temperatures where the crystal phase was stable.

After the solution had come to equilibrium, the flask was removed from the bath and a sample of the clear solution quickly poured into a tared flask and weighed. The weighed solution was then poured into water acidified with dilute nitric acid, the ether removed by evaporation and boiling, and the total bromide concentration determined as silver bromide. All of the solubility measurements were determined by this method and reported in grams of magnesium bromide dissolved in 100 g. of ethyl ether. In a series of experiments, a second sample was weighed in a tared crucible, the ether removed by evaporation on a steam-bath and the residue treated with concentrated sulfuric acid which was later removed by heating on a hot-plate and finally the magnesium sulfate was heated to redness and weighed as such. The determination of magnesium by this method was well suited to the conditions, since the concentrated sulfuric acid destroyed all the organic matter which might interfere with other methods. The disadvantage, aside from the hygroscopic character of anhydrous magnesium sulfate, was that considerable loss of ether from the open crucible occurred before weighing which would lead to higher results than by the bromide method. This was consistently shown in the determinations but, even so, the agreement was quite good.

The results of the analyses are shown in Table I and Fig. 1. The solubility of magnesium bromide at each temperature is the average of at least two individual samples taken from separate preparations. The more important

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(1) Presented before the Inorganic Division of the American Chemical Society at Kansas City, Mo., April, 1936.

(2) "International Critical Tables," New York, Vol. IV, 1928, p. 203.

(3) B. N. Menschutkin, *Z. anorg. Chem.*, **49**, 34 (1906).

(4) W. V. Evans and H. H. Rowley, THIS JOURNAL, **52**, 3523 (1930).

(5) N. Zelinsky, *Chem. Zentr.*, **74**, II, 277 (1903).

Table I

Solubility of $MgBr_2$ in Ethyl Ether

Temp., °C.	Solubility, g. $MgBr_2$/100 g. Et_2O	Temp., °C.	Solubility, g. $MgBr_2$/100 g. Et_2O
Equilibrium Phase:	Crystalline		
—20	0.27	+13.0	1.47
−10	.40	+15.0	1.76
0	.70	+16.5	1.99
+3.0	.84	+18.0	2.14
+7.8	1.05	+20.0	2.52
+10.1	1.19		
Equilibrium Phase:	Immiscible Liquid		
0	2.16	+24.9	3.20
+13.1	2.62	+27.5	3.33
+20.0	2.95	+32.0	3.63

points such as at 0, +16 and +25° were checked by analysis of five or more samples. During the course of the investigation, well over 150 separate preparations were made. The accuracy of the points is ±0.05 g. of magnesium bromide per 100 g. of ether.

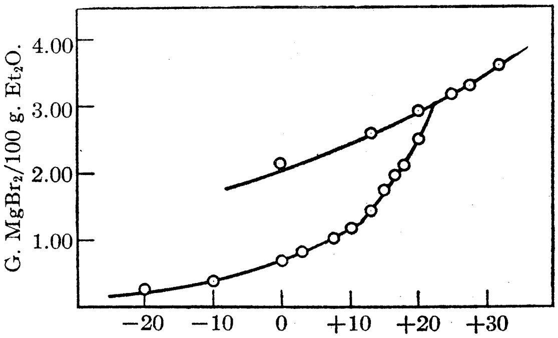

Fig. 1.—Solubility of $MgBr_2$ in ethyl ether.

Factors Influencing Purity

It was found during the investigation that high and inconsistent results were frequently encountered. The possibility of impure reagents was eliminated inasmuch as inconsistent results were often obtained using identically the same materials in successive runs. Since moisture was known to decompose the etherates,[4,6] this was one of the first factors to be investigated.

Effect of Moisture during the Preparation.—Dry, freshly distilled ether was mixed with a known quantity of water and this moist ether was then used in preparing the magnesium bromide solutions in the usual manner. The reaction of bromine on the magnesium was always immediate with moist ether, whereas dry ether required a minute or more before a reaction was visible. With wet ether there appeared to be a gas given off even when the solution was cold. The results of a series of analyses at +24.9° are given in Table II. Small amounts of moisture in the ether during the preparation do not appear to affect the apparent solubility.

Effect of Moisture after the Preparation.—The magnesium bromide was prepared in the usual manner using dry ether. The immiscible layer was crystallized by cooling and the original solution decanted. Ether with a known moisture content was added, the crystals melted and the solution saturated at +24.9°. The amount of magnesium bromide in solution was determined both by the magnesium sulfate and the silver bromide methods. The results of the series are given in Table III and show that the presence of moisture, after the solutions are prepared, definitely raises the apparent solubility of the magnesium bromide.

Table II

Effect of Moisture during Preparation

Analysis at +24.9°

Sample no.	Mols. H_2O/liter Et_2O	Solubility, g. $MgBr_2$/100 g. Et_2O	Remarks
55	0.0001	3.34	Prepd. in daylight
58	.0005	3.36	Prepd. in daylight
60	.01	3.36	Prepd. in daylight
73	.01	3.20	Prepd. in semi-darkness

Table III

Effect of Moisture after the Preparation

Analysis at +24.9°

Sample	Moles H_2O/liter Et_2O	$MgBr_2$/100 g. Et_2O Mg analysis	Br analysis
75	0.001	3.43	3.42
74	.005	3.51	3.45
71	.01	3.59	3.52
59	.02	3.68	3.57

To overcome this source of error, the apparatus and reagents were carefully dried and the reaction flasks fitted with calcium chloride tubes. During the preparation and recrystallization, the flasks were never opened except in an atmosphere of air dried by calcium chloride and concentrated sulfuric acid.

Effect of Light during the Preparation.—The fact that the solubility of the magnesium bromide could be lowered to a constant value by careful recrystallization from fresh ether, indicated that the apparent high solubilities frequently obtained were due to certain conditions existing during the preparation. There seemed to be good indications that ether, not freshly distilled, caused high results but frequently freshly distilled ether also gave somewhat high values not traceable to moisture. In practically all these cases, when the sample was poured into water and the ether boiled off, there was a more or less strong odor of some organic compound or compounds, frequently lachrymatory in nature, that was difficult to boil out of solution. This organic material caused the silver bromide precipitate to be oily and to stick to the side of the beaker. That the high results were not due exclusively to inclusion of this organic material in the silver bromide, is shown by parallel magnesium determinations which also were high. Since the magnesium sample was evaporated to dryness (residue dark when organic matter is present, white when not) then treated with concentrated sulfuric acid and heated to redness, all the organic matter including the combined ether was destroyed.

Believing that this organic matter might be formed by the action of bromine on ethyl ether in the presence of light, a series of runs was made to test this. The room was partially darkened and the sample exposed to strong light

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(6) B. N. Menschutkin, *Chem. Zentr.*, **77**, I, 646 (1906).

for definite intervals during the preparations. A 200-watt daylight gas-filled lamp set in a 30-cm. silver reflector was used as a light source and the sample flask held 15 cm. from the bulb. It was noticed that, during the exposure to a strong light, a gas was given off even though the solution was below room temperature.

During several runs when the concentration of bromine was rather high and the reaction was vigorous, the two-layer system would appear normal after the free bromine color had disappeared but almost immediately the heavy immiscible layer would begin to darken. In ten or fifteen minutes it would be a deep purple and the upper ether layer would acquire a light purple color. On further standing for an hour or so, this would fade to a green and finally the immiscible layer would become clear yellow and the ether layer colorless. During these color changes, the liberation of a gas frequently was observed. In all such cases, the analyses were very high and showed the presence of a large amount of high-boiling organic material. The results of the experiments with light are shown in Table IV. When the strong light was not in use, the samples were not in total darkness but were not exposed to any direct daylight.

TABLE IV

EFFECT OF LIGHT DURING THE PREPARATION

ANALYSIS AT +24.9°

Sample	Exposure to strong light	G. $MgBr_2$/100 g. Et_2O Mg analysis	Br analysis	Remarks
62	None	3.38	3.34	Reaction violent; no color changes
63	None	3.41	3.29	
65	None	3.37	3.23	
66	None	3.28	3.18	
71	None	3.34	3.30	
74	None	3.34	3.30	
64	1 min.	3.22	3.20	
67	1 min.	3.36	3.34	
70	1 min.	3.32	3.29	
69	2 min.	3.53	3.51	Reaction violent; color changes
76	3 min.	3.42	3.43	Slight color changes.
77	3 min.	3.29	3.24	Less Br_2 concn. than No. 76
61	15–20 min.	3.59	3.61	Color changes

A few rough experiments were performed to determine whether ethyl ether did react with liquid bromine to a certain extent in the presence of light. Ether that had been distilled about six days previously and kept over sodium in semi-darkness was used. In total darkness 50 cc. of this ether and 1.8 g. of bromine still showed a strong bromine color after five days. However, exposure of this sample to a strong light caused the color to disappear in less than two hours. Another 75-cc. portion took up about 0.9 g. of bromine in a few hours in daylight giving a colorless solution and another gram of bromine more slowly on exposure to the 200-watt lamp. When colorless, this sample reacted vigorously with magnesium giving a homogeneous solution. Analysis of this solution showed a concentration of 0.0125 mole of magnesium and 0.0135 mole of bromine per 100 g. of solution. There was considerable organic material in both samples.

Discussion

Examination of Fig. 1 shows two discontinuities in the solubility curve of magnesium bromide, one at about +22.5° the other, less distinct, at about 12°. If it is assumed that the heat of solution remains constant over this temperature range, a plot of the logarithm of the solubility against the inverse absolute temperature should give a straight line as long as the phase in equilibrium with the solution does not change. Plotting in this manner, in Fig. 2, straight lines are obtained and show very distinctly a change of crystal phase between +11 and +12°. The solid phase in equilibrium with the ether solution along the line AB is magnesium bromide triethyl etherate.[4]

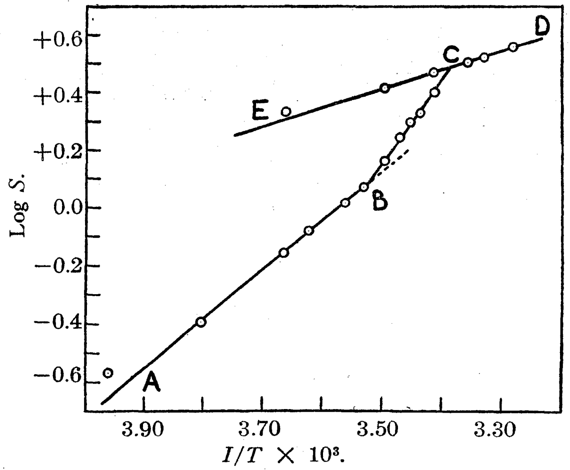

Fig. 2.—Solubility of $MgBr_2$ in ethyl ether.

At approximately +12° (B) the trietherate decomposes to form magnesium bromide diethyl etherate which is the solid phase in equilibrium along BC. The dietherate, which in the absence of excess ether exists to +28°,[3,4] reacts with excess ether at +22.6° (C) and forms an immiscible liquid layer which is the phase in equilibrium along CD. As noted previously, this liquid can be greatly supercooled and the solubility in the metastable state below +22.6° follows along CE.

Though Menschutkin[3] made only a few measurements below +10°, when his data are plotted in the same manner as Fig. 2, a break is also obtained at about +12°. The transition temperature of magnesium bromide triethyl etherate at +12 ± 0.5° as determined from the solubility data agrees very well with the value of +13 ± 0.5° found by Evans and Rowley[4] from vapor pressure measurements. Likewise, the change to a liquid phase of the diethyl etherate of magnesium bromide under ether, as determined in this work, checks Menschutkin's value to within a few tenths of a degree.

From the slope of the lines AB and BC (Fig. 2), the heat of solution of one mole of the crystal phase in an almost saturated ethyl ether solution can be calculated. Thus, the average differential heat of solution is −4.03 kcal. for magnesium bromide triethyl etherate over the temperature range −20 to +10°, while the average differential heat of solution is −6.47 kcal. for the diethyl etherate from +12 to +22°.

The determination at 0° when the immiscible layer is in equilibrium with the solution is known to be somewhat high. It was frequently difficult to obtain absolutely pure samples without recrystallizing the magnesium bromide and since there is little supercooling in a sample that has once been crystallized, the metastable points below +22.6° had to be obtained with fresh samples. Quite a number of samples had to be prepared before the points at +13 and +20° were obtained. Even so, all the values obtained were considerably lower than those found by Menschutkin and reported in the "International Critical Tables"[2] amounting to an average difference of 0.1 g. $MgBr_2$/100 g. Et_2O for the trietherate; 0.2–0.3 g. $MgBr_2$/100 g. Et_2O for the dietherate; and 0.4–0.5 g. $MgBr_2$/100 g. Et_2O for the immiscible layer. Experimental values taken from the smooth curve and compared to the literature values are given in Table V.

TABLE V

SOLUBILITY OF $MgBr_2$ IN ETHYL ETHER

Temp., °C.	G. $MgBr_2$/100 g. Et_2O	Moles % $MgBr_2$ Experimental	"I. C. T."
Solid Phase: $MgBr_2 \cdot 3(C_2H_5)_2O$			
−20	0.22	0.09	..
−10	.40	.16	0.24 (−8°)
0	.70	.28	.32
+10	1.18	.47	.52
Solid Phase: $MgBr_2 \cdot 2(C_2H_5)_2O$			
+14	1.58	0.65	0.67
+16	1.84	.74	.79
+18	2.14	.85	.94
+20	2.50	.99	1.10
+22	2.91	1.16	1.32
Immiscible Liquid Phase			
0(m)	2.04	0.82	0.94
+10(m)	2.47	0.98	1.14
+20(m)	2.95	1.17	1.36
+30	3.49	1.38	1.56

The effect of moisture on the purity of the sample shows, in Table II, that the presence of a slight amount of moisture during the preparation does not materially affect the result. This might be expected since the free bromine would probably combine with the water to give hydrobromic acid which would react immediately with the magnesium, forming magnesium bromide and free hydrogen.

However, the presence of traces of moisture after the magnesium bromide is prepared affects the apparent solubility as shown in Table III. It is well known that water will displace completely the ethyl ether from etherates.[4,6] Possibly small amounts of water would displace only part of the solvated ether, giving rise to mixed solvates. These mixed solvates might be expected to be somewhat soluble in ether and in turn have little effect on the solubility of unchanged magnesium bromide etherate so that the net result would be an increase of magnesium and bromide in the solution. The analysis of magnesium by magnesium sulfate and of bromide by silver bromide would not distinguish between these two compounds in solution. In all cases when moist ether was used to crystallize the magnesium bromide, there appeared to be a white solid mixed with the immiscible layer. Menschutkin[6] claimed that small amounts of water give $Mg(OH)Br \cdot MgBr_2 \cdot 2(C_2H_5)_2O$ which is practically insoluble in ethyl ether. Possibly this compound is more soluble than he thought.

Summary

1. The solubility of magnesium bromide in ethyl ether was measured from −20 to +30°.

2. Two discontinuities in the solubility curve were found: one at +12 ± 0.5° where $MgBr_2 \cdot 3(C_2H_5)_2O$ decomposes to form $MgBr_2 \cdot 2(C_2H_5)_2O$; the other at +22.5 ± 0.5° where $MgBr_2 \cdot 2(C_2H_5)_2O$ melts under ether to form an immiscible liquid layer.

3. The average differential heat of solution for $MgBr_2 \cdot 3(C_2H_5)_2O$ over the temperature range −20 to +10° was calculated to be −4.03 kcal. The average differential heat of solution for $MgBr_2 \cdot 2(C_2H_5)_2O$ from +12 to +22° was calculated to be −6.47 kcal.

4. The values of the solubility of magnesium bromide were found to be consistently lower than those reported in the "International Critical Tables."

5. The purity of the magnesium bromide prepared in ethyl ether solutions was studied and it was found that traces of moisture during the prepa-

ration had little effect on the solubility values, whereas the presence of very small amounts of water after the preparation was complete caused an increase in the apparent solubility.

6. The effect of light during the preparation was studied and the conclusion reached that bromine reacted to a certain extent with recently distilled ethyl ether in the presence of light giving rise to side reactions and impurities.

EVANSTON, ILLINOIS RECEIVED APRIL 13, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. LOUIS UNIVERSITY]

A Study of Some Reactions between Dry Inorganic Salts. III*

BY E. B. THOMAS WITH LYMAN J. WOOD

In two previous papers[1,2] the authors have reported results obtained from a study of a few of the possible reactions occurring between the dry alkali halides in the fused state. The remaining 42 of the 60 possible reactions have now been studied and some of the previously reported reactions have been studied in greater detail. Also 12 new salt pairs having a common ion have been examined in order to determine in which cases solid solutions can be formed. These solid solubility relationships as well as the course of the reactions mentioned above have been determined by the method of x-ray crystal analysis.

The general plan of the work was very similar to that followed in the previous work. The material to be examined was melted and held in the molten condition for a short time, after which it was quenched and quickly placed in a desiccator to avoid the possible absorption of water. The mixture was then ground to a fine powder (approximately 200-mesh) and placed in a small, thin-walled glass tube of 0.6–0.7 mm. inside diameter, in which container it was exposed to the x-ray beam. The molybdenum K_α doublet, filtered through zirconia, was used for all exposures, the scattered rays being photographed according to the well-known powder method of Debye, Scherrer and Hull.

Those mixtures which showed a tendency to absorb water were handled in a "Dry Box" to which rubber sleeves were attached, or were ground in a mortar on a hot-plate from which the small tubes were filled. The chloride, bromide and iodide of lithium and the fluorides of rubidium and cesium were found to be extremely hygroscopic, and the fluoride of potassium moderately so.

Results

In order to supplement the table of miscibilities previously published,[2] all the binary mixtures of salts having a common ion, in which the percentage deviation from the mean cube edge is less than 10, have been examined in order to determine in which cases solid solutions are formed. The results obtained are shown in Table I. As is to be seen, no solid solutions have been observed in any case in which the per cent. deviation from the mean cube edge is greater than 8.20.

In Table II are assembled the results for the 42 new reactions not reported in the previous papers. These results were found to be in excellent agreement with the former findings. In each case the reaction goes to completion in such a direction that the average cube edge of the stable pair is less than that of the reciprocal pair. In each case the stable pair has the cation of smaller atomic weight united with the anion of smaller atomic weight, and the cation of larger atomic weight united with the anion of larger atomic weight. In each case the sum of the heats of formation of the stable pair is greater than that of the reciprocal pair. With the exception of the lithium salts one member of the stable pair always has the highest melting point of the four compounds involved.

It should be mentioned that the value for the cube edge of sodium bromide used in this paper is a little larger than the previously used value of 5.940 Å. which is listed by Wyckoff[3] as the favored value. A survey of the literature showed that Davey[4] reported a value of 5.936 Å. for the cube edge of sodium bromide, that Wyckoff[5] reported a value of 5.95 Å., while Ewald's "Structurbericht" lists the value of 5.962 Å. A very careful com-

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(*) Read at the Kansas City Meeting of the American Chemical Society.

(1) E. B. Thomas and Lyman J. Wood, THIS JOURNAL, **56**, 92 (1934).

(2) E. B. Thomas with Lyman J. Wood, *ibid.*, **57**, 822 (1935).

(3) Wyckoff, "The Structure of Crystals," Second edition, The Chemical Catalog Co., New York, 1931.

(4) W. P. Davey, *Phys. Rev.*, **21**, 143 (1923).

(5) R. W. G. Wyckoff, *J. Wash. Acad. Sci.*, **11**, 429 (1921).

TABLE I

SHOWING RESULTS OF X-RAY ANALYSIS OF BINARY MIXTURES HAVING A COMMON ION

Comp. in mol, %	Cube edges, Å.	[a]	Phase A	Phase B	Cube edge 50% solid soln., calcd.	Remarks
50LiCl	5.140	9.10	5.149		5.384	Completely immiscible
50NaCl	5.628			5.628		
50LiBr	5.489	8.20	5.489		5.724	Completely immiscible
50NaBr	5.959			5.948		
50LiI	6.000	7.41	6.049		6.231	Limited miscibility
50NaI	6.462			6.415		
50NaI	6.462	8.74	6.462		6.757	Completely immiscible
50KI	7.052			7.048		
50KF	5.328	5.51	5.469	Only one phase	5.479	Completely miscible
50RbF	5.630					
50KI	7.052	3.80	7.185	Only one phase	7.188	Completely miscible
50RbI	7.325					
50LiCl	5.140	6.57	5.310	Only one phase	5.315	Completely miscible
50LiBr	5.489					
50LiBr	5.489	8.90	5.491		5.745	Completely immiscible
50LiI	6.000			5.999		
50KBr	6.570	7.07	6.962		6.811	Limited miscibility
50KI	7.052			6.641		
50RbBr	6.868	6.45	7.092	Only one phase	7.091	Completely miscible
50RbI	7.325					
50CsBr	4.290	6.15	4.425	Only one phase	4.426	Completely miscible
50CsI	4.562					

[a] $(A_1 - A_2) \times 100/0.5(A_1 + A_2)$.

parison of sodium bromide with sodium chloride in our laboratory gave a value very near to 5.951 Å. Because of the greater density of the sodium bromide this value must be smaller than the value that would have been obtained by mixing the sodium chloride directly with the sodium bromide, which of course could not be done since the two salts are known to form solid solutions with each other. Some electrolytic copper was filed to a fine powder and mixed directly with the sodium bromide. Using a value of 3.605 Å. for the cube edge of copper, a value of 5.959 Å. was obtained for the cube edge of sodium bromide. This latter value has been substituted for the previously used value of 5.940 Å.

For reactions 31, 32, 33, 34, 39, 40, 41, 42, 52, 54 and 56, two interference patterns were obtained in each case which corresponded, respectively, to the pure components of the stable pair. In each of these cases it is known that at least one solid solution is formed between one of the components of the stable pair and one of the components of the reciprocal pair. It may be concluded that all of these reactions go to completion, since if such were not the case interference patterns corresponding to solid solutions would have been obtained, rather than the patterns corresponding to the pure components of the stable pair. In this way quite small amounts of unchanged components of reciprocal pairs could have been detected since very small changes in cube edges are easily measured.

The fact that reaction mixtures 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 43, 44, 45, 46, 47, 48, 49, 50 and 51 gave no evidence of becoming moist after fusion, despite the fact that at least one member of the reciprocal pair is definitely hygroscopic, may be regarded as an indication that reaction has proceeded to completion, although such evidence is not nearly as conclusive as that presented above.

No solid solutions are formed between the compounds involved in reactions 35, 36, 37, 38, 53, 55, 57, 58, 59 and 60. However, had reaction not gone to completion in these cases, four patterns should have been obtained instead of only the two which were observed. Although the mere absence of two patterns is not to be regarded as such satisfactory evidence for completeness of reaction as that described in the foregoing cases, it is very unlikely that both patterns (for the reciprocal pair) would be missed if present in even small quantities, since the scattering power of one member of the reactant pair compares favorably in each of these cases with that of one of the members of the stable pair.

TABLE II

RESULTS OF DOUBLE DECOMPOSITIONS

Reaction	Stable pairs	Accepted cube edge, Å.	Observed cube edges, Å. Phase I	Observed cube edges, Å. Phase II	Change in mean cube edge	Diff. in sums of hts. of formation
19	LiF	4.014	4.015		−0.059	
	NaCl	5.628		5.627		+10.18
20	LiF	4.014	4.014		− .087	
	KCl	6.280		6.281		+18.32
21	LiF	4.014	4.010		− .093	
	RbCl	6.570		6.571		+19.79
22	LiF	4.014	4.012		−1.512	
	CsCl	4.110		4.111		+22.53
23	LiF	4.014	4.018		−0.068	
	NaBr	5.959		5.943		+11.85
24	LiF	4.014	4.011		− .117	
	KBr	6.570		6.573		+21.74
25	LiF	4.014	4.014		− .118	
	RbBr	6.868		6.860		+24.56
26	LiF	4.014	4.016		−1.596	
	CsBr	4.290		4.292		+27.31
27	LiF	4.014	4.018		−0.072	
	NaI	6.462		6.461		+13.71
28	LiF	4.014	4.005		− .131	
	KI	7.052		7.052		+25.20
29	LiF	4.014	4.012		− .146	
	RbI	7.325		7.325		+18.01
30	LiF	4.014	4.018		−1.716	
	CsI	4.562		4.562		+32.33
31	LiCl	5.140	5.137		−0.009	
	NaBr	5.959		5.943		+ 1.67
32	LiCl	5.140	5.142		− .035	
	KBr	6.570		6.565		+ 3.42
33	LiCl	5.140	5.148		− .025	
	RbBr	6.868		6.860		+ 4.78
34	LiCl	5.140	5.138		− .084	
	CsBr	4.290		4.290		+ 4.68
35	LiCl	5.140	5.144		− .013	
	NaI	6.462		6.460		+ 3.33
36	LiCl	5.140	5.138		− .044	
	KI	7.052		7.050		+ 6.88
37	LiCl	5.140	5.136		− .553	
	RbI	7.325		7.320		+ 8.23
38	LiCl	5.140	5.140		− .204	
	CsI	4.562		4.562		+ 9.70
39	LiBr	5.489	5.486		− .004	
	NaI	6.462		6.456		+ 1.86
40	LiBr	5.489	5.488		− .014	
	KI	7.052		7.047		+ 3.47
41	LiBr	5.489	5.496		− .027	
	RbI	7.325		7.315		+ 3.47
42	LiBr	5.489	5.492		− .119	
	CsI	4.562		4.560		+ 5.02
43	NaF	4.620	4.618		− .028	
	KCl	6.280		6.268		+ 8.13
44	NaF	4.620	4.621		− .034	
	RbCl	6.570		6.565		+ 9.60
45	NaF	4.620	4.616		−1.453	
	CsCl	4.110		4.112		+12.45
46	NaF	4.620	4.621		−0.048	
	KBr	6.570		6.567		+ 9.89
47	NaF	4.620	4.620		−0.050	
	RbBr	6.868		6.858		+12.72
48	NaF	4.620	4.619		−1.528	
	CsBr	4.290		4.289		+15.46
49	NaF	4.620	4.626		−0.059	
	KI	7.052		7.048		+11.50
50	NaF	4.620	4.615		−0.073	
	RbI	7.325		7.317		+14.30
51	NaF	4.620	4.622		−1.644	
	CsI	4.562		4.562		+18.62
52	KF	5.328	5.330		−0.006	
	RbCl	6.570		6.561		+ 1.46
53	KF	5.328	5.330		−1.425	
	CsCl	4.110		4.111		+ 4.31
54	KF	5.328	5.331		−0.002	
	RbBr	6.868		6.859		+ 2.82
55	KF	5.328	5.322		−1.480	
	CsBr	4.290		4.289		+ 5.57
56	KF	5.328	5.331		−0.015	
	RbI	7.325		7.322		+ 2.80
57	KF	5.328	5.334		−1.585	
	CsI	4.562		4.561		+ 7.12
58	RbF	5.630	5.629		−1.419	
	CsCl	4.110		4.110		+ 2.85
59	RbF	5.630	5.630		−1.476	
	CsBr	4.290		4.288		+ 2.75
60	RbF	5.630	5.632		−1.570	
	CsI	4.562		4.560		+ 4.32

Of the eighteen reactions previously reported[2] three reactions (Nos. 10, 14 and 16) were found not to go to completion in the direction of the minimum average cube edge as did the other 15 reactions and as the 42 additional reactions, which have now been studied, have been found to go. Reaction No. 10

$$\mathrm{RbBr} + \mathrm{KCl} \rightleftharpoons \mathrm{KBr} + \mathrm{RbCl}$$

has not been further investigated since the data and discussion previously given appeared to be adequate. In the case of reaction No. 14

$$\mathrm{KBr} + \mathrm{RbI} \rightleftharpoons \mathrm{KI} + \mathrm{RbBr}$$

the interference lines were found to correspond to two phases of which the cube edge of phase I was 6.710 Å. and the cube edge of phase II was 7.165 Å. It has been found possible to calculate the composition of the equilibrium mixture by assuming that 6.710 Å. is the cubic edge of a binary solid solution of potassium bromide and rubidium bromide and 7.165 Å. is the cube edge of a ternary solid solution of potassium iodide, rubidium iodide and rubidium bromide. The calculations were carried out by solving the simultaneous equations

$$6.570\,\frac{x}{1-y} + 6.868\,\frac{1-x-y}{1-y} = 6.710$$

$$7.325\,\frac{x}{1+y} + 7.052\,\frac{1-x}{1+y} + 6.868\,\frac{y}{1+y} = 7.165$$

where x is the moles of potassium bromide in the binary solid solution and y is the moles of rubidium bromide in the ternary solid solution and the numbers 6.570, 6.868, 7.325 and 7.052 are the respective cube edges of potassium bromide, rubidium bromide, rubidium iodide and potassium iodide.

The results of the calculations are shown in Table III. The hypothesis upon which these calculations rest was tested in the laboratory by preparing and melting a mixture having the composition of 47.48 mol % potassium iodide, 45.80 mol % rubidium iodide and 6.72 mol % rubidium bromide. Upon analyzing this mixture the interference pattern indicated the presence of only one

TABLE III

SHOWING THE RESULTS AND CALCULATIONS FOR THE REACTION $KBr + RbI \longrightarrow KI + RbBr$ (REACTION NO. 14)

	Cube edge, Å.	Calculated molecular ratio	Composition in mol, %
Phase I	6.710	0.491:0.437 = KBr:RbBr	KBr 51.00 RbBr 49.00
Phase II	7.165	0.509:0.491:0.072 = KI:RbI:RbBr	KI 47.48 RbI 45.80 RbBr 6.72
Ternary mix having comp. of Phase II	7.172		

component having a cube edge of 7.172 Å., which is to be compared with the value 7.165 Å. which has been assumed to be the cube edge for a ternary solid solution of potassium iodide, rubidium iodide and rubidium bromide (Table III). The composition calculated for the equilibrium mixture is represented by the equation

$$0.491\ KBr + 0.491\ RbI \rightleftarrows 0.509\ KI + 0.509\ RbBr$$

It is quite interesting to note that the equilibrium mixture is very close to an equimolecular mixture of the four kinds of molecules and that there is only 0.02 kcal./mole difference in the sums of the heats of formation of the two reciprocal pairs.

The equilibrium mixture for reaction 16 was previously reported as being approximately

$$0.64\ RbCl + 0.64\ CsBr \rightleftarrows 0.36\ RbBr + 0.36\ CsCl$$

although the agreement between the equilibrium composition when calculated from phase I and when calculated from phase II was not very close. The average cube edge of phase I and phase II is smaller than the average cube edge of the pair RbBr–CsCl and greater than that of the pair RbCl–CsBr indicating that the reaction should probably go to completion in the direction of RbCl–CsBr. Several new laboratory determinations have been made but thus far the results obtained do not deviate from the values previously reported.

At the present time reactions occurring between the dry alkali halides below the fusion point are being studied. The free energy change has been calculated for one such reaction, *viz.*

$$NaBr + KCl \longrightarrow KBr + NaCl$$

and has been found to be

$$\Delta F = \Delta H - T\Delta S = -1.93 \text{ kcal./mole at } 25°$$

This calculation is in agreement with the x-ray evidence previously reported[2] for the reaction occurring between sodium bromide and potassium chloride below the fusion point.

The reaction

$$TlCl + KI \longrightarrow TlI + KCl$$

has been examined by Chernomordik,[6] using thermal methods and has been found to be irreversible in the direction indicated. The average cube edge of the pair TlCl–KI is 5.446 Å. and that of the pair TlI–KCl is 5.239 Å. Furthermore, the large cation is united with the large anion and the small cation with the small anion. This fact as well as the decrease in average cube edge is in agreement with the generalizations described above for 57 of the 60 reactions studied.

Summary

Reactions occurring between the dry halides of lithium, sodium, potassium, rubidium and cesium in the fused state have been studied.

1. Of the 60 possible reactions, 57 have been found to go completely in such a direction that the average cube edge of the stable pair is less than that of the reciprocal pair.
2. In each of these 57 cases the sum of the heats of formation of the stable pair is greater than the sum of the heats of formation of the reciprocal pair.
3. In each case the stable pair has the cation of larger atomic weight united with the anion of larger atomic weight, and the cation of smaller atomic weight united with the anion of smaller atomic weight.
4. In the case of the other three reactions in which there is either no difference in the average cube edge or no difference in the sum of the heats of formation of the stable and reciprocal pairs, equilibrium has been found to be established. In two of the three cases the equilibrium mixture was composed of very nearly equimolecular quantities of the four kinds of molecules involved in the reaction.

ST. LOUIS, MISSOURI RECEIVED APRIL 21, 1936

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[6] Chernomordik, *J. Gen. Chem.* (U. S. S. R.), **4**, 456–465 (1934).

[CONTRIBUTION FROM BEACON LABORATORY OF THE TEXAS COMPANY]

An Azeotropic Mixture of Acetylene and Ethane at Atmospheric Pressure

BY WALLACE A. MCMILLAN

During work on the development of precision methods for the analysis of complex hydrocarbon gases, considerable difficulty was encountered occasionally in the separation of ethylene from ethane by ordinary low temperature fractional distillation methods. Continued work on such separations resulted in the isolation of an azeotropic mixture of acetylene and ethane of minimum boiling point. The existence of such a mixture has been established previously[1] for high but not for low pressures. With the increasing use of low temperature fractionation as an analytical method it was felt that constants for the mixture, at atmospheric pressure and low temperature, should be established.

Experimental

Acetylene.—Commercial acetylene was washed successively with distilled water, 40% potassium hydroxide, and 30% sulfuric acid, then passed through soda-lime and dried with anhydrous magnesium perchlorate. The dried gas was condensed by liquid air in the kettle of a special low temperature fractionating column,[2] the fixed gases pumped off, and the acetylene distilled at 1.5 atmospheres, discarding both end fractions. Two subsequent distillations, discarding heads and tails, were made before use. Hydrogenation of the pure material gave a value of 100% for the unsaturation.

Ethane.—Commercial ethylene-free ethane was purified by successive washings through 30% fuming sulfuric acid, and 98 and 79% sulfuric acid, followed by two washings with 43% potassium hydroxide, a soda-lime tower, and dried by anhydrous magnesium perchlorate. It was likewise distilled through a special low temperature column, retaining only the middle portion each time. After four redistillations, the purified material showed a constant boiling point (−88.3°) and the end fractions showed constant vapor pressures when tested in a Shepherd differential manometer.[3] Hydrogenation of the pure material showed no unsaturation.

Mixtures.—Mixtures of the two components were made by blending in the gas phase in an evacuated all-glass system. They were then condensed into the kettle of a special low temperature fractionating column[2] and distilled. The first mixture, containing 70% ethane and 30% acetylene, distilled at −94.5° until 73.5% had come over, at which point the temperature broke sharply to −88.3° and the remainder of the ethane came over at that temperature. In the case of a 70% acetylene–30% ethane mixture, 50.2% distilled at −94.5° at which point the column froze solid with acetylene and it was necessary to go to 1.5 atmospheres to continue the distillation.

When analyzed by catalytic hydrogenation of the acetylene over a reduced nickel catalyst,[4] each of the azeotropic mixtures boiling at −94.5° gave 40.8% acetylene and 59.2% ethane. Check determinations on five additional samples distilled at pressures from 752 to 766 mm. gave a boiling range of −94.5 ± 0.1° and a composition range of: acetylene, 40.75 ± 0.25%; ethane, 59.25 ± 0.25%.

Redistillations of the constant boiling mixtures did not change either the boiling points or compositions.

An azeotropic mixture isolated from reformed refinery gases gave, after redistillation, a boiling point of −94.4° and a composition of: acetylene, 40.7%; ethane, 59.3%; thus checking the existence and identity of the mixture.

Discussion

The isolation and identification of this mixture is of interest inasmuch as reports in the technical literature show acetylene determined by auxiliary reagent methods even though no acetylene had been observed on fractional distillation of the sample.[5] This phenomenon can be accounted for by the analysts disregarding irregularities usually found in Podbielniak distillations, especially when run at accelerated rates. It also explains, at least in part, the appearance of so-called "carbon dioxide plugs" which develop from time to time during ethane separations even though the original gases have been scrubbed with fresh caustic. The white solid which separates in such cases is usually not carbon dioxide but acetylene and can be identified by Ilosvay solution[6] or some other acetylene reagent.

Summary

The existence and composition of an azeotropic mixture of acetylene and ethane at atmospheric pressure have been determined.

BEACON, N. Y. RECEIVED MAY 12, 1936

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[1] Kuenan, *Phil. Mag.*, **40**, 173 (1895); **44**, 174 (1897); *Z. physik. Chem.*, **24**, 667 (1897).

[2] McMillan, U. S. Patent 2,005,323.

[3] Martin Shepherd, *Bur. Standards J. Research*, **2**, 1156 (1929).

[4] McMillan, Cole and Ritchie, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 105 (1936).

[5] Groll, *Ind. Eng. Chem.*, **25**, 784 (1933); Frey and Hepp, *ibid.*, **25**, 441 (1933); *et al.*

[6] Pietsch and Kotowski, *Z. angew. Chem.*, **44**, 509 (1931).

[Contribution from the Chemical Laboratory of the University of Missouri]

Reaction of Esters with Ammonia[1]

By H. E. French, O. H. Johnson and Eula Ratekin[2]

Numerous reports appear in the literature on the effect of structural variations on the reactivities of esters. In this connection it seemed of interest to determine the effect on the ease of reaction with ammonia caused by varying the structure of the alcohol radical of the ester. Preliminary experiments showed no reaction between the esters and gaseous ammonia at 100° and under pressures up to 8 atmospheres. Somewhat milder conditions with small amounts of water also present, likewise failed to cause reaction. It was therefore decided to use an aqueous alcohol solution of ammonia as the reagent, although the presence of the water would undoubtedly cause a certain amount of hydrolysis as a side reaction.

Reagents.—The reagent used was a forty per cent. solution (by weight) of alcohol in water, saturated at 25–30° with ammonia.

The *n*- and *i*-butyl acetates were prepared by refluxing one mole of the alcohol with one and one-half moles of the acid. Six cc. of concentrated sulfuric acid per 100 cc. of the mixture was also present. After six to eight hours of refluxing, the esters were washed with water, dried over anhydrous calcium chloride, over potassium carbonate, then fractionated through a 90-cm. column filled with glass rings.

The *s*-butyl acetate was prepared by refluxing a mixture of acetic anhydride and acetic acid with 0.6 cc. of concentrated sulfuric acid per 100 cc. of the mixture. The ester was purified by the process used with the normal ester.

The tertiary butyl acetate was prepared by refluxing equal volumes of the alcohol and acetic anhydride with one gram of zinc dust for a period of ten to twelve hours. The ester was purified in the manner described above. The boiling points and densities at 25° for the esters were as follows: *n*-butyl acetate, 123.7–123.8° at 737 mm., 0.8734; *i*-butyl acetate, 116.1–116.3° at 741 mm., 0.8683; *s*-butyl acetate, 110.4–111.2° at 740 mm., 0.8627; *t*-butyl acetate, 95.3–95.7° at 737 mm., 0.8654.

Procedure.—Two volumetric flasks of 250-cc. capacity were used for each ester. Twenty-five cc. of ester, measured with a pipet, was placed in each flask, which was then filled to the mark with the aqueous ethyl alcohol solution of ammonia. The reaction mixtures were kept at 25°, and at twenty-four-hour intervals, 50-cc. portions were removed by means of a pipet and diluted with 70 cc. of water. This usually caused the separation of unused ester. In order to remove the excess of ammonia, the solutions were heated to 65–70° on a water-bath and a rapid stream of purified air was bubbled through them till there was no further test with litmus.

The solutions were then diluted to 100 cc. in volumetric flasks and 25-cc. portions were analyzed for ammonium acetate and acetamide in the following manner. Each sample was placed in a Kjeldahl flask, diluted to a volume of 300 cc., and a paste consisting of 2 g. of magnesium oxide in 20 cc. of water was added. The ammonia liberated from the ammonium acetate was distilled into standard acid and the excess acid titrated with 0.1 *N* base. The contents of the Kjeldahl flask were then cooled, again diluted to 300 cc., and 20 cc. of 40% sodium hydroxide solution was added and the solution was boiled. The ammonia liberated by the hydrolysis of the acetamide was distilled into standard acid and determined in the usual manner. This analytical procedure[3] gave results on known solutions of acetamide of less than 0.2% error, indicating but little hydrolysis during the distillation with the magnesium oxide. Each determination was made in duplicate from different original reaction mixtures.

When the samples for analysis were diluted with water, unused ester usually separated. As would be expected, the heating to 65° to remove the ammonia caused additional reaction. In order to correct for this, blank determinations were run. Each sample analyzed contained 5 cc. of ester or the reaction products from that amount. Therefore, samples of 5, 3 and 1 cc. would represent the amounts of ester remaining when reaction had proceeded 0, 40 and 80% toward completion. In making the blank determinations, these quantities, 5, 3 and 1 cc. of each ester were dissolved in

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[1] Presented at the Kansas City meeting of the American Chemical Society, April, 1936.

[2] This paper is an abstract of the theses submitted by Mr. Johnson and Miss Ratekin in partial fulfilment of the requirements for the degree of Master of Arts at the University of Missouri.

[3] Pucher, Vickery and Leavenworth, *Ind. Eng. Chem., Anal. Ed.*, **7**, 152 (1935).

enough of the original aqueous ethyl alcohol solution of ammonia to make a volume of 50 cc. (the amount always taken for analysis), then diluted with 70 cc. of water, aerated at 65° and analyzed for acetamide and ammonium acetate. The blanks were run in duplicate, and the averages of the results were plotted. The analysis of any sample from a run indicated the extent of reaction and by reference to the graph the necessary correction could be made. Acceptable results could be obtained from this part of the procedure only by a careful control of conditions, such as the size of the openings in the water-bath, rate of the air current, etc.

The results are summarized in the accompanying graphs. With the exception of the *t*-butyl acetate, the reactions of each ester are represented by two pairs of curves. The lower pair represents the hydrolysis reaction in each case, and the upper pair the ammonolysis reaction. In any pair of curves, the upper curve corresponds to the total reaction as determined by the analyses. The lower curve is obtained by subtracting the corrections as described above, and represents the reaction taking place at 25°. With the *t*-butyl acetate, the corrections, which are not shown on the graph, were of the same order of magnitude as those for the *s*-butyl ester. Each point on each curve is an average of two determinations made from different reaction mixtures, rather than from two samples of the same reaction mixture. The agreement among the check determinations was good, showing a variation in two-thirds of the cases of less than 0.5%. The products from the reactions at 25° from the different esters were distributed as indicated in the table.

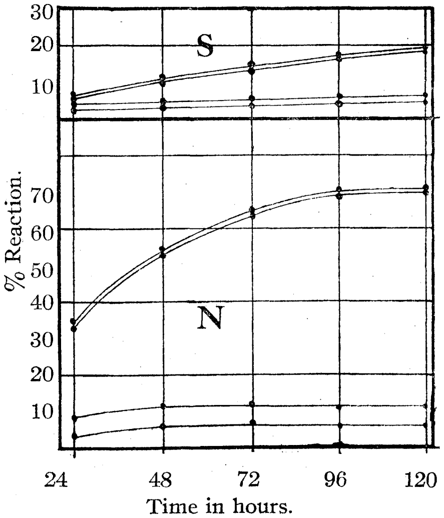


Fig. 1a.—S, *s*-butyl acetate; N, *n*-butyl acetate.

TABLE I

REACTION PRODUCTS FORMED AT 25°

Ester	Hours	% yield amide	% yield salt	Ratio amide : salt[a]
n-Butyl acetate	120	69.7	6.1	11.4:1
Isobutyl acetate	120	68.8	7.7	8.9:1
s-Butyl acetate	120	18.6	4.8	3.8:1
t-Butyl acetate	360	2.9	2.1	1.4:1

[a] These were the ratios at the end of the reaction period.

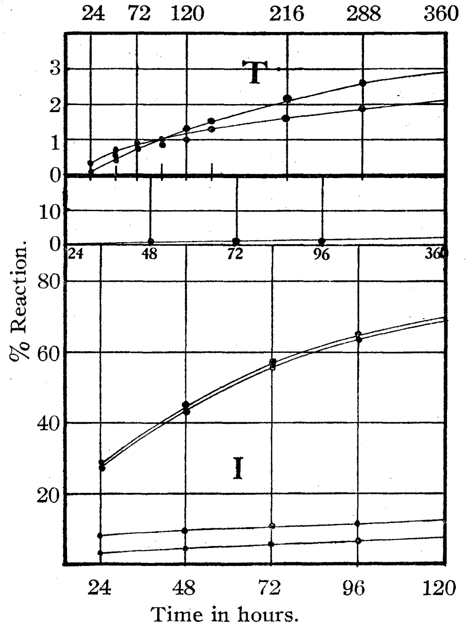


Fig. 1b.—T, *t*-butyl acetate; I, *i*-butyl acetate.

Summary

1. The action of aqueous ethyl alcohol solutions of ammonia on the four butyl acetates was studied.

2. The relative reactivities of the primary, secondary and tertiary butyl acetates toward ammonia was found to be of the order of 24:6:1.

3. A certain amount of hydrolysis took place in each reaction, and increased in importance with the secondary and tertiary butyl acetates.

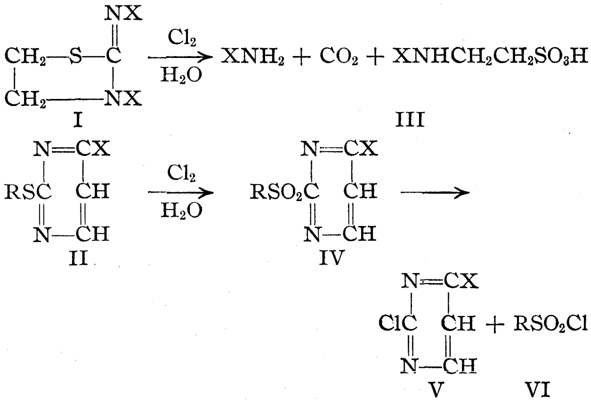
COLUMBIA, MISSOURI RECEIVED APRIL 30, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

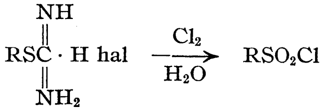
A New Method for the Preparation of Alkyl Sulfonyl Chlorides

BY TREAT B. JOHNSON AND JAMES M. SPRAGUE[1]

2-Imido-4,5-dihydrothiazoles I (X = H, CH_3, etc.) and 2-mercaptopyrimidines II (R = CH_3, C_2H_5, etc., X = H, CH_3, C_2H_5) are characterized by their chemical behavior when subjected to the action of chlorine and bromine in aqueous solution. The thiazoles[2] I undergo complete degradation by the action of either of these halogens with formation of an amine, carbon dioxide, and a taurine derivative III. A mercaptopyrimidine II interacts with chlorine under the same experimental conditions to give the corresponding sulfone derivative IV without degradation of the pyrimidine ring. This reaction with chlorine proceeds still further in the case of certain mercaptopyrimidines leading to replacement of the sulfone grouping by halogen V and formation of an alkyl sulfonyl chloride VI. Furthermore, it has been shown that this oxidation reaction is applicable to both 2- and 6-mercaptopyrimidines[3] yielding the corresponding sulfones, respectively.



Because of the similarity in constitution of the imido-4,5-dihydrothiazoles I and the 2-mercaptopyrimidines II, respectively, and the accepted ammonium structure of the S-alkyl-isothiourea salts[4] VII, the behavior of these latter acyclic substances toward chlorine has now been investigated. We find, when chlorine gas is passed into a cold aqueous solution of these S-alkyl-isothiourea salts VII, that the corresponding alkyl sulfonyl chlorides VI are formed in good yields. In fact, this method of synthesis opens up a new and practical procedure for the replacement of a halogen atom in an aliphatic halide by the sulfonyl chloride grouping ($-SO_2Cl$). If bromine is used instead of chlorine the corresponding sulfonyl bromide ($-SO_2Br$) is formed. This process introduces thiourea in place of phosphorus halide as the key reagent for the preparation of aliphatic sulfonyl chlorides, and also furnishes an interesting and instructive field for further study, which hitherto has received little notice. This program will receive further attention in this Laboratory.[5]


VII VI

$$\mathrm{RS}\overset{\overset{\displaystyle \mathrm{NH}}{\|}}{\underset{\underset{\displaystyle \mathrm{NH_2}}{\|}}{\mathrm{C}}}\cdot\mathrm{H\ hal}\ \xrightarrow[\mathrm{H_2O}]{\mathrm{Cl_2}}\ \mathrm{RSO_2Cl}$$

Rathke[6] observed the formation of ethylsulfonic acid from S-ethyl-N,N-diphenyl-isothiourea salts by the action of chlorine or bromine. The formation of sulfonic acids from S-alkyl-isothioureas by oxidation with potassium chlorate is also reported in the literature.[7] The direct formation of alkyl sulfonyl halides by the action of halogen on S-alkyl-isothiourea salts has not, however, been previously reported. The cleavage of a carbon–sulfur linkage by chlorine with the formation of an alkyl sulfonyl chloride or sulfonic acid has been observed with other types of sulfur compounds.[8]

The yields of alkyl sulfonyl chlorides obtained from the various alkyl-isothiourea salts are given in Table I. Since bromine also reacts with these salts to form alkyl sulfonyl bromides, it was necessary first to remove the hydrobromic acid when using the hydrobromide salts for preparation of sulfonyl chlorides by treatment with chlorine gas.

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[1] Sterling Professorship of Chemistry Research Assistant, 1935–1936.

[2] (a) Gabriel, *Ber.*, **22**, 1142 (1889); (b) Avenarius, *ibid.*, **24**, 266 (1891); (c) Andreasch, *Monatsh.*, **8**, 411 (1888); see also *Ber.*, **23**, 158 (1890).

[3] Sprague and Johnson, THIS JOURNAL, **57**, 2252 (1935); **58**, 423 (1936).

[4] (a) Taylor, *J. Chem. Soc.*, **111**, 650 (1917); (b) Werner, *ibid.*, **57**, 283 (1890); (c) Wheeler and Merriam, *Am. Chem. J.*, **29**, 482 (1903); (d) Wheeler and Bristol, *ibid.*, **33**, 440 (1905); (e) Lecher *et al.*, *Ann.*, **438**, 169 (1924); **445**, 35, 77 (1925).

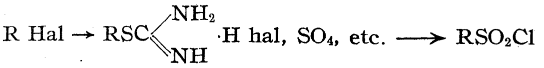
[5] United States patent application, Serial No. 72983, filed April 6, 1936.

[6] Rathke, *Ber.*, **14**, 1774 (1881).

[7] (a) Andreasch, *Monatsh.*, **1**, 446 (1880); **4**, 131, 142 (1883); (b) Kucera, *ibid.*, **35**, 145 (1914).

[8] (a) Spring and Winssinger, *Bull. soc. chim.*, [2] **49**, 72 (1888); *Ber.*, **15**, 447 (1882); (b) Gabriel and Heymann, *ibid.*, **23**, 158 (1890); (c) Gabriel, *ibid.*, **22**, 1154 (1889).

TABLE I



$$\mathrm{R\ Hal} \rightarrow \mathrm{RSC}\begin{matrix}\nearrow \mathrm{NH_2}\\ \searrow \mathrm{NH}\end{matrix}\cdot\mathrm{H\ hal,\ SO_4,\ etc.} \longrightarrow \mathrm{RSO_2Cl}$$

R =	Salt Acid =	Yield, %	B. p. or m. p., °C.	Mm.	n^{25}D
CH_3—	SO_4	76	B. 60.5–61.5	21	1.4490
C_2H_5—	Cl	66			
	Br[a]	82	B. 77–77.5	26	1.4506
	SO_4	78			
i-C_3H_7—	Cl	40	B. 74–75	19	1.4525
	Br[a]	54			
i-C_4H_9—	Br[a]	53	B. 73–75	11	1.4520
n-C_7H_{15}—	Br[a]	50	B. 124–126	9	1.4564
	Acetate	80			
1,2-C_2H_4—	Br[a]	63	M. 91–92		
	Cl	74			
	Acetate	72			
$C_6H_5CH_2$—	Cl	92	M. 91–92		
	SO_4	96			
	NO_3	91			
$C_6H_5CH_2CH_2$—	Cl	89–95	B. 121–123 M. 32–33	3	1.5390^{35}

[a] The bromine was removed with an equivalent of silver nitrate before treatment with chlorine.

Otherwise a mixture of sulfonyl chloride and bromine was obtained.[9]

With branched alkyl groups, as isopropyl and isobutyl, lower yields of sulfonyl halides were obtained. Both the low (148°) and the high melting (174°) forms of S-benzyl-isothiourea hydrochloride[4a,e] behaved identically on chlorination.

Although the S-alkyl-isothiourea[4] hydrobromides are easily prepared from the alkyl bromides and thiourea, the simple alkyl chlorides react very slowly with thiourea under similar conditions.[10] Since the practicability of the method here described for the preparation of alkyl sulfonyl chlorides depends on the ease of preparation of the S-alkyl-isothiourea salts, an attempt was made to improve the preparation of the hydrochlorides. This may be accomplished by heating the respective alkyl chloride with thiourea in an autoclave (see ethyl and isopropyl, Table II). However, a more convenient process is that used by Stevens[10] for the preparation of S-ethyl-isothiourea hydrochloride. This investigator found that this salt could be obtained by heating thiourea hydrochloride with ethyl alcohol. We have now found that this procedure may be applied with success to the higher aliphatic alcohols.

$$\mathrm{ROH + HCl + NH_2CSNH_2 = \underset{VII}{RSC({=}NH)NH_2 \cdot HCl}}$$

The S-alkyl-isothiourea hydrochlorides VII were not isolated from this reaction but were treated directly with chlorine in aqueous solution. The maximum yields of sulfonyl chlorides were obtained after heating the above reaction mixture for three or four days on a steam-bath. The lower yields of ethyl, isopropyl and isobutyl compounds may be attributed to several factors, such as temperature of the reaction, boiling point of the alcohol, volatility of the alkyl chloride and the effect of a branched chain (compare Table I). The results of this method are summarized in Table II. The yields are based on the amount of thiourea used.

Methyl, ethyl and *n*-heptyl sulfonyl bromides were prepared by the action of bromine on the corresponding S-alkyl-isothiourea salts in yields of 43.5, 64.8 and 36%, respectively.

The identity of the nitrogenous product resulting from the preparation of the alkyl sulfonyl halides from S-alkyl-isothioureas, and the mechanism of these transformations, are being studied further and will be discussed in a future paper from this Laboratory.

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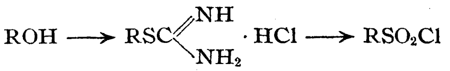
(9) In our first experiments silver nitrate was employed to replace the bromine ion, thereby forming the corresponding isothiourea nitrate which reacted smoothly with chlorine. This method of precipitation, however, cannot be recommended for practical synthesis and we have found that organic acid salts of isothiourea serve our purpose well when bromine is a conflicting reagent. Very little attention has been paid to the study of this class of salts but we have found in this Laboratory that they can perform a practical service in many operations. Treatment of an alkyl-isothiourea hydrobromide, for example, with potassium acetate leads to the quantitative formation of the acetate of the alkylisothiourea which interacts smoothly with chlorine to give the desired alkyl sulfonyl chloride. Other organic acid salts react in a similar manner and with production of the sulfonyl chlorides in excellent yields. The description of a series of these characteristic organic acid salts is given in a paper from This Laboratory by Dr. John J. Donleavy (THIS JOURNAL, **58**, 1004 (1936)).

(10) Stevens, *J. Chem. Soc.*, **81**, 79 (1902).

TABLE II



$$\mathrm{ROH} \longrightarrow \mathrm{RSC}(=\mathrm{NH})\mathrm{NH_2}\cdot\mathrm{HCl} \longrightarrow \mathrm{RSO_2Cl}$$

R =	Hours	Yield, %	B. p., °C.	Mm.	$n^{25}\mathrm{D}$
C_2H_5—	72	30	70–71	20	1.4508
	120	61			
n-C_3H_7—	24	50	66–68	9	1.4518
	48	72			
	120	82			
i-C_3H_7—	120	15.5	61–62	9	1.4522
n-C_4H_9—	120	47	73–75	10	1.4517
i-C_5H_{11}—	24	54	87–88.5	9	1.4530
	48	76			
	72	81			
	120	83			

Experimental Part

S - Alkyl - isothiourea Salts, $RSC(NH_2)=NH\cdot HCl$.—The following salts which were used in this investigation have been prepared previously: S-methyl-isothiourea sulfate,[4a] S-ethyl-isothiourea sulfate,[4a] S-ethyl-isothiourea hydrobromide,[4c] S-isobutyl-isothiourea hydrobromide,[4d] S,S-ethylenedi-isothiourea hydrobromide,[7] S-benzyl-isothiourea hydrochloride,[4a] nitrate[4a] and sulfate.[4a]

The general procedure for the preparation of the S-alkyl-isothiourea hydrohalide salts is that described by Wheeler and Bristol.[4d] A volume of alcohol equal to the volume of alkyl halide was used, except in the cases of ethylene dibromide and ethylene dichloride. In these cases 3 or 4 volumes of alcohol was used and the insoluble S,S-ethylenedi-isothiourea salts were filtered off. After the thiourea had dissolved completely, the alcohol solutions were heated at water-bath temperature until a sample gave no silver sulfide precipitate with ammoniacal silver nitrate. S,S-Ethylenediisothiourea hydrochloride has been prepared previously from the hydrobromide.[7a]

S-n-Heptyl-isothiourea hydrobromide was obtained in a crystalline form by shaking a concentrated alcohol solution of the salt with ether. S-n-Heptyl-isothiourea acetate was prepared by treating a concentrated aqueous solution of the hydrobromide with a saturated solution of potassium acetate. The precipitated acetate was recrystallized from water. S,S-Ethylenedi-isothiourea acetate was prepared and purified in an analogous manner. S-β-Phenylethyl-isothiourea hydrochloride was recrystallized from concentrated hydrochloric acid.

Ethyl chloride and isopropyl chloride in several volumes of alcohol were refluxed for weeks with thiourea without complete transformation to the corresponding S-alkyl-isothioureas. On heating at 110–120° for six to ten hours in an autoclave there was still unchanged thiourea. However, these crude reaction products were chlorinated and with successful formation of the corresponding alkyl sulfonyl chlorides (Table I). The analytical data on new compounds prepared in this research are recorded in Table III.

Alkyl Sulfonyl Chlorides.—(A) The S-alkyl-isothiourea salts (0.05–1.0 mole) were dissolved in water (50–135 cc.) and the solution cooled to 10°, or below, in an ice-bath. Chlorine gas was conducted into this aqueous solution at such a rate that the temperature did not rise above 15° in order to avoid hydrolysis of the sulfonyl chloride with formation of a sulfonic acid. An occasional rise of temperature to 20° did not seriously lower the yields. The treatment with chlorine was continued until the oil (sulfonyl chloride) had completely settled out and the aqueous layer was distinctly green due to the excess of chlorine. This operation usually required about twenty to thirty minutes. The oil (sulfonyl chloride) was then extracted with ether and the excess of chlorine removed by washing several times with small portions of dilute sodium bisulfite solution (5%). After washing with water the ether extract was dried over calcium chloride and distilled.

Benzyl sulfonyl chloride, $C_6H_5CH_2SO_2Cl$, and ethane-1,2-disulfonyl chloride precipitated as solids directly during the chlorine treatment. They were dried over sulfuric acid and purified by crystallization from chloroform or benzene. However, the melting points of the crude material were only a degree or two lower than those of the purified substances.

The low melting β-phenylethyl sulfonyl chloride ($C_6H_5CH_2CH_2SO_2Cl$, m. p. 32–33°) was occasionally obtained as a solid directly, but usually it was necessary to extract with ether as directed above. On removing the ether a solid was always obtained. This sulfonyl chloride also may be purified by distillation.

The bromine of the S-alkyl-isothiourea hydrobromides was removed by adding an equivalent of silver nitrate and the resulting solution concentrated to the desired volume. Chlorination and ether extraction were carried out as previously described. However, with S-n-heptyl-isothiourea hydrobromide and S,S′-ethylenedi-isothiourea hydrobromide this procedure was unsatisfactory because of the

TABLE III

ANALYSES OF NEW COMPOUNDS

Compound	B. p. or m. p., °C.	Mm.	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Halogen, % Calcd.	Halogen, % Found
S-Isopropyl-isothiourea hydrobromide	M. 76–78		14.07	14.10	...	...	40.16	40.42
S-n-Heptyl-isothiourea hydrobromide	M. 92–94		10.97	10.90	...	...	31.33	31.62
S-n-Heptyl-isothiourea acetate	M. 136–137		11.95	11.80	...	...	...	...
β-Phenylethyl-isothiourea hydrochloride	M. 113–114		12.92	13.03	...	...	16.36	16.57
S,S-Ethylenedi-isothiourea hydrochloride	M. 247–248		22.30	22.18	...	...	28.23	28.33
S,S-Ethylenedi-isothiourea acetate	M. 157–158		18.78	18.81	...	...	...	...
n-Heptylsulfonyl chloride	B. 124–126	9	...	...	...	...	17.85	17.62
n-Heptylsulfonamide	M. 74–75		7.81	7.66	17.90	18.21	...	...
β-Phenethylsulfonyl chloride	B. 121–123	3						
	M. 32–33		...	...	...	...	17.32	17.38
β-Phenethyl sulfonamide	M. 121.5–122.5		7.56	7.44	17.31	17.55	...	...

sparing solubility of the resulting nitrates. The use of a large volume of solution to dissolve the nitrate at the low temperature (10–15°) resulted in a low yield of the sulfonyl chloride. Consequently, in these two cases the acetates were used. These organic salts are more soluble in water than the nitrates. The addition of a small volume of strong hydrochloric acid aids the solution of these salts, (see Table I).

Alkyl Sulfonyl Chlorides.—(B) Seventy-five cubic centimeters of the alcohol containing 4.5–5.0 g. of hydrogen chloride and 7.6 g. (0.1 mole) of finely powdered thiourea were heated on a steam-bath under a reflux condenser for various lengths of time as recorded in the second column of Table II. With frequent vigorous shaking the thiourea dissolved within a few minutes after heat was applied. Some hydrogen sulfide is evolved during the reaction. At the end of the heating period the excess of alcohol was removed under diminished pressure and the viscous residue dissolved in warm water (75–100 cc.). Tests applied to these aqueous solutions with alkaline lead acetate or ammoniacal silver nitrate showed that the thiourea had disappeared completely after seventy-two to ninety-six hours in the case of *n*-propyl-, *n*-butyl and isoamyl alcohol. With ethyl, isopropyl and isobutyl alcohols unchanged thiourea was present after five days of digestion. No attempt was made to isolate the respective S-alkyl-isothiourea hydrochlorides from these reactions. The solution was cooled to the desired temperature and the chlorination operation applied as directed under (A).

That concentrated aqueous hydrochloric acid solution may be used instead of dry hydrochloric acid gas was shown in one experiment: 75 cc. of *n*-butyl alcohol, 10 cc. of concentrated hydrochloric acid and 7.6 g. of thiourea were heated together for forty-eight hours. A yield of 72% of *n*-butyl sulfonyl chloride was obtained as compared to 76% with hydrochloric acid gas. These results are recorded in Table II. The yields given are based on the quantity of thiourea used.

The alkyl sulfonyl chlorides described in (A) and (B) were characterized by chlorine analyses and by melting points of their corresponding acid amides or anilides.[11]

n-Heptyl sulfonamide was prepared by shaking the corresponding sulfonyl chloride with concentrated ammonia. The amide separated in crystalline form and was purified by crystallization from an ether–petroleum ether mixture. β-Phenylethyl sulfonamide was prepared in a similar manner and recrystallized either from dilute alcohol or an ether–petroleum ether mixture.

Ethyl Sulfonyl Bromide, $C_2H_5SO_2Br$.[12]—S-Ethyl-isothiourea hydrobromide (18.5 g.) or sulfate (15.3 g.) was dissolved in 200 cc. of water and the solution cooled to 0–5°. During vigorous stirring 125 g. (0.78 mole) of bromine was added from a dropping funnel during one hour. The temperature was not allowed to rise above 5°, and the solution was stirred for two to three hours at this temperature after the final addition of the bromine. The oil (sulfonyl bromide) was extracted with ether and the excess of bromine removed by washing with 5% sodium bisulfite solution. After washing with water the ether extract was dried over calcium chloride and distilled. The yield was 11.21 g. (64.8%); b. p. 85–86° (18 mm.); n^{25}_D 1.5010. *Anal.* Calcd. for $C_2H_5O_2SBr$: Br, 46.19. Found: Br, 45.93.

The use of a larger amount of bromine did not greatly increase the yield. For example, 150 g. (0.94 mole) gave a yield of 67.6%. However, the use of less than 125 g. of bromine gave lower yields: 108 g. gave a yield of 60% of the sulfonyl bromide. Higher reaction temperatures also reduced the yield. Ethyl sulfonyl bromide decomposes with evolution of sulfur dioxide when distillation is applied at ordinary pressure.

Methyl Sulfonyl Bromide, CH_3SO_2Br.[12]—S-Methyl-isothiourea sulfate (13.9 g.) was treated with 125 g. of bromine as described above except that the stirring period after final addition of bromine was increased to five hours. A shorter period of stirring gave a lower yield. The yield was 6.92 g. (43.5%); b. p. 80–80.5° (22 mm.); n^{25}_D 1.5080. *Anal.* Calcd. for CH_3O_2SBr: Br, 50.27. Found: Br, 50.25.

***n*-Heptyl Sulfonyl Bromide.**—S-*n*-Heptyl-isothiourea hydrobromide (25.5 g.) under the above conditions gave a 36% yield of this sulfonyl bromide of b. p. 135–137° at 9 mm. There was some decomposition on distillation. The sulfonamide melted at 74–75°.

Action of Chlorine on Hydrobromides of S-Alkyl-isothioureas

An aqueous solution of S-ethyl-isothiourea hydrobromide (18.5 g.) was treated with chlorine as described for the preparation of alkyl sulfonyl chlorides. The chlorination was continued until the bromine color had completely disappeared. The resulting oil was then extracted with ether, washed and dried as previously described. There was obtained 14–16 g. of material of b. p. 90–92° at 23 mm., n^{25}_D 1.4960–1.4970. This product contained bromine and a comparison of the refractive index and results of sulfur and halogen analyses indicated a mixture of ethyl sulfonyl chloride (8–12%) and ethyl sulfonyl bromide (88–92%). Ethyl sulfonamide was prepared from the mixture melting at 59°. An aqueous solution of S,S-ethylenediisothiourea hydrobromide on chlorination gave a solid product containing bromine melting at 95–96° after crystallization from chloroform.

Summary

1. S-Alkyl-isothiourea salts interact in aqueous solution at low temperature with chlorine and bromine to form the corresponding alkyl sulfonyl chlorides and sulfonyl bromides, respectively, in good yields.

2. An alkyl halide and thiourea serve as key reagents in this reaction.

3. A method has been developed for preparing alkyl sulfonyl chlorides directly from an aliphatic alcohol and thiourea as key reagents. Advantage is taken here of an old observation made by Stevens for the preparation of pseudothioureas.

4. The new method of synthesis is superior to

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[11] Dugeut, *Rec. trav. chim.*, **21**, 76 (1902); **25**, 215 (1906).

[12] Cherbuliez and Schnauder, *Helv. Chim. Acta*, **6**, 249 (1923).

any technique involving the use of phosphorus halides for conversion of sulfonic acids to their sulfonyl halides.

5. This investigation is to be continued in this Laboratory.

NEW HAVEN, CONN. RECEIVED APRIL 13, 1936

[CONTRIBUTION FROM THE ABBOTT LABORATORIES]

Some Alkyl and Aryl Amides and Ureides as Hypnotics[1]

BY E. H. VOLWILER AND D. L. TABERN

A considerable number of simple and substituted acetamides and acetyl ureas have been prepared from time to time and subjected to pharmacologic study. Many have been found to possess distinct hypnotic activity, and at least five, Adalin (bromodiethylacetyl urea), Neodorm (isopropylethylacetamide), Bromural (bromo-isovaleryl urea), Sedormid (allylisopropylacetyl urea), and Novonal (diethylallyl acetamide), are employed in medical practice. In their properties, these compounds appear to stand intermediate between the comparatively powerful barbiturates and the milder bromides, being chiefly used as sedatives in neuropsychic disorders.

Recent studies in the field of barbiturate hypnotics have demonstrated that certain members, particularly those containing secondary amyl groups in addition to ethyl or allyl, possess unique properties. The member most extensively investigated clinically, ethyl-1-methylbutylbarbituric acid, has been found to be characterized by its unusual rapidity of action, and by the fact that while its hypnotic action is intense, it disappears quite rapidly. As has been repeatedly pointed out,[2] this rapidity of recovery from depressant effects, is a valuable property when the drug is to be used as a preanesthetic sedative. Again, clinical reports indicate that in certain of these higher members, the sedative as contrasted to the true hypnotic properties seem to be accentuated.

It seems desirable, therefore, to prepare a series of acetyl ureas and acetamides, and the bromo analogs, containing the 1-methylbutyl and other similar secondary alkyl groups, in order to see whether the typical properties just enumerated are retained.

Experimental

The requisite malonic esters were prepared in the usual way, in absolute alcohol, employing the respective alkyl bromides (in the case of the diethylcarbinyl derivatives the *p*-toluene sulfonyl ester was utilized), and purified by fractionation.

Certain of the higher esters were very difficult to hydrolyze, prolonged refluxing with 40% potassium hydroxide in dilute alcohol being necessary. After removing the alcohol *in vacuo*, the solid mass was dissolved in cold water and carefully neutralized with hydrochloric acid until permanently acid to congo, the organic acids extracted with ether, heated to eliminate carbon dioxide, and distilled *in vacuo*. Bromo acids were synthesized essentially according to the method of "Organic Syntheses."[3]

The acetic acids were then converted to the acid chlorides by a 10% excess of thionyl chloride at room temperature and purified by fractionation *in vacuo*. No attempt was made to secure highest purity.

For the preparation of the amides, a solution of ammonium hydroxide saturated at 10° was prepared and the acid chlorides gradually dropped in at this temperature, or below, ammonia concentration being maintained by passage of a slow stream of ammonia gas. After several hours of stirring, the solid was filtered off, dried and recrystallized either from dilute alcohol, or a mixture of ether and petroleum ether, or in most cases both.

A generally more satisfactory method of preparing the amides lies in the use of the cyanoacetic esters.[4] For example: ethyl cyanoacetate was condensed by sodium ethylate in absolute alcohol by adding somewhat more than one mole of 1-ethylpropyl bromide ($\alpha^{20}\text{D}$ 1.4440) at below 60°. The separation of sodium bromide was rapid. Next morning the mass was heated to boiling and allowed to stand overnight. The ester boiled at 150–160° at 35 mm. This was ethylated by ethyl bromide and sodium ethylate, the reaction again proceeding readily. The ethyl-1-ethylpropylcyanoacetic ethyl ester boiled at 150–155° at 32 mm.

One hundred grams of this ester was refluxed with 100 g. of potassium hydroxide and 200 cc. water for twelve hours or longer. The solvent was distilled *in vacuo*, the cyanoacetic acid liberated by an excess of hydrochloric acid and extracted with benzene. On distillation through a tall column, carbon dioxide was evolved and the redistilled nitrile boiled at 190–200°.

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[1] The material covered in this paper was presented in part at the Cleveland meeting of the American Chemical Society, September, 1934, and in part at the New York meeting, April, 1935.

[2] (a) Barlow, *Arch. Surg.*, **29**, 527 (1934); (b) Waddy, "The Fear of Anaesthesia," Thesis, University of Manchester, 1934.

[3] "Organic Syntheses," Coll. Vol. I, 1932, p. 108.

[4] See U. S. Patent 1,482,343 (1934).

Sixty grams of the nitrile was refluxed for ten to fifteen hours with 120 g. of potassium hydroxide in 600 cc. of 95% alcohol. The solvent was removed *in vacuo* and ice added. The separated and washed solid was redissolved in methanol. This ethyl-1-ethylpropylacetonitrile hydrolyzed with much more difficulty than most of the cyanides and liquid residues were therefore subjected to further hydrolytic treatment.

All halogen-free amides were colorless solids quite soluble in organic solvents, but relatively insoluble in water. α-Bromoethyl-1-methylbutylacetamide was an oil at room temperature.

We have found that sodamide or finely divided sodium in boiling benzene converts the halogen-free amides quantitatively into sodium salts which are soluble in the solvent and react readily with alkyl halides. The structure of the resultant amides was established by their synthesis from the acid chlorides and the requisite alkylamine.

These N-substituted amides are oils or low melting solids which may be distilled at 15 to 20 mm. They are quite insoluble in water but in the presence of starch or acacia are readily emulsified.

The acetyl ureas were prepared by heating the acid chlorides with a large excess (2.5 moles) of dry urea to 110–135°. After the main reaction, two layers were formed, the lower soon turning solid. After several additional hours of heating, the powdered mass was broken up under dilute alkali and finally recrystallized from dilute alcohol or another appropriate solvent. Another convenient method is to extract with boiling alcohol and pour into cold water kept permanently alkaline by sodium hydroxide. In several instances, appreciable quantities of higher melting substances, insoluble in cold ether, were formed.

A simpler but in general less satisfactory method for the preparation of the acetyl ureas is to heat a solution of the sodium salt of the appropriate barbituric acid in a sealed tube at 100° for several days, filter off the precipitated acetyl urea, and repeat the process.

TABLE I

Acetic acids	B. p. of acetic acids, °C.	Press., mm.	B. p. of acetyl chlorides, °C.	Press., mm.
Mono-1-methylbutyl	208–210	755	83–85	60
Ethyl-1-methylbutyl	225–230	755	103–108	45
			190	755
Allyl-1-methylbutyl	195–200	755	190–195	755
n-Butyl-1-methylbutyl	185–190	55	140	55
Ethyl-*n*-amyl	232–238	750	195–200	750
α-Bromo-1-methylbutyl			110–120	40
Ethyl-α-bromo-1-methylbutyl			138–150	50
Ethyl-α-bromo-*s*-butyl			130–135	50
Ethyl-2-ethylpropyl				

TABLE II

No.	Compound	Nitrogen, % Calcd.	Nitrogen, % Found	M. p., °C.
1	1-Methylbutylacetyl urea	16.3	16.48	180
2	Ethyl-1-methylbutylacetyl urea	14.0	13.79	133
3	α-Bromo-1-methylbutylacetyl urea	11.2	11.48	108–110
4	Ethyl-α-bromo, 1-methylbutylacetyl urea	10.0	7.56	Oil
5	Ethyl-*s*-butylacetyl urea	14.9	14.74	172
6	Isoamylethylacetyl urea	13.9	14.07	130
7	Allyl-1-methylbutylacetyl urea	13.1	13.20	123
8	Butyl-1-methylbutylacetyl urea	12.2	12.0	123
9	*n*-Butyl-ethylacetyl urea[a]	15.0	14.76	157
10	Phenyl-ethylacetyl urea[a]	13.5	13.69	137
11	Phenyl-allylacetyl urea	12.6	12.73	133–134
12	Ethyl-1-ethylpropylacetyl urea	14.0	13.98	148–150
13	Ethyl-1-methylbutylacetamide	8.91	9.12	97–98
14	α-Bromo-1-methylbutylacetamide	6.74	7.03	112–114
15	Allyl-1-methylbutylacetamide	8.2	8.35	90–91
16	Ethyl-α-bromo-1-methylbutylacetamide	5.95	6.2	Oil
17	Butyl-1-methylbutylacetamide	7.5	7.75	97–98
18	*n*-Amyl-ethylacetamide	8.91	8.9	96
19	Isoamyl-ethylacetamide[a]	8.91	9.0	106–108
20	Phenyl-ethylacetamide	8.6	8.7	85–87
21	Phenylallylacetamide	8.0	8.10	63
22	Ethyl-1-ethylpropylacetamide	8.91	8.89	123–125
23	Ethyl-1-methylbutyldiethylamide	6.56	6.31	Oil
24	α-Bromo-1-methylbutylmethylacetamide	6.27	6.44	90
25	Diethylmalonic acid monoallylamide	7.05	6.92	105
26	Ethyl-1-methylbutyl-N-methylacetamide	8.2	8.5	Oil
27	Ethyl-isopropyl-N-methylacetamide	9.8	10.0	72–75
28	Ethyl-1-methylbutyl-N-allylacetamide	7.1	7.3	Oil
29	Ethyl-isopropyl-N-allylacetamide	8.3	8.1	58–60
30	Ethyl-*s*-butyl-N-allylacetamide	7.65	7.4	Oil
31	Ethyl-isopropyl-N-ethylacetamide	8.9	9.0	Oil

[a] Described previously.

The distribution coefficients of three therapeutically promising members of the series were determined as previously described.[5]

TABLE III

Barbiturate	Distrib. coeff.
Ethyl-1-methylbutylacetamide	1.6
Ethyl-*s*-butylacetyl urea	1.1
Ethyl-isopropylacetyl urea	1.1

For the pharmacological studies of these compounds, we are indebted to Prof. A. L. Tatum of the University of Wisconsin. While he will re-

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(5) Tabern and Shelberg, THIS JOURNAL, **55**, 328 (1933).

port the results in detail elsewhere, a few general observations may be indicated here.

The efficiencies of the compounds vary among themselves as much as five-fold, and the toxicities even more widely. Of those active in moderate dosage, particular interest would seem to attach, as had been anticipated, to ethyl 1-methylbutylacetyl urea and the corresponding amide. These have respectively safety margins of 18 and 11, as compared with a range from 2 to 5 for known barbiturates, and 6 for the commercial analog tested allyl isopropylacetyl urea (Sedormid).

In the N-alkyl series it was observed that when the N-substituent group was methyl, prolonged mild sedation was secured. When it was larger, excitement rather than sedation resulted.

A very interesting point is the relatively great analgesic action shown by certain of the amides, this being produced without a correspondingly deep hypnotic effect as in the barbiturates. There are also definite variations among individual members of the series.

Two chemically related substances, diethyl malonic mono-allyl amide and the bis (diethylamide) of ethyl-1-methylbutylmalonic acid, showed no true hypnotic action; the second produced local anesthesia and on oral administration clonic convulsions.

Conclusions

An extended series of simple and substituted alkyl amides and ureas has been synthesized in connection with a study of their use as sedatives and hypnotics. Considered in connection with the N-aryl and N-alkyl barbiturates described in a companion paper the results indicate the wide value of secondary butyl, amyl and hexyl groups in conferring to such compounds valuable therapeutic properties.

North Chicago, Ill. Received May 8, 1936

[Contribution from the Abbott Laboratories, North Chicago, Ill.]

N-Alkyl and N-Aryl Substituted Barbituric Acids[1]

By D. L. Tabern and E. H. Volwiler

Although Fischer and Dilthey described several simple N-substituted barbituric acids as long ago as 1904,[2] until recently little systematic study has been made of higher homologs. Dox and his group[3] reported upon certain intermediate members of the series, but did not prepare compounds containing certain secondary butyl, amyl and hexyl groups, which in the simple barbiturates[4] and thiobarbiturates[5] have been found frequently to confer valuable therapeutic properties. Such compounds are among the most effective yet produced and are characterized by a prompt and intense action of short duration.

Apparently the early N-alkyl and aryl barbiturates did not attract attention because preliminary studies failed to reveal anything of especial interest; they are in general but little more active than the analogs derived from urea itself, and in certain members tend to produce pre-anesthetic excitement, paraplegia and convulsions rather than hypnosis.

More recently, however, 5,5-ethylphenyl-N-methylbarbituric acid has been reported to possess a somewhat specific action in epilepsy without the production of pronounced hypnosis, and another, 5,5-methylcyclohexenyl-N-methylbarbituric acid, has been found to have an extremely short but intense period of hypnotic activity. These interesting facts pointed to the need for a more careful study of promising compounds containing one or more secondary alkyl groups in the 5-position with particular reference to rapidity of onset, duration of action, degree of sedation or hypnosis, route and rapidity of elimination, etc. It also seemed of interest to prepare certain members containing secondary and tertiary groups attached to the nitrogen in position "1," none of these ever having been described.

Chemical

The thirty-five barbiturates of this series were prepared by one or more of the following methods: (1) reaction of the dialkylmalonic esters with the appropriate substituted urea in the presence of sodium ethylate at 100–110°; (2) reaction of the dialkyl cyanoacetic esters with a substituted

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(1) Presented at the Kansas City Meeting of the American Chemical Society, April 16, 1936.

(2) Fischer and Dilthey, *Ann.*, **335**, 334 (1904).

(3) (a) Dox and Hjort, *J. Pharmac.*, **31**, 455 (1927); (b) Hjort and Dox, *ibid.*, **35**, 155 (1929); (c) Dox and Jones, This Journal, **51**, 316 (1929).

(4) Volwiler and Tabern, *ibid.*, **52**, 1676 (1930).

(5) Tabern and Volwiler, *ibid.*, **57**, 1961 (1935).

urea followed by hydrolysis with 15–20% sulfuric acid for ten hours; or (3) the action of allyl bromide on the sodium salt of the simple barbituric acid in water at 100°.[3c] The presence of copper sulfate as a catalyst seems greatly to increase the speed of the latter alkylation. The alkali soluble fraction in each case was extracted and distilled at 2 to 5 mm., passing over below 200°. In the case of reaction 3, there was always a small amount of unchanged dialkyl acid which boiled over 210° under the same conditions and could thus be separated with reasonable accuracy.

The intermediate primary alkyl ureas were best prepared by the action of the corresponding amines upon nitrourea in water or in alcohol at about 80°. After the evolution of nitrogen was at an end, the solvent was removed *in vacuo* and the urea dried and used directly or recrystallized from a suitable solvent, such as acetone or ethyl acetate. Tertiary butyl urea was synthesized by the action of tertiary butyl chloride on urea in the presence of lead carbonate.[6] It was found desirable to carry out the reaction with good stirring, adding the white lead slowly.

Many of the barbituric acids studied were very viscous liquids, insoluble in water but soluble in organic solvents, including petroleum ether; even after long standing, they could not be induced to crystallize and indeed prevented the crystallization of intentionally added portions of the corresponding dialkylbarbituric acids. They are soluble in alkalies, and solid alkali metal salts may be prepared by evaporation *in vacuo* of an absolute alcohol solution. Aqueous solutions of such salts are strongly hydrolyzed and have a *p*H of approximately 10 to 10.5.

Most of the malonic esters have been described previously. The purified barbiturates were analyzed for nitrogen and values obtained agreeing closely with the calculated.

Pharmacologic[7]

While the more promising of the N-substituted derivatives have been studied upon several species and on man, for sake of brevity and uniformity only the results of intravenous injections in rabbits will be indicated here. The figures given represent milligrams per kilogram body weight.

Barbituric acid derivatives			M. p., °C.	Minimum effective dose	Minimum lethal dose
Methyl	1-methylbutyl	N-methyl	105–108	15	90
Methyl	1-methylbutyl	N-ethyl	Oil	30	>100
Methyl	1-methylbutyl	N-allyl	Oil	30	>160
Ethyl	1-methylbutyl	N-methyl	Oil	15	30
Ethyl	1-methylbutyl	N-phenyl	Oil	200	...
Methyl	1-ethylpropyl	N-methyl	[e]	20	130
Ethyl	1-ethylpropyl	N-methyl	Oil	8	80
Methyl	Cyclohexenyl	N-methyl[a]	[e]	10	110
Methyl	*s*-butyl	N-methyl	81–83	20	200
Methyl	*s*-butyl	N-ethyl	[e]	40	>180
Methyl	*s*-butyl	N-2-methylallyl	130	30	...
Ethyl	*s*-butyl	N-methyl	Oil	20	85
Allyl	*s*-butyl	N-methyl	Oil	20	35
Methyl	Isopropyl	N-methyl	113–114	50	250–300
Methyl	Isopropyl	N-ethyl	106–107	60	100[b]
Ethyl	Isopropyl	N-methyl	124–125	30	135
Ethyl	Isopropyl	N-ethyl	[e]	30	> 80
Methyl	2-ethylbutyl	N-methyl	98–100	15	>120
Ethyl	2-ethylbutyl	N-methyl	63–65	10[b]	...
Methyl	1-methylamyl	N-methyl	Oil	20	70
Ethyl	Ethyl	N-*s*-butyl	83–85	>200	>200
Ethyl	Ethyl	N-*t*-butyl	98	>200	>200
s-Butyl		N-*n*-butyl	Oil	80	150[b]
Methyl	1-methylbutyl	N-*t*-butyl		Ineffective	
Methyl	1-methylbutyl	N-*n*-butyl	Oil	Ineffective	
Mono	1,3-dimethylbutyl		235	>165	...
Methyl	1,3-dimethylbutyl		205	45	170
Ethyl	1,3-dimethylbutyl		175	1–3[c]	7[b]
Methyl	1,3-dimethylbutyl	N-methyl[d]	Oil	12–16[b]	

[a] Evipal. [b] Convulsions. [c] Stimulation. [d] See Shonle, THIS JOURNAL, **58**, 585 (1936). [e] Partially crystallized material.

The hypnotic effect comes on very rapidly, with deep hypnotic doses the animal being asleep by the time of completion of the injection. Recovery is likewise rapid, the animal awakening in from fifteen minutes to two hours. Sufficient depth of hypnosis and analgesia may be secured to permit surgical procedures but in this respect the best members of the series seem in-

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[6] Schneegans, *Arch. Pharm.*, **231**, 677 (1893).

[7] For the tests here described we are indebted to Mr. H. C. Spruth of the Pharmacologic Department of the Abbott Laboratories.

ferior to the secondary substituted thiobarbiturates previously reported by us.[5] Given orally they are relatively ineffective in animals and in man.

In general, most satisfactory compounds are secured where one group attached to the 5-carbon is secondary, the other is methyl, and the N-substituent also methyl. The attachment of large primary or of secondary and tertiary groups on the nitrogen leads to compounds of low hypnotic power. There is some indication that the N-alkyl acts additively in the production of the convulsions characteristic of barbiturates containing certain 6- and 7-carbon atom groups (benzyl, etc.). For instance, methyl-(1,3-dimethylbutyl)-barbituric acid could be given in a dosage of 170 mg./kg. without producing convulsions while both its N-methyl derivative and ethyl (1,3-dimethylbutyl)-barbituric acid produced convulsions in the range of 7 to 15 mg.

Conclusion

A series of N-alkyl and N-aryl barbiturates containing secondary and tertiary groups has been prepared. Pharmacologically, certain members offer some promise as short acting intravenous hypnotics and anesthetics.

NORTH CHICAGO, ILL. RECEIVED MAY 8, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Effect of the Composition of the Medium upon the Growth of Yeast in the Presence of Bios Preparations. I. The Effect of Magnesium Salts[1]

BY ELLIS I. FULMER, L. A. UNDERKOFLER AND JAMES B. LESH

Schopmeyer and Fulmer[2] found that the growth of certain molds on synthetic media, with glycerol or sucrose as substrates, formed materials which accelerated the growth of yeast. Recently, in the study of the growth accelerants produced by *Aspergillus niger* upon sucrose media, attempts were made to separate the active substances into the Bios I and Bios II of Miller and co-workers[3–5] who identified Bios I as *i*-inositol.

The properties of the fractions obtained were determined by their effect upon the growth of yeast in Medium C developed by Fulmer, Nelson and Sherwood.[6] When the activity of the Bios II fraction in Medium C was compared with its activity in Clark's medium, which was used by Miller, it was found that the same amount of stimulant gave a much larger growth in the latter medium. Medium C contains, per 100 cc.: 0.188 g. ammonium chloride, 0.100 g. dipotassium phosphate, and 10 g. of sucrose. Clark's medium contains, per 100 cc.: 0.834 g. of ammonium nitrate, 0.417 g. of potassium dihydrogen phosphate, 0.071 g. of calcium chloride, 0.208 g. of magnesium sulfate and 10 g. of sucrose.

Preliminary results showed that the addition of magnesium sulfate to Medium C had a marked effect upon the growth of yeast in the presence of the bios preparation. The addition of calcium chloride, or the replacement of ammonium chloride by ammonium nitrate had no influence upon the bios activity. The effect of magnesium salts was then further investigated.

The yeast employed was a strain of *Saccharomyces cerevisiae* isolated several years ago from a cake of Fleischmann yeast, and deposited with the American Type Culture Collection as No. 4226. The numbers of cells were determined by means of the Thoma-Zeiss counting chamber. The initial inoculation was made to a count of one (250,000 cells per cubic centimeter) from an actively growing culture. The final counts were made after twenty-four hour incubation at 30°. The Bios II added was equivalent to 2.0 cc. of the original extract per 100 cc. of medium. Inositol, where added, was used in concentration of 3.2 mg. per 100 cc. of medium.

In Table I are given data showing the effect of magnesium sulfate upon the growth of the yeast in several media. The inositol was Eastman's ash-free *i*-inositol. The Bios II preparations were made according to the procedure given by Lucas.[3]

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(1) This research was supported in part from a grant received from the Rockefeller Fluid Research Funds administered by the Iowa State College.

(2) H. Schopmeyer and E. I. Fulmer, *J. Bact.*, **22**, 23 (1931).

(3) G. H. W. Lucas, *J. Phys. Chem.*, **28**, 1180 (1924).

(4) Edna V. Eastcott, *ibid.*, **32**, 1094 (1928).

(5) W. L. Miller, Edna V. Eastcott and J. E. Maconachie, THIS JOURNAL, **55**, 1502 (1933).

(6) E. I. Fulmer, V. E. Nelson and F. F. Sherwood, *ibid.*, **43**, 191 (1921).

Series A involved Bios II prepared from malt sprouts and in series B the Bios II was prepared from a synthetic medium which had supported the growth of *Aspergillus niger* on sucrose as substrate. It is evident that the addition of magnesium sulfate to Medium C, in the same concentration as that in Clark's medium, very markedly increases the growth of the yeast in the presence of Bios II. The addition of the salt to Medium C, without the bios, does not increase the growth, a result in harmony with previous reports from this Laboratory.[6,7]

TABLE I

The effect of Bios II and of inositol upon the growth of yeast in several media. Series A involves Bios II from malt sprouts; in series B the Bios II was prepared from a medium which supported the growth of *Aspergillus niger*. The control contained neither Bios II nor inositol.

	Count					
	Medium C		0.20%	Medium C + $MgSO_4 \cdot 7H_2O$	Clark's medium	
	A	B	A	B	A	B
Control	9	7	9	5	1	6
Control + inositol	8	..	9	...	1	...
Control + Bios II	52	71	191	194	248	255
Control + Bios II + inositol	54	74	284	215	256	311

The data of Table II show that the salt is effective in very low concentrations. The addition of inositol alone does not increase the growth of the yeast, but the growth is increased by the addition of inositol to the medium containing Bios II. This result agrees with the findings of Miller and co-workers.[3-5]

TABLE II

The effect of varying concentrations of magnesium sulfate upon the growth of yeast in Medium C in the presence of Bios II from malt sprouts.

	Count	
Molarity of $MgSO_4 \cdot 7H_2O$	Inositol absent	Inositol present
0	29	34
8×10^{-6}	44	53
8×10^{-5}	150	157
8×10^{-4}	142	147
8×10^{-3}	172	215
8×10^{-2}	192	313

The question at once arises as to whether the above phenomenon is common to all magnesium salts or whether the sulfate radical is involved. Data in Table III show that magnesium chloride and magnesium nitrate are practically without effect, while potassium sulfate gives some increase in growth. The combination of the potassium sulfate with magnesium sulfate is no more effective than is the latter salt alone. In adding the potassium sulfate the concentration of potassium is likewise increased. When ammonium sulfate is substituted for the ammonium chloride, the former salt gives about the same increase in growth as was evidenced by the potassium sulfate. Addition of magnesium chloride or of magnesium nitrate to the medium containing ammonium sulfate gives the same increase in activity of the bios as that shown by magnesium sulfate alone. The above data show that both magnesium and sulfate are involved in the phenomenon.

TABLE III

The effect of several salts upon the growth of yeast in Medium C in the presence of Bios II from malt sprouts.

	Count			
	Medium C		Medium C	NH_4Cl replaced by $(NH_4)_2SO_4$
Salt added (0.017 molar)	Inositol absent	Inositol present	Inositol absent	Inositol present
Control	28	34	47	89
$MgSO_4$	161	257	163	228
$MgCl_2$	30	34	146	204
$Mg(NO_3)_2$	27	31	155	210
K_2SO_4	68	80		
$MgSO_4 + K_2SO_4$	153	228		

Miller and co-workers state that neither Bios I (inositol) nor Bios II produce much increase in the growth of their yeast when used alone, but that the combination gives greatly enhanced growth. It is evident that Bios II alone increases the growth of the yeast employed by us although the effect is further enhanced by the addition of *i*-inositol (Bios I). Lucas,[3] Williams, Warner and Roehm,[8] Stantial,[9] Williams and Saunders[10] and Farrell[11] have called attention to great differences in the response of various strains of yeast toward bios preparations. Preliminary experiments in our laboratory with various strains of yeasts, show that with some yeasts the addition of magnesium sulfate does not increase the activity of the Bios II but actually decreases the growth. However, if inositol be added in the presence of the Bios II a marked increase in growth is evident with all the strains tested. Full details will be published in a later communication.

Summary

For the strain of yeast employed, the presence of magnesium sulfate markedly increases the growth of the yeast in the presence of a bios preparation

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[7] F. F. Sherwood and E. I. Fulmer, *J. Phys. Chem.*, **30**, 738 (1926).

[8] R. J. Williams, M. E. Warner and R. R. Roehm, THIS JOURNAL, **51**, 2764 (1929).

[9] Helen Stantial, *Trans. Roy. Soc. Can.*, **28**, Sec. III, 163 (1932).

[10] R. J. Williams and D. H. Saunders, *Biochem. J.*, **28**, 1887 (1934).

[11] Leone N. Farrell, *Trans. Roy. Soc. Can.*, **29**, Sec. III, 167 (1935).

(Bios II). Magnesium chloride or nitrate does not show the above phenomenon while potassium or ammonium sulfate gives some increase in activity. Combinations of magnesium chloride or nitrate with potassium or ammonium sulfate give about the same increase in growth in the presence of the bios preparation as does magnesium sulfate.

AMES, IOWA RECEIVED APRIL 27, 1936

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

Di- and Trialkyl Barbituric Acids

BY H. A. SHONLE AND WILBUR J. DORAN

During the past several years, a number of new dialkyl substituted barbituric acids have been prepared in this Laboratory for the purpose of studying the relationship of the pharmacological action to the chemical structure.[1] Since the intermediate malonic esters were available, it seemed advantageous to extend this study to include certain trialkyl substituted barbituric acids. During the course of the preparation of the trialkyl barbituric acids, several undescribed dialkyl barbituric acids were prepared.

A considerable number of 1-alkyl-5,5-dialkyl barbituric acids have been described since Fischer and Dilthey[2] prepared N-methyldiethylbarbituric acid.[3]

The various malonic esters were made in the usual manner by adding the alkyl halide, usually the bromide, to an absolute alcoholic solution of sodiomalonic ester or sodioalkylmalonic ester, refluxing until the reaction was completed and purifying the malonic ester by fractional distillation *in vacuo*. Table I summarizes some of the physical properties of the malonic esters.

Most of the barbituric acids were prepared by condensing the di-substituted malonic ester with urea, methyl urea, or ethyl urea, in the presence of an alcoholic solution of sodium ethoxide, after which they were precipitated and purified, usually by recrystallization from dilute alcohol. In some instances, however, the barbituric acid was an oil which would not readily crystallize, so that its purification had to be effected by fractional distillation *in vacuo*. Table II summarizes the properties of the various barbituric acids prepared.

TABLE I

	Ethyl malonate	B. p., °C.	Mm.	n^{25}_D
1	3-Methylbutylmethyl[a]	103–104	3	1.4248
2	*n*-Hexylmethyl	125	3.5	1.4280
3	1-Methylpentylmethyl	126	6	1.4323
4	1-Methylpentylallyl	139	5	1.4442
5	2-Ethylhexylmethyl	126	1.5	1.4353
6	*n*-Pentylmethyl	99	8	1.4254
7	1-Methylbutylmethyl	124	10	1.4288
8	*n*-Propyl-2-methylbutyl	100	1	1.4319

[a] Sommaire [*Bull. soc. chim.*, **33**, 189–95 (1923)] describes this ester as boiling at 242–247°.

The di- and trialkyl barbituric acids were converted into their sodium salts by the addition of a 50% solution of sodium hydroxide to an alcoholic solution of the barbituric acid, followed by the removal of the alcohol by vacuum distillation. Solutions of the sodium salts of these barbituric acids were studied pharmacologically on several varieties of laboratory animals. The results obtained by the intraperitoneal injection into white rats are summarized in Table II, wherein the minimum anesthetic dose (M. A. D.) and the minimum lethal dose (M. L. D.) are reported. The detailed pharmacological study will be reported elsewhere.[4] From the pharmacological data, it appears, in general, that the introduction of a third alkyl group lessens the duration of the action. In some instances, alkylating the nitrogen group made the barbituric acids less effective.

We wish to thank Mr. E. E. Swanson and Mr. W. E. Fry for the pharmacological assays, and Mr. John H. Waldo, Miss Anna K. Keltch and Dr. E. C. Kleiderer for assistance in the preparation of several of these barbituric acids.

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[1] Swanson, *Proc. Soc. Exptl. Biol. Med.*, **31**, 961 (1934); U. S. Patent, 1,996,627; Shonle, Waldo, Keltch and Coles, THIS JOURNAL, **58**, 585 (1936).

[2] Fischer and Dilthey, *Ann.*, **335**, 334 (1904); U. S. Patent, 782,742.

[3] Among the various investigators who have reported in this field are: Dox and Hjort, *J. Pharmacol.*, **31**, 455 (1927); Hjort and Dox, *ibid.*, **35**, 155 (1929); Dox and Jones, THIS JOURNAL, **51**, 316 (1929); Kleiderer and Shonle, *ibid.*, **56**, 1772 (1934); Tabern and Volwiler, Kansas City Meeting, American Chemical Society, April 16, 1936.

[4] Swanson, in press.

TABLE II

Compounds numbers 9, 14, 15 and 18 were reported by Tabern and Volwiler, Kansas City Meeting, American Chemical Society, April 16, 1936. The nitrogen determinations were obtained by the micro-Dumas method.

	Barbituric acid	M. p., °C.	%, Nitrogen Calcd.	Found		M. A. D. mg./kg.	M. L. D. mg./kg.	Av. duration of symptoms of surviving rats, min.
1	3-Methylbutylmethyl[a]	124.5–125.2	13.20	12.96	12.76	1000	1500	447
2	*n*-Hexylmethyl	168–169	12.38	12.57	12.58	150	450	260
3	1-Methylpentylmethyl	173–174	12.38	12.50	12.41	150	400	227
4	1-Methylpentylallyl[b]	Oil	11.11	11.47	11.41	60	150	108
5	2-Ethylhexylmethyl	132–132.5	11.02	11.14	11.06	125	250	223
6	*n*-Propyl-2-methylbutyl	129–130.5	11.67	11.58	11.55	110	220	165
7	N-methyl *n*-propylethyl	94.5–95.0	13.20	13.03	13.02	140	200	570
8	N-methyl 2-methylpropylethyl	90–91	12.38	12.48	12.24	140	200	228
9	N-methyl 1-methylpropylethyl[c]	94–95	12.38	12.44	12.44	90	120	764
10	N-methyl *n*-pentylmethyl	108–109	12.38	11.82	11.69	1000	None	...
11	N-methyl *n*-pentylethyl[d]	Oil	11.67	11.40	11.42	90	190	191
12	N-methyl 3-methylbutylmethyl	106–107	12.38	12.01	12.03	None	2000	...
13	N-ethyl 3-methylbutylethyl[e,f]	Oil	11.02	11.33	11.45	150	300	68
14	N-methyl 1-methylbutylmethyl	116–117	12.38	12.58	12.55	150	350	240
15	N-methyl 1-methylbutylethyl[c,g]	Oil	11.67	11.75	11.87	70	140	205
16	N-methyl 1-methylbutylallyl[h]	Oil	11.11	11.08	11.15	60	120	133
17	N-ethyl 1-methylbutylethyl[e,h]	Oil	11.02	10.87	10.88	150	340	224
18	N-methyl 1-methylpentylmethyl[i]	Oil	11.67	11.75	11.61	150	400	152
19	N-methyl 1-methylpentylallyl	Oil	10.53	10.18	10.13	80	170	313
20	N-methyl *n*-hexylmethyl[j]	Oil	...	...	...	...	...	...
21	N-methyl 2-ethylhexylmethyl[k]	Oil	...	...	...	...	...	...
22	N-methyl 2-ethylhexylethyl[c]	Oil	...	...	...	...	...	...

[a] Sommaire [*Bull. soc. chim.*, **33**, 189–195 (1923)] gives the m. p. of this barbiturate as 108°. [b] B. p. 218–220° at 7 mm. [c] Prepared by the action of dimethyl sulfate on the sodium salt of the corresponding 5,5-dialkylbarbituric acid. All of the other N-methylbarbiturates were prepared by condensation of the dialkylmalonic esters and methyl urea. [d] B. p. 155–156° at 1 mm. [e] Prepared from ethyl urea and the dialkylmalonic ester and also by the action of diethyl sulfate on the sodium salt of the corresponding 5,5-dialkylbarbituric acid. [f] B. p. 192–194° at 13 mm. [g] B. p. 188–190° at 7 mm. [h] B. p. 148–150° at 1 mm. [i] B. p. 180° at 3 mm. [j] The barbituric acid was obtained as an oil which decomposed on distillation with the formation of the acetyl urea, b. p. 189° at 3 mm., m. p. 63–64°. Kropp and Taub (German patent 606,499, Dec. 4, 1934) give 183–185° at 1.5 mm. as the b. p. of the barbituric acid. % nitrogen for *n*-hexylmethylacetylmethyl urea, calcd., 13.08, found, 13.24 and 13.18. The acetyl urea exhibited no demonstrable hypnotic action. [k] The barbituric acid was obtained as an oil which on standing at room temperature decomposed into 2-ethylhexylmethylacetylmethyl urea, m. p. 65–70°. % nitrogen, calcd., 11.57, found, 11.63 and 11.89. 750 mg. per kg. produces ataxia only in rats. Kropp and Taub (German patent 606,499) report the preparation of this barbituric acid.

Summary

The preparation of a number of new dialkyl malonic esters and di- and trialkyl barbituric acids has been described, and the pharmacological action of the latter summarized.

INDIANAPOLIS, IND.

RECEIVED MAY 25, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

Some New Local Anesthetics Containing the Morpholine Ring. III. Esters of 2-Alkoxycinchoninic Acids

BY JOHN H. GARDNER AND WARREN M. HAMMEL

Extending the investigation of esters of morpholine alcohols as local anesthetics,[1] a series of esters of 2-alkoxycinchoninic acids has been prepared. These compounds are analogs of the series of alkamine esters prepared from diethylaminoethyl alcohol and 2-alkoxycinchoninic acids by Wojahn.[2]

In this investigation, β-4-morpholineethanol and γ-4-morpholinepropanol were prepared by the method of Gardner and Haenni.[1] 2-Chlorocinchoninic acid was prepared by the method of Camps[3] and this was converted into a series of 2-alkoxycinchoninic acids by reaction with solutions of sodium alcoholates in the corresponding alcohol.[3] From these, the acid chlorides, esters and finally the ester hydrochlorides were prepared.

These ester hydrochlorides have been found to show local anesthetic action when tested on the tongue, but no pharmacological measurements have been made.

Experimental

2-Alkoxycinchoninic Acids.—Methoxy, ethoxy, *n*-propoxy and *n*-butoxycinchoninic acids were prepared. To a solution of sodium in the alcohol, using 40 cc. of alcohol per gram of sodium there was added twice the weight of sodium of 2-chlorocinchoninic acid. The solution was boiled a half hour. The alcohol was evaporated and the residue dissolved in water. Dilute hydrochloric acid was added to the filtered solution to precipitate the 2-alkoxycinchoninic acid. This was filtered out, dried and crystallized from benzene. Yields and properties of the individual acids are given in Table I.

TABLE I

Cinchoninic acid	Yield, %	M. p.,[4] °C.	M. p. (Literature), °C.
2-Methoxy	77	177–178	178–179[a]
2-Ethoxy	82	142.2–143.8	145–146[b]
2-*n*-Propoxy	63	138–139.4	136[b]
2-*n*-Butoxy	60	96.6–97.6	111[b,c]

[a] Mulert, *Ber.*, **39**, 1901 (1906). [b] Ref. 2. [c] *Anal.* Calcd. for $C_{14}H_{15}O_2N$: C, 68.54; H, 6.17. Found: C, 68.35; H, 6.27.

2-Alkoxycinchoninyl Chlorides.—To solutions of the alkoxycinchoninic acids in benzene, using about 7 cc. of benzene per gram of the acid, there was added 4 to 5 g. of thionyl chloride per gram of the acid. The mixture was heated at 55–60° for ten minutes. After cooling, the benzene solution was filtered and the insoluble portion, which was largely 2-alkoxycinchoninic acid hydrochloride, washed well with benzene. The benzene solution was evaporated to dryness in a vacuum desiccator, the residue extracted with ligroin and the filtered ligroin solution evaporated to dryness in a vacuum desiccator. Yields, melting points and analyses of the individual acid chlorides are given in Table II.

TABLE II

Cinchoninyl chloride	Yield, %	M. p., °C.,	Analyses, % Calcd. C	H	Found C	H
2-Methoxy	43	45.6–6.5	59.59	3.64	59.79	3.65
2-Ethoxy	41	86–86.5	61.14	4.28	61.47	4.46
2-*n*-Propoxy	51	54–55	62.51	4.85	62.38	4.77
2-*n*-Butoxy	37	35.5–7.5	63.74	5.35	64.95	5.57[a]

[a] Probably not obtained entirely pure.

Morpholinealkyl 2-Alkoxycinchoninates.—To a solution of the alkoxycinchoninyl chloride in about eight times its weight of benzene there was added, with stirring, a slight excess of the morpholine alcohol dissolved in a small volume of benzene. The mixture was heated to 60° for one and a half hours, cooled and filtered. The benzene solution was extracted with dilute hydrochloric acid. The

TABLE III

Ester β-4-Morpholineethyl ( )-cinchonate	M. p., °C.	Analyses, % Calcd. C	H	Found C	H
2-Methoxy	Oil	64.52	6.38	64.39	6.49
2-Ethoxy	44–6	65.42	6.72	65.69	6.93
2-*n*-Propoxy	Oil	66.24	7.03	66.26	7.11
2-*n*-Butoxy	Oil	67.00	7.32	66.91	7.30
γ-4-Morpholinepropyl ( )-cinchonate					
2-Methoxy	Oil	65.42	6.72	65.50	6.77
2-Ethoxy	57–8	66.24	7.03	66.85	7.08
2-*n*-Propoxy	Oil	67.00	7.32	66.72	7.27
2-*n*-Butoxy	Oil	67.70	7.58	67.73	7.53

TABLE IV

Hydrochloride β-4-Morpholineethyl ( )-cinchoninate	Yield, %	M. p., °C.	Cl Analyses, % Calcd.	Found
2-Methoxy	54	198–9	10.05	9.70
2-Ethoxy	27	147.0–6	9.67	10.35
2-*n*-Propoxy	54	150.6–1.2	9.31	9.19
2-*n*-Butoxy	45	150.5–1.4	8.98	9.25
γ-4-Morpholinepropyl ( )-cinchoninate				
2-Methoxy	81	155–60	9.67	9.91
2-Ethoxy	90	157	9.31	9.31
2-*n*-Propoxy	55	174.7–5.6	8.98	9.24
2-*n*-Butoxy	73	149.2–6	8.68	8.54

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(1) Gardner and Haenni, THIS JOURNAL, **53**, 2763 (1931); Gardner, Clarke and Semb, *ibid.*, **55**, 2999 (1933).

(2) Wojahn, *Arch. Pharm.*, **269**, 422 (1931).

(3) Camps, *ibid.*, **237**, 659 (1899).

(4) All melting points in this paper are corrected.

solid precipitate which had collected on the filter was dissolved in a small amount of water and this solution was added to the hydrochloric acid extract. The ester was precipitated by the addition of sodium carbonate. Melting points and analyses of the individual esters are given in Table III.

Morpholinealkyl 2-Alkoxycinchoninate Hydrochlorides.—Solutions of the esters in benzene were treated with the calculated quantity of a benzene solution of hydrogen chloride. The mixture was allowed to stand for several hours and the precipitated hydrochloride was filtered out, washed with benzene and dried in a desiccator. Yields, melting points and analyses of the individual compounds are given in Table IV.

Summary

1. Eight new morpholinealkyl esters of 2-alkoxycinchoninic acids and their hydrochlorides have been prepared.

2. The hydrochlorides are local anesthetics.

ST. LOUIS, MO.

RECEIVED APRIL 10, 1936

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Chemical Studies of the Mechanism of the Narcosis Induced by Hypnotics. II. The Synthesis of Colored Derivatives of Phenobarbital[1]

BY ALAN E. PIERCE AND MARY M. RISING

The pharmacological and histological study of of a hypnotic which shows the property of selectively staining nerve cells may be found to give insight into the mechanism of hypnosis. With the synthesis of such a dye-hypnotic as an object, the work described in this paper consisted of the preparation of several colored derivatives of phenobarbital, or 5-phenyl-5-ethylbarbituric acid, $(C_6H_5)(C_2H_5)\underline{CCONHCONHCO}$, which is itself a white compound. Several investigators[2] have attempted the preparation of physiologically active, colored derivatives of cocaine or procaine with varying degrees of success. It was hoped that phenobarbital would also be suitable for such a study.

In the first paper of this series,[3] the syntheses of four dye derivatives of phenobarbital by means of coupling diazotized 5-*m*-aminophenyl-5-ethylbarbituric acid with various phenolic compounds separately were described. Not one of these products, however, exhibited satisfactory hypnotic properties.

In the present investigation two colored derivatives of phenobarbital were prepared by the coupling of diazotized 5-*m*-aminophenyl-5-ethylbarbituric acid with *m*-phenylenediamine to form 5-*m*-(2,4-diaminophenylazo)-phenyl-5-ethylbarbituric acid, $(NH_2)_2C_6H_3N{=}NC_6H_4(C_2H_5)\underline{CCONHCONHCO}$, and with 5-*m*-hydroxyphenyl-5-ethylbarbituric acid to form *x*-hydroxyazobenzene-*x*,3′-bis-(5-ethylbarbituric acid), $\underline{CONHCONHCOC}(C_2H_5)C_6H_4{-}N{=}N{-}(OH)C_6H_3(C_2H_5)\underline{CCONHCONHCO}$. A third colored derivative is *m*-diazoamino-5-phenyl-5-ethylbarbituric acid, $\underline{CONHCONHCOC}(C_2H_5)C_6H_4{-}N{=}N{-}NHC_6H_4(C_2H_5)\underline{CCONHCONHCO}$. In this synthesis it was hoped by means of linking two ureide nuclei to ensure the preservation of the physiological effect of phenobarbital.

In addition to 5-*m*-nitrophenyl-5-ethylbarbituric acid, obtained by the nitration of phenobarbital, the para nitro compound was isolated in small quantity and identified, but was not used in the syntheses.

For the pharmacological study of the compounds prepared in this work the writers are indebted to several investigators. The work was done in part by Dr. A. L. Tatum, Professor of Pharmacology, University of Wisconsin, and in part by Dr. H. A. Shonle and Mr. E. E. Swanson of the Eli Lilly Company, Indianapolis. Intraperitoneal administration of the sodium salts of the various compounds to rabbits and white mice produced no sedative action without undesirable effects. Neither the three colored compounds nor 5-*m*-hydroxyphenyl-5-ethylbarbituric acid were effective in sub-lethal doses. The 5-*p*-nitrophenyl-5-ethylbarbituric acid was not tested, since the meta isomer has been found to be physiologically inert.[4]

Experimental

5-*m*-Nitrophenyl-5-ethylbarbituric Acid.—The method of Bousquet and Adams[4] was followed in the nitration of

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(1) This article is abstracted from the dissertation presented by Alan E. Pierce in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Chicago.

(2) (a) Ehrlich and Einhorn, *Ber.*, **27**, 1872 (1894); (b) Fulton, *Am. J. Physiol.*, **57**, 158 (1921); (c) Gardner and Joseph, THIS JOURNAL, **57**, 901 (1935).

(3) Rising, Shroyer and Stieglitz, *ibid.*, **55**, 2818 (1933).

(4) Bousquet and Adams, *ibid.*, **52**, 224 (1930).

phenobarbital. Several recrystallizations of the crude nitrated material from 95% alcohol gave a 60% yield of 5-*m*-nitrophenyl-5-ethylbarbituric acid, m. p. 283–284°. The position of the nitro group in this product has been previously proved.[5]

5-*p*-Nitrophenyl-5-ethylbarbituric Acid.—The alcoholic mother liquors from the recrystallizations of 5-*m*-nitrophenyl-5-ethylbarbituric acid were evaporated to dryness. The residue (7.0 g. from 20 g. crude nitro-ureide) was dissolved in the least possible amount of dilute sodium hydroxide solution, and, with rapid stirring of this solution, enough dilute hydrochloric acid to neutralize three-fourths the alkali used was slowly added to the solution. The white precipitate which formed was brought upon a filter, washed with water, and recrystallized several times, from either 95% alcohol or water, until a product of m. p. 216–217° was obtained. Further crystallization from alcohol, water or toluene did not change this melting point; yield 1.2 g. *Anal.* Calcd. for $C_{12}H_{11}N_3O_5$: C, 51.96; H, 4.00; N, 15.17. Found: C, 52.12, 51.93; H, 4.08, 3.99; N, 15.17, 15.22.

The position of the nitro group in the substance just described was determined through alkaline permanganate oxidation of the material. The pure product (5.0 g.) was dissolved in 300 cc. of 1% potassium hydroxide solution. This solution was refluxed for twelve hours, as 25.0 g. of potassium permanganate was added in portions. When all permanganate color of the reaction mixture had disappeared, the solution was filtered from the manganese dioxide, evaporated to 40 cc., strongly acidified with concentrated hydrochloric acid and chilled. The product which separated was brought upon a filter, washed with water, and recrystallized from hot water with Norite added, yielding 1.2 g. of white crystals, m. p. 239–239.5°. The yield was 40% of the theoretical amount of nitrobenzoic acid. A mixture of the oxidation product and pure *p*-nitrobenzoic acid melted at 239–240°. The oxidation product was reduced with ammonium sulfide, yielding a white crystalline substance, m. p. 186–187°. A mixture of the reduction product and pure *p*-aminobenzoic acid melted at 186–187°.

5-*m*-Aminophenyl-5-ethylbarbituric Acid.—This was prepared by the catalytic reduction of 5-*m*-nitrophenyl-5-ethylbarbituric acid according to the directions of Bousquet and Adams[4]; yield 90%, m. p. 208–209°.

5-*m*-Hydroxyphenyl-5-ethylbarbituric Acid.—Bousquet and Adams[4] attempted to prepare this substance. Our procedure follows. 5-*m*-Aminophenyl-5-ethylbarbituric acid (2.47 g.) was diazotized at 5° in a solution of 5 cc. of concentrated hydrochloric acid in 50 cc. of water, a 10% sodium nitrite solution being used. At the end of the diazotization the excess nitrous acid present was destroyed by the addition of urea. The solution was now heated rapidly and boiled as long as nitrogen was evolved. During this heating the solution assumed a red color. The beaker containing the reaction mixture was vigorously shaken in an ice-bath until a red gummy substance gathered on the sides of the vessel and the liquid itself was practically colorless. At this point the mixture was filtered quickly, and pink crystals soon formed in the filtrate. This product was brought on a filter, washed with water, and recrystallized from hot water with Norite added. The white crystalline material so obtained was a dihydrate, but was easily dehydrated at 110°; yield 77%, m. p. 199.5–200° (anhydrous product). *Anal.* (anhydrous product). Calcd. for $C_{12}H_{12}N_2O_4$: C, 58.04; H, 4.88; N, 11.29. Found: C, 57.96, 58.06; H, 4.93, 4.88; N, 11.27, 11.48. Hydrate, calcd. for $2H_2O$, 12.68. Loss of weight at 110°, 12.68.

5-*m*-(2,4-Diaminophenylazo)-phenyl-5-ethylbarbituric Acid.—5-*m*-Aminophenyl-5-ethylbarbituric acid (2.47 g.) was diazotized in the manner described in the preparation of 5-*m*-hydroxyphenyl-5-ethylbarbituric acid, only 2.5 cc. of concentrated hydrochloric acid being used. To the solution of the diazonium salt was added a cold solution of 1.9 g. of *m*-phenylenediamine dihydrochloride in 20 cc. of water. After this solution was stirred for fifteen minutes a solution of 6.9 g. of sodium acetate in 50 cc. of water was added slowly, the reaction mixture being kept well cooled. After it was stirred for another half hour, the mixture was heated to boiling and filtered. The orange crystals remaining on the filter were purified by solution in hot dilute hydrochloric acid, followed by the addition of sodium acetate to this solution. The tarry material which first formed was separated by quick filtration of the solution. The addition of more sodium acetate to the filtrate caused the separation of the desired product. After a second solution and precipitation in this manner the final product was crystallized from hot water, in which it is slightly soluble. The pure compound consisted of orange crystals, m. p. 221–222°, yield 70%. *Anal.* Calcd. for $C_{18}H_{18}N_6O_3$: C, 58.98; H, 4.96; N, 22.95. Found: C, 58.77, 58.88; H, 5.00, 4.99; N, 22.89, 23.00.

Coupling of Diazotized 5-*m*-Aminophenyl-5-ethylbarbituric Acid with 5-*m*-Hydroxyphenyl-5-ethylbarbituric Acid.—5-*m*-Aminophenyl-5-ethylbarbituric acid (1.0 g.) was suspended in 50 cc. of water and diazotized as previously described, 2.0 cc. of concentrated hydrochloric acid being used. To the solution of the diazonium salt, made just alkaline to litmus with dilute sodium hydroxide solution, was added dropwise with stirring a cold solution of 1.1 g. of 5-*m*-hydroxyphenyl-5-ethylbarbituric acid dihydrate in 25 cc. of water to which just enough alkali had been added to dissolve the ureide. After fifteen minutes, a dye was precipitated from solution by the gradual acidification with normal hydrochloric acid, stirring being continued. The yellow solid was brought upon a filter, washed with water, and purified by solution in dilute sodium hydroxide, and reprecipitation with hydrochloric acid; yield 92%, dec. approx. 280°.

Anal. Calcd. for $C_{24}H_{22}N_6O_7$: C, 56.89; H, 4.38; N, 16.60. Found: C, 56.70, 56.89; H, 4.54, 4.42; N, 16.10, 16.05.

***m*-Diazoamino-5-phenyl-5-ethylbarbituric Acid.**—5-*m*-Aminophenyl-5-ethylbarbituric acid (2.0 g.) was suspended in 100 cc. of water and diazotized as previously described, using 2.0 cc. of concentrated hydrochloric acid. To the solution of the diazotized amine was added a cold solution of 1.9 g. of 5-*m*-aminophenyl-5-ethylbarbituric acid in 75 cc. of water containing 1 cc. of concentrated hydrochloric acid. A solution of 4.9 g. of sodium acetate in 25 cc. of

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(5) (a) Bush and Johnson, This Journal, **55**, 3894 (1933). (b) Rising and Pierce, *ibid.*, **55**, 3895 (1933); the melting point of the nitro-ureide was erroneously stated in this communication to be 279–280°.

water was added dropwise with stirring. The yellow precipitate which separated was brought upon a filter, washed with water, and purified by solution in dilute alkali and reprecipitation by the slow addition of dilute hydrochloric acid to a point faintly acid to litmus. The solid was collected, washed and dried at 110°; yield 75%, dec. 210°.

Anal. Calcd. for $C_{24}H_{23}N_7O_6$: C, 57.00; H, 4.59; N (total), 19.41; N (diazoamino), 5.55. Found: C, 56.80, 56.98; H, 4.57, 4.60; N (total), 19.32, 19.33; N (diazoamino, according to procedure to be described), 5.47, 5.44.

The Microdetermination of Diazoamino Nitrogen

The method of Houben-Weyl[6] for analyzing diazoamino compounds was modified and adapted to the micro scale. The modified method should be applicable to substances which evolve nitrogen when heated with hydrochloric acid.

The apparatus (Fig. 1) was constructed from a piece of 10-mm. Pyrex glass tubing 15 cm. long. When in use, it was connected to the carbon dioxide generator, at the end near A, and to the azotometer, at the end near B, by flexible connections, each made by joining together several short pieces of 1-mm. capillary tubing with clean rubber connections. A precision microazotometer, described by Pregl,[7] was used.

The sample to be analyzed was deposited in the bulb A and 0.5 cc. of freshly boiled concentrated hydrochloric acid in the bend of the tube at B. The tube was supported in the position shown, connected with generator and azotometer, and thoroughly flushed with a stream of pure carbon dioxide, until the bubble residues in the azotometer were no longer of significant size.[7] The gas stream was adjusted to the rate of one bubble per second, and the apparatus tilted so that the acid in B ran down upon the sample in A. By heating the chamber A, the acid was boiled for a few minutes, decomposing the diazoamino compound with the liberation of nitrogen. The source of heat was withdrawn and the tube swept out with carbon dioxide. The collection and measurement of nitrogen and the subsequent calculation were made according to Pregl's directions.

This micro method was tested by analyzing four diazoamino compounds, whose purity was initially established by duplicate total nitrogen determinations. In the analyses for diazoamino nitrogen the sample size varied between 2.5 and 6 mg. The results are shown in Table I.

TABLE I

-Azoamino benzenes[8]	Total N, % Calcd.	Found		Diazoamino N, % Calcd.	Found	
Di-	21.32	21.36	21.23	14.21	14.26	14.38
p-Methyldi-	19.90	19.90	19.84	13.25	13.26	13.35
p-Nitrodi-	23.14	23.03	23.09	11.57	11.47	11.55
p,p'-Dichlorodi-	15.80	15.77	15.90	10.53	10.60	10.51

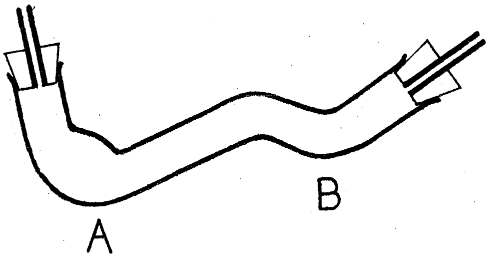

Fig. 1.

Summary

1. In a further attempt to prepare a nerve-cell staining hypnotic derivative of 5-phenyl-5-ethylbarbituric acid, three new colored derivatives of the ureide have been synthesized. These products did not exhibit the desired physiological action. 5-*m*-Hydroxyphenyl-5-ethylbarbituric acid, a white substance used as an intermediate, also was shown to be devoid of hypnotic activity.

2. A method for the microdetermination of diazoamino nitrogen has been devised and tested.

BOUND BROOK, N. J. RECEIVED MAY 18, 1936

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[6] Houben-Weyl, "Die Methoden der organischen Chemie," Second edition, Leipzig, Vol. IV, 1924, p. 668.

[7] Pregl, "Quantitative Organic Microanalysis," second ed. (Fyleman), P. Blakiston's Son, Philadelphia, 1930.

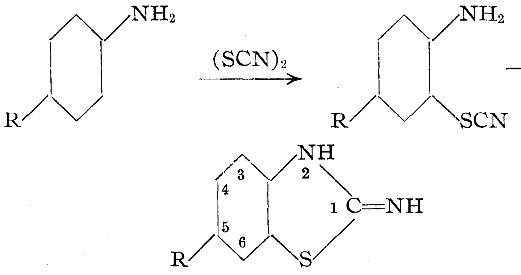
[8] The pure diazoamino compounds were kindly prepared by Mr. W. A. Erickson.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Studies on the Thiazoles Obtained by Direct Thiocyanogenation[1]

BY R. Q. BREWSTER AND F. B. DAINS

Considerable interest has been shown recently in the direct thiocyanogenation of aromatic amines. In the procedure[2] followed by most investigators the amine (1 mole) and ammonium thiocyanate (2 moles) were dissolved in glacial acetic acid and bromine or a chloramide was slowly added. The liberated thiocyanogen substituted in the position para to the amino group or, if that were occupied, in the ortho position. Such ortho thiocyanogenated products were of special interest to us because they automatically rearrange to substituted iminobenzthiazoles similar to others which have been studied previously in this Laboratory.



Our experiments dealing with the extension of this type of reaction and a study of the thiazoles thus produced may be described under four headings as follows:

(A) **General Application of the Method.**—Previous investigators have shown (1) that in the reaction indicated above the group R may be of almost any character (alkyl, halogen, carboxyl, nitro, etc.) but (2) that the reaction fails entirely if the amino group is acetylated or converted to a urethan. Both of these observations have been verified in our experiments. In addition we have found (1) that monoalkylated amines (ethyl-*p*-toluidine, benzyl-*p*-toluidine, etc.) undergo thiocyanogenation smoothly with rearrangement to the alkylated benzthiazoles, (2) that the reaction may also be applied to many disubstituted aminobenzenes such as 3-nitro-4-methylaminobenzene, 2,4-dimethylaminobenzene, 2-bromo-4-methylaminobenzene, and 2-methyl-4-nitroaminobenzene but (3) that the process fails in the case of 2-chloro-4-nitroaminobenzene and 2-nitro-4-methylaminobenzene where "steric hindrance" forces are quite large.

(B) **Alkylation.**—The imino-benzthiazoles undergo alkylation at position 2 upon boiling with alkyl halides for six to eight hours giving products identical with those obtained by direct thiocyanogenation of mono-N-alkylanilines.

(C) **Condensation with Loss of Ammonia.**—Fusion of the iminobenzthiazoles with aniline (or other primary aromatic amines) resulted in evolution of ammonia and production of 1-arylimino-benzothiazoles.

(D) **Formation of Thiazoles from Aryl Thioureas.**—Disubstituted thioureas of the type RNHCSNHR′ react with bromine in chloroform solution giving 1-aryliminobenzthiazoles which in many cases are identical with those obtained by condensation with loss of ammonia as mentioned in the preceding paragraph.

Experimental

A typical procedure for the preparation of one of those iminobenzthiazoles by direct thiocyanogenation is described as follows.

2,4-Dimethylaminobenzene (12.1 g., 0.1 mole) and 16.2 g. (0.2 mole) of sodium thiocyanate were dissolved in 150 cc. of glacial acetic acid, cooled in ice and stirred mechanically while a solution of 16 g. of bromine in 25 cc. of acetic acid was slowly added drop by drop. External cooling was applied throughout the process to keep the temperature below 10° and the stirring was continued for thirty minutes after all of the bromine had been added. The precipitate of 1-imino-3,5-dimethylbenzthiazole hydrobromide[3] was removed by filtration at the pump, dissolved in warm water and the base precipitated with alkali. For purification it was recrystallized from alcohol or ligroin, yield 13 g. The melting points and analyses of this and other benzthiazoles not recorded in the literature which have been prepared by this method are shown in Table I.

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[1] Presented at the San Francisco Meeting of the Society, August, 1935.

[2] Dyson, Hunter and Morris, *J. Chem. Soc.*, **130**, 1186 (1927); Kaufmann, *Arch. Pharm.*, **266**, 197 (1928); Likhosherstov and Petrov, *J. Gen. Chem.* (U. S. S. R.), **3**, 183 (1933); Kaufmann and Kuchler, *Ber.*, **67**, 944 (1934).

[3] In some instances the precipitate is a thiocyanate or a mixture of thiocyanate and hydrobromide.

TABLE I

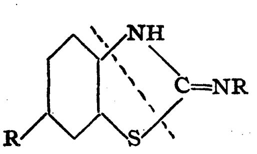
No.	Benzthiazole	Source	M. p., °C.	%, N Calcd.	Found	
I	1-Imino-5-nitro	*p*-Nitraniline	252	21.54	21.20	21.35
II	1-Imino-4-nitro-5-methyl	3-Nitro-4-methylaniline	257	20.10	19.95	
III	1-Imino-3,5-dimethyl	2,4-Dimethylaniline	140	15.93	15.74	15.81
IV	1-Imino-3-bromo-5-methyl	2-Bromo-4-methylaniline	211	11.52	11.50	11.44
V	1-Imino-3-methyl-5-nitro	2-Methyl-4-nitroaniline	280	20.10	20.04	
VI	1-Imino-2-ethyl-5-methyl	Ethyl-*p*-toluidine	106	14.58	14.53	14.60
VII	1-Imino-2-benzyl-5-methyl	Benzyl-*p*-toluidine	80	11.02	11.24	11.14
VIII	1-Imino-2,5-dimethyl	Methyl-*p*-toluidine	51	15.73	15.70	15.81

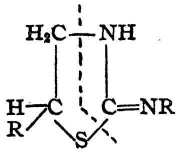
Alkylation of the Benzthiazoles

For these experiments 1-imino-5-methylbenzthiazole was used since it is easily obtained in quantity by thiocyanogenation of *p*-toluidine. 1-Imino-5-methylbenzthiazole (16.4 g., 0.1 mole) when boiled with 10 cc. of ethyl iodide and 50 cc. of ethyl alcohol on the water-bath for ten hours gave 17 g. of the slightly soluble hydriodic acid salt of 1-imino-2-ethyl-5-methylbenzthiazole. Solution of this salt in hot water and addition of alkali gave the free base, m. p. 106°. The location of the ethyl radical at position 2 was established by the fact that a mixture of this substance and compound VI, Table I, showed no depression of the melting point. Analysis of the hydriodic acid salt gave I, 39.50, 39.40. Calculated for $C_{10}H_{13}NSI$: I, 39.68.

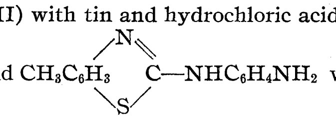
Methylation of the 1-imino-5-methylbenzthiazole by the above method using either methyl iodide or methyl sulfate likewise gave a 2-methyl derivative identical with compound VIII. Its hydriodic acid salt is quite insoluble in cold water and analysis showed 41.35% I. Calculated for $C_9H_{11}NSI$: I, 41.53.

Benzylation of the 1-imino-5-methylbenzthiazole by eight hours of boiling with benzyl chloride in ethyl alcoholic solution gave the 2-benzyl derivative identical with compound VII. In none of the alkylations did the alkyl group unite with the nitrogen atom at position 1. Such benzthiazoles (with substituents at position 1) were made by another method shown in a following section. If the hydrogen at either position 1 or position 2 has been replaced by one radical, no further alkylation occurs even upon long heating. Thus 1-*o*-chlorophenylimino-5-methylbenzthiazole (XV) was not ethylated by ethyl iodide either by boiling for several days or by heating in a sealed tube at 150° for six hours. Other compounds in this series behaved similarly. In each case the original benzthiazole (XV) was recovered unchanged. Such difficulty of alkylation is analogous to the behavior of the 2-arylimino-5-alkylthiazolines as observed by Dains and Eberly.[4]

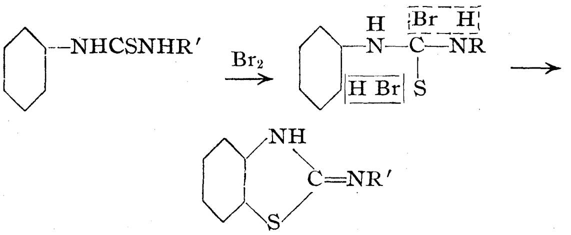




Condensations with Loss of Ammonia.—Fusion of 1-imino-5-methylbenzthiazole (8.2 g., 0.05 mole) with 8 g. (excess of 0.05 mole) of aniline[5] at 220° for thirty minutes resulted in the evolution of ammonia and the production of 11 g. of 1-phenylimino-5-methylbenzthiazole[6] which after crystallization from alcohol melted at 167°. Such condensations are typical of these substances and the following compounds which were prepared by this method and which are not listed in the literature are here reported.

Reduction of 1-*p*-nitrophenylimino-5-methylbenzthiazole (XIII) with tin and hydrochloric acid gave the amino compound  $CH_3C_6H_3\underset{S}{\overset{N}{\lessgtr}}C\text{—}NHC_6H_4NH_2$ which was purified by crystallization from ligroin; m. p. 147°; N, 16.47. Found: N, 16.40, 16.25. It was more conveniently prepared by boiling its acetyl derivative (XIV) with 15% hydrochloric acid for one hour and precipitation of the base with alkali. This compound has a close relation in structure to primuline and its diazotized solution was found to be substantive to cotton cloth and couples on the fiber with phenol or naphthol to give colors of almost the same shade as with primuline.

Formation of Benzthiazoles from Substituted Thioureas and Bromine.—Hugerschoff[7] has shown that thiocarbanilide reacts with bromine in chloroform solution to give the hydrobromide salt of 1-phenyliminobenzthiazole.



This process has heretofore been used only to prepare thiazoles from symmetrical thioureas. We have used unsymmetrical thioureas in order to obtain a check on the constitution of the benzthiazoles shown in Table II. Our observations show that in the conversion of a thiourea of the type RNHCSNHR′ to the substituted benzthiazoles the more positive of the two groups (R and R′) takes the

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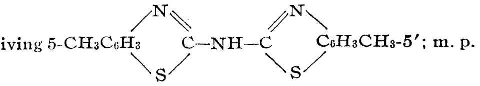
[4] Dains and Eberly, not yet published.

[5] If monomethylaniline is substituted for aniline no reaction occurs.

[6] On heating alone to 270° for thirty minutes, 1-imino-5-methylbenzthiazole evolves 1 mole of ammonia from 2 moles of the benzthiazole giving  $5\text{-}CH_3C_6H_3\underset{S}{\overset{N}{\lessgtr}}C\text{—}NH\text{—}C\underset{S}{\overset{N}{\gtrless}}C_6H_3CH_3\text{-}5'$; m. p. 278°; N, 13.50. Found: N, 13.30, 13.36. This compound is very slightly soluble in the usual solvents and is often a by-product in the formation of the substances shown in Table II.

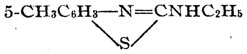
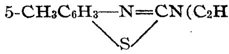
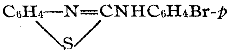
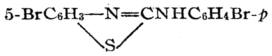
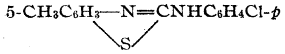
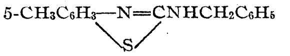
[7] Hugerschoff, *Ber.*, **36**, 3121 (1903).

TABLE II

No.	Benzthiazole	Source	M. p., °C.	%, N Calcd.	Found	
IX	1-Phenylimino-5-methyl	5-Me-benzthiazole + aniline	167	11.66	11.55	
X	1-Phenylimino-5-bromo	5-Br-benzthiazole + aniline	188	9.18	9.10	9.24
XI[a]	1-*p*-Anisylimino-5-methyl	5-Methylbenzthiazole + *p*-anisidine	160	10.36	10.41	10.54
XII[a]	1-*p*-Tolylimino-5-methoxy	5-Methoxybenzthiazole + *p*-toluidine	160	10.36	10.30	10.68
XIII	1-*p*-Nitrophenylimino-5-methyl	5-Methylbenzthiazole + *p*-nitraniline	272	14.63	14.50	
XIV	1-*p*-Acetaminophenylimino-5-methyl	5-Methylbenzthiazole + *p*-aminoacetanilide	220	14.12	13.92	14.02
XV	1-*p*-Chlorophenylimino-5-methyl	5-Methylbenzthiazole + *p*-chloroanilin	197	10.20	10.10	9.98

[a] A mixed melting point shows that XI and XII are not identical.

TABLE III

No.	Thiazole	Source	M. p., °C.	Nitrogen, % Calcd.	Found	
XVI[a]	 $\underbrace{5\text{-}CH_3C_6H_3\text{—}N{=}C}_{S}NHC_2H_5$	*p*-$CH_3C_6H_4NHCSNHC_2H_5$	133	14.58	14.38	14.49
XVII[b]	 $\underbrace{5\text{-}CH_3C_6H_3\text{—}N{=}C}_{S}N(C_2H_5)_2$	*p*-$CH_3C_6H_4NHCS(C_2H_5)_2$	Oil	..		
XVIII	 $\underbrace{C_6H_4\text{—}N{=}C}_{S}NHC_6H_4Br\text{-}p$	$C_6H_5NHCSNHC_6H_4Br\text{-}p$	210	9.12	8.98	9.04
XIX	 $\underbrace{5\text{-}BrC_6H_3\text{—}N{=}C}_{S}NHC_6H_4Br\text{-}p$	*p*-$BrC_6H_4NHCSNHC_6H_4Br\text{-}p$	256	7.25	7.41	7.21
XX[c]	 $\underbrace{5\text{-}CH_3C_6H_3\text{—}N{=}C}_{S}NHC_6H_4Cl\text{-}p$	*p*-$CH_3C_6H_4NHCSNHC_6H_4Cl\text{-}p$				
XXI[d]	 $\underbrace{5\text{-}CH_3C_6H_3\text{—}N{=}C}_{S}NHC_6H_4NHCOCH_3\text{-}p$	*p*-$CH_3C_6H_4NHCSNHC_6H_4NHCOCH_3\text{-}p$				
XXII	 $\underbrace{5\text{-}CH_3C_6H_3\text{—}N{=}C}_{S}NHCH_2C_6H_5$	*p*-$CH_3C_6H_4NHCSNHCH_2C_6H_5$	159	11.02	11.17	11.10

[a] Isomeric but not identical with VI. [b] Picrate, m. p. 174°. Platinum salt ($C_{24}H_{34}N_4S_2PtCl_6$): Pt, 22.92. Found: Pt, 22.72. [c] Identical with XV by mixed melting point test. [d] Identical with XIV. Preparation of this compound from the *p*-tolyl-*p*-acetaminophenylthiourea is the most convenient method.

position 1[8] and the more negative forms the ring closure with the sulfur atom. The results of several experiments are shown in Table III.

Summary

New methods for the preparation of the benzthiazoles and their derivatives have been developed and the properties of these compounds have been studied. In several cases substituted benzthiazoles have been obtained both by the direct thiocyanogenation of aromatic amino compounds and also by the action of bromine upon disubstituted thioureas. The behavior of these substances upon alkylation is also reported.

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[8] See table by Kharasch and Flenner, THIS JOURNAL, **54**, 678 (1932). If the two groups (R and R′) are close together in the table, such as phenyl and *p*-tolyl, a mixture of both possible isomeric benzthiazoles results which is practically impossible of separation.

It was also found in this Laboratory that disubstituted thioureas react with ethylene dibromide giving thiazoles in accordance with the same principle as above; *viz.*, the ring closure forming with the more electronegative group. Dains *et al.*, *ibid.*, **47**, 1987 (1925).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Electron Affinity of Free Radicals. XI. The Free Energy of Addition of Sodium to Ketones and Unsaturated Hydrocarbons

BY HENRY E. BENT AND NORMAN B. KEEVIL

The previous paper of this series[1] describes a potentiometric method for determining the free energy change associated with the addition of sodium to an organic compound. The method has been tested on reactions involving the addition of sodium to several free radicals by comparing the value obtained by the potentiometric method with the value obtained by an analysis of the equilibrium mixture. In order to determine whether or not the potentiometric method may be used in studying other types of compounds, namely, ketones and unsaturated hydrocarbons, the investigation of these reactions by a direct analysis of the equilibrium mixture has been undertaken. In a later paper we hope to compare these results with the results by the potentiometric method. The data are interesting in themselves and shed light on the structure of ketyls.

The experimental procedure is essentially that described in earlier papers of this series.[2] The equilibrium is approached from both sides and the concentrations of the reactants and products determined by analysis. The activity of sodium in the amalgam is adjusted to give a reaction which is approximately 50% complete.

Purification of Materials

Benzophenone was purified by fractional distillation under reduced pressure. The product was recrystallized twice from absolute methyl alcohol, giving large white crystals which melted at 47.7°.

Fluorenone obtained from Eastman Kodak Company was recrystallized from 95% alcohol and stored in a desiccator. The melting point was raised from 180–182 to 183°.

Dibiphenyl ketone, synthesized from phosgene and *p*-bromobiphenyl, melted at 229°.

Tetraphenylcyclopentadienone was prepared in connection with work reported in the fourth paper of this series.

Tetraphenylethylene was very kindly supplied by Mr. E. L. Martin. After recrystallization it melted at 220–221°.

Stilbene and anthracene were used as supplied by Eastman Kodak Company.

Ether was stored either over sodium benzophenone prepared from sodium–potassium alloy, or over sodium fluorenone prepared from dilute amalgam. The latter method of drying the ether does away with the hazard associated with the use of sodium–potassium alloy.

Experimental Results

Benzophenone.—The experimental results are recorded in Table I. Some difficulty was encountered due to the fact that the ketyl sometimes precipitated and was not easily dissolved by repeated washing with solvent. In the latter runs the volume of the solution was considerably increased in order to avoid this precipitation. The equilibrium constant refers to the reaction $(C_6H_5)_2CO + Na = (C_6H_5)_2CONa$. (When we have information on the amount of pinacolate present we will recalculate our results if this becomes necessary.) The concentrations of the ketone and ketyl may be expressed in any units. The activity of the sodium is referred to the pure metal as the standard state. In runs 11 to 15 the ketyl was prepared by shaking benzophenone with 40% amalgam. This leads to the formation of the disodium derivative which was then poured onto a slight excess of ketone, forming the monosodium derivative.[3] This change is accompanied by a change in color from the clear purple of the disodium derivative to the blue of the monosodium derivative. The solution of the monosodium derivative was then poured onto mercury and shaken until equilibrium was established. In run 18 the ketyl was prepared by shaking the ketone with a saturated amalgam (about 1%). Run 13 was carried out at 0° and the rest at 25°. In run 16 benzene was the solvent. The solubility of ketyl in ether seems to be about 10^{-5} moles per liter and in benzene about 5×10^{-3} moles per liter. Exact values cannot be given due to the tendency of the solution to supersaturate, and the slowness with which the precipitate dissolves. The last four runs are probably the best. In approaching the equilibrium by adding sodium directly to the ketone an amalgam was used in which the mole fraction of sodium was 0.0008.

Fluorenone forms a monosodium derivative. The insolubility of the ketyl again introduced some experimental difficulties. In order to avoid error from possible precipitation during the reac-

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[1] Bent and Keevil, THIS JOURNAL, **58**, 1228 (1936).

[2] Dorfman, *ibid.*, **57**, 1455 (1935).

[3] When the monosodium derivative was prepared by this indirect method the amount of ketone at equilibrium was obtained by evaporation of the solution to dryness and correcting for the amount of ketyl determined by titration.

TABLE I

EQUILIBRIUM DATA ON BENZOPHENONE-SODIUM

No.	Direction of approaching equilibrium	Moles Na in mercury	Moles of Na in ether	Moles of mercury	Moles of ether	Moles of ketone at equilibrium	$-\Delta F$
11	Removal of Na	6.72×10^{-5}	6.08×10^{-4}	0.2561	0.3399	8.08×10^{-4}	22.3
12	Removal of Na	4.08×10^{-5}	1.708×10^{-4}	.2088	.3964	5.17×10^{-4}	22.0
13[a]	Removal of Na	1.83×10^{-5}	2.296×10^{-4}	.2531	.4609	7.20×10^{-4}	20.7
14	Removal of Na	8.54×10^{-7}	2.81×10^{-5}	.1977	.4671	2.64×10^{-4}	23.6
15	Removal of Na	6.59×10^{-6}	1.30×10^{-4}	.2557	.3854	2.64×10^{-4}	23.4
16	Removal of Na	1.79×10^{-4}	1.23×10^{-3}[b]	.3560	.2635[b]	1.79×10^{-4}	23.2
22	Addition of Na	1.27×10^{-5}	9.02×10^{-5}	.1153	2.275	3.40×10^{-4}	22.2
23	Addition of Na	7.33×10^{-4}	2.265×10^{-4}	1.3181	2.135	2.170×10^{-4}	22.1
24	Addition of Na	2.172×10^{-5}	1.38×10^{-4}	0.229	1.067	3.36×10^{-4}	22.5
18	Removal of Na	5.34×10^{-5}	5.33×10^{-5}	2.066	2.104	3.70×10^{-4}	22.7
						Average of all results at 25°	22.7
						Average of last four	22.4
			Data on Benzophenone-Potassium				
17	Addition of K	4.17×10^{-5}	2.80×10^{-4}	0.7515	0.880	2.80×10^{-4}	27.8

[a] Temp. = 0°. [b] Benzene as solvent.

TABLE II

EQUILIBRIUM DATA ON FLUORENONE-SODIUM

No.	Direction of approaching equilibrium	Moles Na in mercury	Moles Na in ether	Moles of mercury	Moles of ether	Moles of ketone at equilibrium	$-\Delta F$
11	Removal of Na	2.81×10^{-6}	6.71×10^{-4}	0.4308	0.4659	5.07×10^{-4}	24.9
12	Removal of Na	4.27×10^{-6}	6.64×10^{-4}	.3906	.4202	6.13×10^{-4}	24.4
13	Removal of Na	3.05×10^{-6}	3.40×10^{-4}	.6767	.2544	4.83×10^{-4}	24.7
14	Removal of Na	2.22×10^{-4}	3.59×10^{-4}	2.8344	2.0708	1.0×10^{-5}	25.3
21	Addition of Na	1.34×10^{-5}	5.60×10^{-5}	.6600	2.448	1.0×10^{-5}	25.0
23	Addition of Na	3.17×10^{-6}	2.54×10^{-4}	.2973	2.281	1.77×10^{-4}	24.6
24	Addition of Na	4.88×10^{-7}	1.41×10^{-4}	.2550	1.684	2.80×10^{-4}	25.0
						Average	24.8

TABLE III

EQUILIBRIUM DATA ON DIBIPHENYL KETONE

22	Addition of Na	3.78×10^{-4}	1.99×10^{-4}	0.7043	2.175	1.14×10^{-5}	23.8
23	Addition of Na	3.44×10^{-4}	1.86×10^{-4}	.6784	1.659	2.0×10^{-6}	24.8
24	Addition of Na	6.40×10^{-5}	1.64×10^{-4}	.3368	2.078	3.0×10^{-5}	23.7
25	Addition of Na	2.99×10^{-5}	1.51×10^{-4}	.6760	1.882	3.47×10^{-5}	24.4
17	Removal of Na	3.71×10^{-5}	4.30×10^{-5}	3.103	1.756	6.59×10^{-5}	24.0
18	Removal of Na	7.45×10^{-5}	7.23×10^{-5}	3.1518	2.073	1.04×10^{-4}	23.7
						Average	24.1

tion the concentration of ketone was determined by evaporation of the solution to dryness after titration of the sodium as in the case of benzophenone. The various runs are of unequal importance due to the fact that in some cases the concentration of one of the reactants was very low. The large negative value for ΔF for the reaction of addition of sodium to these ketones necessitates working with very dilute amalgams. These ketones exhibit about the greatest stability which can be studied by this method.

Dibiphenyl Ketone.—This ketone behaved in much the same way as the two discussed above, forming a monosodium derivative. In preparing the ketyl for removal of sodium with dilute amalgam a saturated amalgam was used.

Tetraphenylcyclopentadienone.—This ketone is remarkable in that it adds more than one equivalent of sodium even when shaken with very dilute amalgam. The rate of addition of sodium, however, is very slow and we were not able to add as much as two equivalents of sodium even after shaking the ketone with 40% amalgam for fifteen days.

Tetraphenylethylene.—This unsaturated hydrocarbon and the two following compounds exhibit a much smaller tendency to add sodium than any compounds which we have studied hitherto. The sodium derivatives are so unstable as to be completely decomposed by a saturated sodium amalgam. They might be studied by means of solid sodium amalgams but probably better still by means of the potentiometric method. We will

TABLE IV

PRELIMINARY DATA ON UNSATURATED COMPOUNDS

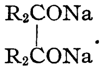
Compound	No.	Procedure	Moles Na in mercury	Moles Na in ether	Moles of mercury	Moles of ether	Moles of ketone at equilibrium	$-\Delta F$
Tetraphenylethylene	1	Out with mercury	2.15×10^{-4}	2.80×10^{-6}	0.3645	0.4413	1.48×10^{-4}	30.2
Tetraphenylethylene	2	Out with mercury	2.49×10^{-4}	3.42×10^{-6}	.6258	.5903	1.77×10^{-4}	30.5
Tetraphenylethylene	3	Out with 1% amalgam	6.61×10^{-3}	1.15×10^{-5}	.7553	.5913	1.96×10^{-4}	28.0
Tetraphenylethylene	4	Out with 1% amalgam	7.72×10^{-3}	6.1×10^{-6}	.1471	.886	2.60×10^{-4}	24.3
Stilbene	1	Out with 1% amalgam	3.29×10^{-3}	2.80×10^{-5}	.0552	.2793	1.66×10^{-4}	24.8
Stilbene	2	Out with 1% amalgam	4.28×10^{-3}	2.84×10^{-5}	.0801	.6572	6.9×10^{-5}	25.5
Anthracene	1	Out with mercury	3.35×10^{-4}	6.10×10^{-6}	.3513	.6134	9.21×10^{-4}	13.7
Anthracene	2	Out with 1% amalgam	8.96×10^{-3}	7.12×10^{-5}	.1787	.9397	4.55×10^{-4}	12.4

reserve comment on these compounds until we have more exact quantitative data. The results reported in Table IV are of interest in indicating the most negative value which ΔF can assume. These are minimum values only, the true value lying nearer to zero. The reaction to which ΔF refers is $2\mathrm{Na} + (\mathrm{C_6H_5})_2\mathrm{C{=}C}(\mathrm{C_6H_5})_2 = (\mathrm{C_6H_5})_2\mathrm{CNaCNa}(\mathrm{C_6H_5})_2$.

Stilbene.—Saturated amalgam did not remove as much of the sodium in the case of stilbene as it did with tetraphenylethylene. It is possible, therefore, that the value in the last column of the table is the correct value for this compound. Since we have not approached the equilibrium from both sides, however, it is safer to consider this a maximum value for $-\Delta F$.

Anthracene.—This compound is remarkable in that it is an unsaturated hydrocarbon and yet differs from the two just discussed in that it will combine with one atom of sodium. This reaction we hope to investigate further and until we have quantitative data will reserve further comment. The values given in the last column of the table are again maximum values for $-\Delta F$. They are approximately half of those given for the two previous compounds since only one atom of sodium is involved and the reaction is written $\mathrm{Na} + \mathrm{C_{14}H_{10}} = \mathrm{NaC_{14}H_{10}}$.

Discussion of Results

The free energy data reported indicate that fluorenone combines with sodium more readily than dibiphenyl ketone, which in turn combines with sodium more readily than benzophenone. This is not the order in which the groups attached to the carbonyl group are effective in promoting dissociation of ethanes but is the order in which free radicals containing these groups combine with sodium. It therefore appears that the problem is not a simple one and that there must be at least two factors involved. It is doubtless too early to state these factors with certainty but since the facts can readily be explained by two factors which must be of importance one is tempted to suggest an explanation. In the first place we will assume that the addition of sodium first forms a free radical, the sodium being attached to the oxygen to give a molecule of the formula $\mathrm{R_2\underset{|}{C}ONa}$. Such a molecule will have a stability which is determined partly by resonance.[4] We would, therefore, expect dibiphenyl ketone to combine more readily with sodium on account of the greater resonance energy of the biphenyl group. In the case of fluorenone, however, we must look for another explanation. Bachman has presented evidence to show that these free radicals double up to form pinacolates of the formula  $\begin{array}{c}\mathrm{R_2CONa}\\ |\\ \mathrm{R_2CONa}\end{array}$. This reaction will not affect the above argument involving resonance if the sodium addition compound is largely in the form of the pinacolate. In the case of fluorenone, however, another factor must be considered. The data on the heat of oxidation and hydrogenation of hexaphenylethane[5] indicate that steric hindrance is an important factor in determining the stability of free radicals. The large association of phenylfluoryl may therefore be due to the fact that the tying together of the two benzene rings decreases the steric hindrance and gives rise to a more stable bond. If this be assumed then it is easy to see why fluorenone combines more readily with sodium than the other ketones. The decreased steric hindrance results in the formation of more pinacolate which removes the product of the reaction and therefore shifts the equilibrium in the direction of formation of the ketyl.

The next point to be discussed is the location of the sodium atom in the ketyl molecule. Recently Wooster[6] has considered the possibility of

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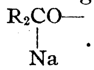
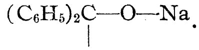
(4) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

(5) Bent, Dorfman, Cuthbertson and Leary, THIS JOURNAL, **58**, 165 (1936); *ibid.*, **58**, 170 (1936).

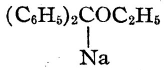
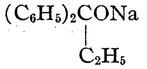
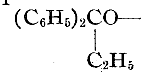
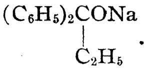
(6) Wooster, *ibid.*, **57**, 112 (1935).

the sodium being attached to the carbon, forming an oxygen free radical of the formula  $\begin{array}{l}R_2CO\text{—}\\ \ \ |\\ Na\end{array}$. Our experimental results lead us to the conclusion that the sodium is attached to oxygen and not to carbon. If we compare the free energy of addition of sodium to carbon and to oxygen we find that there is a large difference which is in favor of sodium being attached to oxygen. Thus sodium may be readily removed when attached to carbon free radicals by dilute sodium amalgam while we were not able to remove even a trace of sodium from the oxygen free radical derived from 9-chloro-10-phenanthrol with the aid of mercury.[7] This indicates that the free energy of addition of sodium to a free radical is at least 5 kcal. more negative in the case of the oxygen free radical. Hence we conclude that sodium is much more firmly attached to oxygen than to carbon and that therefore the ketyl should be represented as a carbon free radical with the sodium on the oxygen  $(C_6H_5)_2\underset{|}{C}\text{—}O\text{—}Na$.

Another entirely different approach to the problem leads to the same conclusion. Thus the negative ion formed from the ketyl can be represented by the structures $(C_6H_5)_2\underset{\cdot}{C}:\underset{\cdot\cdot}{\ddot{O}}:$ and $(C_6H_5)_2\underset{\cdot\cdot}{C}:\underset{\cdot\cdot}{\ddot{O}}\cdot$ in which the odd electron may be either on the carbon or the oxygen. Many other structures would have to be included to form the complete wave equation, these structures involving quinonoid rings. The ion must be considered to be the sum of all of these structures with, however, a preponderance of the structure of lowest energy. Since the electron affinity of oxygen is greater than that of carbon,[8] we may expect the first structure given above to be that of greatest importance. This corresponds to the negative charge being localized on the oxygen and hence would lead to an ion pair in which the sodium is attached to oxygen. Finally, a third factor which promotes the addition of sodium to oxygen is to be found in the coulomb interaction of the sodium ion and the electrons which may be considered to give rise to resonance in the molecule as a result of their wandering around in the benzene rings. This coulomb interaction will tend to localize an electron pair in the vicinity of the sodium atom.[9] Here we find a pronounced difference in the effect of such a pair being localized on the carbon or on the oxygen. If the pair is localized on the oxygen the odd electron on the carbon is still free to wander. On the other hand, if the pair is localized on the carbon the free electron on the oxygen is not free to wander and hence this structure would be less stable on account of the smaller amount of resonance energy in the molecule.

The above three lines of evidence lead us to the conclusion that the sodium is attached to oxygen in the ketyl. No shift of the sodium is then required in forming the double molecule.[10]

If our point of view is correct the question arises as to what is the probable answer to each of the lines of evidence which Wooster brings out, leading to the opposite conclusion.

Wooster's first evidence arises from the fact that  $\begin{array}{l}(C_6H_5)_2COC_2H_5\\ \ \ \ \ \ \ \ \ |\\ \ \ \ \ \ \ Na\end{array}$ does not rearrange to give the compound  $\begin{array}{l}(C_6H_5)_2CONa\\ \ \ \ \ \ \ \ |\\ \ \ \ \ \ C_2H_5\end{array}$ and he therefore concludes that the initial product of the reaction of sodium-benzophenone with ethyl bromide is the free radical  $\begin{array}{l}(C_6H_5)_2CO\text{—}\\ \ \ \ \ \ \ \ |\\ \ \ \ \ \ C_2H_5\end{array}$ and that this reacts with a second molecule of ketyl to give  $\begin{array}{l}(C_6H_5)_2CONa\\ \ \ \ \ \ |\\ \ \ \ C_2H_5\end{array}$. We agree that a reaction of the oxygen free radical with sodium benzophenone would be expected as our experiments have shown that sodium cannot be removed from an oxygen free radical by mercury while it can be removed very readily from sodium benzophenone. This difference is due in large measure to the fact that when the sodium is removed from the ketone a single bond between oxygen and carbon is changed into a double bond and it is this process which permits the sodium to be removed so readily from the ketone. Wooster's suggestion that because the ethyl group adds to carbon the sodium must originally have been on the carbon does not seem conclusive in the absence of other evidence. We quite agree with Wooster, however, that the course of the alkylation may be determined by a configuration which is not that of the normal molecule and in this case may be that in which the charge is on the carbon.

The second evidence presented by Wooster has to do with the relative ionization of sodium benzhydrylate, sodium benzophenone and sodium triphenylmethyl. Wooster informs us that he

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(7) Bent, Dorfman and Bruce, THIS JOURNAL, **54**, 3250 (1932).

(8) Glockler, *Phys. Rev.*, **46**, 111 (1934).

(9) There seems to be no way at present of estimating the magnitude of this effect. We hope to study this problem in more detail experimentally.

(10) Bachman, THIS JOURNAL, **55**, 1179 (1933).

expects in the near future to give a different interpretation of these data so that this argument no longer concerns us here. Recent correspondence indicates that Wooster's views and ours are not in complete accord. The question of the degree of localization of the sodium ion in the ion pair is answered by the data of Kraus and Fuoss on the compounds C_6H_5ONa (2.70), C_6H_5SNa (4.95) and $C_{10}H_7ONa$ (2.9–3.1). The values given in parentheses are for the distance "a," multiplied by 10^8, which is characteristic of the distance of closest approach of the two ions. It is apparent that the change from an oxygen to a sulfur atom produces a much greater change in "a," than the addition of several carbon and hydrogen atoms. We therefore conclude that in such an unsymmetrical anion the sodium is localized, in this case near the oxygen or sulfur and the anion cannot be treated as spherically symmetrical. This is the justification for the formulation of the ion pair with the sodium attached to oxygen rather than a more general formula which does not localize it at any point in the molecule.

The third line of evidence suggested by Wooster has to do with the ease with which sodium may be removed from sodium benzophenone and from sodium triphenylmethyl. Wooster gives data to show that these two compounds are about equally stable, the free energy change for the process of transferring the sodium from ketone to the free radical being within 0.5 kcal. of zero. Our data also indicate the free energy change for this reaction is small, from 0.7 to 1.0 kcal. Wooster finds that the sodium is held slightly more firmly by benzophenone while we find that triphenylmethyl has a slightly greater affinity for sodium. The difference is not significant, however, and we may consider the two sets of data in substantial agreement. Wooster concludes from these data that the sodium is attached to carbon in both cases. As we have pointed out above, however, the loss of sodium from the ketone leads to the formation of a double bond between the carbon and oxygen and therefore contributes nearly 100 kcal. to the process. If sodium were attached to carbon in both compounds we would expect (from this factor alone neglecting resonance energy) that it would be liberated from the ketone more easily by 100 kcal. This would mean that the ketyl would not be formed at all. We have calculated the heat of formation of the ketyl assuming the sodium to be on the oxygen, adding up single bond energies and estimating the magnitude of the resonance energies involved. We do not wish to present these figures in detail owing to their very rough qualitative nature, but they give the right order of magnitude for the experimental energy. When one assumes that the sodium is attached to carbon the agreement with the experimental value is very poor, as is indicated above. We, therefore, are led to the conclusion that sodium adds to the benzophenone forming a ketyl with sodium attached to oxygen which then forms a pinacolate.

Summary

1. Data are given for ΔF for the reaction of addition of sodium to benzophenone, dibiphenyl ketone, fluorenone, tetraphenylcyclopentadienone, tetraphenylethane, stilbene and anthracene.

2. The data are correlated with previous experiments which indicate the significance of resonance energy and steric hindrance.

3. Evidence is presented to show that sodium is attached to oxygen in sodium-benzophenone.

CAMBRIDGE, MASS. RECEIVED MAY 23, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE SAN FRANCISCO JUNIOR COLLEGE]

Radioactive Manganese as an Indicator in Testing for Possible Equilibria between Several Valences of Manganese[1]

BY MILTON J. POLISSAR

Equilibria Assumed to Exist in a Permanganate–Manganic Oxalate Mixture.—The kinetics of the reaction between permanganate and oxalate ions was studied by Harcourt and Esson,[2] and later by Schilow[3] and Skrabal.[4] Recently Launer[5] has shown that Skrabal's mechanism for the reduction of manganic ion by oxalate ion is not in complete accord with experimental facts. Launer and Yost[6] have proved conclusively that the earlier mechanism for the reactions taking place in a permanganate–manganic oxalate complex mixture is incorrect.

Launer and Yost proposed another mechanism, based on the very plausible assumption that the following equilibria exist in a solution containing permanganate ion and manganic oxalate complex ion

$2MnO_4^- + 3Mn^{++}$ (always present in $KMnO_4$) $+ 16H^+ = 5Mn^{++++} + 8H_2O$ (rapid equilibrium or sum of equilibria) (1)

$Mn^{++++} + Mn^{++} = 2Mn^{+++}$ (rapid, reversible) (2)

$Mn^{+++} + 2C_2O_4^{--} = Mn(C_2O_4)_2^-$ (rapid, reversible) (3)

A little later, Polissar[7,8] has shown that the immeasurably fast reaction taking place on mixing permanganate, oxalate and manganous ions is in need of a new interpretation. He showed that the mechanism of this reaction may be explained with the use of the equilibria assumed by Launer and Yost.

Until very recently there was no other evidence as to the reversibility of reaction (1) in acid solutions. With the discovery of radioactive manganese,[9] it became possible to test for the existence of such equilibria, using marked manganese atoms. The present paper deals with the method of attack used by the writer in carrying out such tests.

The Use of Marked Atoms in Testing for Equilibria.—The method of attack will be illustrated by means of a concrete example. Assuming that it is possible to trace the identity of atoms, one can rewrite equation (1) as follows

$2MnO_4^- + 3{}^*Mn^{++} = 2Mn^{IV} + 3{}^*Mn^{IV}$ (rapid, reversible) (4)

The marked substances are contaminated with radioactive substances chemically identical with them. For the sake of simplicity, the equation is not completely balanced. In this and in the following equations the substances whose exact formulas are not known will be indicated simply by the valence number of the manganese in them. Precipitated manganese dioxide will be represented by the formula MnO_2, even though it is known that the latter is hydrated.

If we start with ordinary permanganate and marked manganous ion, then, provided equilibrium (4) actually exists, the radioactivity should spread into the permanganate, through the operation of the reverse of reaction (4). Thus, we have a means of carrying out a crucial test for the existence of this equilibrium. (1) Mix a *small* amount of marked manganous ion with a *large* amount of ordinary permanganate ion in acid solution. (2) After allowing the mixture to stand for the desired length of time, add enough sodium hydroxide to make the mixture neutral or slightly basic. Filter off the manganese dioxide from the large excess of permanganate ion. If there is a rapid equilibrium, then *most* of the radioactivity should be found in the *filtrate*. On the other hand, if there is no exchange, then *none* of the activity should be found in the filtrate.

All the experiments in this investigation were carried out in the same manner: a highly radioactive filtrate indicates an exchange reaction; an inactive filtrate indicates the absence of an exchange reaction.

Experimental Procedure and Results

The Preparation of Marked Manganous Ion. Analysis for Radioactivity.—Radioactive manganese was prepared by bombarding metallic manganese for about forty-five minutes with a 4-microampere beam of 5.8 m. v. deuterons

$$25^{Mn^{55}} + 1^{H^2} = 25^{Mn^{56}} + 1^{H^1} \qquad (5)$$

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[1] This work is part of a project supported by a grant from the National Research Council.

[2] Harcourt and Esson, *Phil. Trans. Roy. Soc.* (London), **156**, 193 (1866).

[3] Schilow, *Ber.*, **36**, 2735 (1903).

[4] Skrabal, *Z. anorg. Chem.*, **42**, 1 (1904).

[5] Launer, THIS JOURNAL, **54**, 2597 (1932).

[6] Launer and Yost, *ibid.*, **56**, 2571 (1934).

[7] Polissar, *J. Chem. Ed.*, **13**, 40 (1936).

[8] Polissar, *J. Phys. Chem.*, **39**, 1057 (1935).

[9] Amaldi *et al.*, *Proc. Roy. Soc.* (London), **A149**, 522 (1935).

The radioactive layer was dissolved in a solution containing perchloric acid and ordinary manganous sulfate. The solution so obtained was analyzed for its total content of manganous ion. Enough sodium hydroxide, ordinary manganous sulfate, and water was added to give 50 cc. of 0.01 M *$MnSO_4$.

The preparation of the various reaction mixtures and the methods of precipitating out one of the valences will be described in connection with the respective experiments. The precipitated manganese dioxide was in each case filtered off rapidly through asbestos, in a Gooch crucible. After separation, the solid phase and the filtrate were each treated with 25 cc. of buffered hydrogen peroxide (approx. 4 M NaAc + 2 M HAc + 0.25 M H_2O_2). The resulting solutions were accurately diluted to 100 cc., a 20.0-cc. portion was removed, and a 20.0-cc. portion of 1 M $MnSO_4$ was added. Thus, all solutions to be tested for radioactivity had approximately the same concentrations of manganous ion, sodium acetate, acetic acid and hydrogen peroxide; they differed only in the concentration of radioactive manganous ion.

The solutions were tested for radioactivity in a special apparatus.[10] If the solution to be tested was found to be too active for measurement, it was diluted with another one containing the proper concentrations of manganous sulfate, sodium acetate, acetic acid and hydrogen peroxide. Frequent measurements were made to check the "background" count of the apparatus.

The experimental results are shown in Fig. 1. The ordinates in the diagram show the number of counts per minute given by each individual solution, corrected for the "background" of the Geiger counter, and for dilution. The abscissas give the time of day at which the respective measurements were made. The four circles marked with short arrows give the measurements on a control solution containing as much marked manganous sulfate as was used in every experiment. The heavy line is the best semi-logarithmic line drawn through these four points, with a slope corresponding to the half-life of radioactive manganese (two hours and forty min.). The lines running parallel to it across the diagram correspond to 80%, down to 0.1% of the activity of the control solution. They make it possible to estimate directly the fraction of the original activity present in a given solution.

The tie lines each connect the two points obtained from a single experiment. In each case the circle corresponding to the filtrate is plain. The circle corresponding to the precipitate is blackened. The radius of each circle is drawn approximately to scale, to indicate the maximum error in the measurement of the radioactivity.

Shortly before 10 P. M. the amplifying circuit of the counter stopped functioning. The last five measurements were made by placing each solution, in an Erlenmeyer flask, over the aluminum window of an electroscope. All five values of the activity, expressed in divisions per minute, were multiplied by a constant factor, selected in such a way as to bring the third control point (11:05 P. M.) on the 100% line.

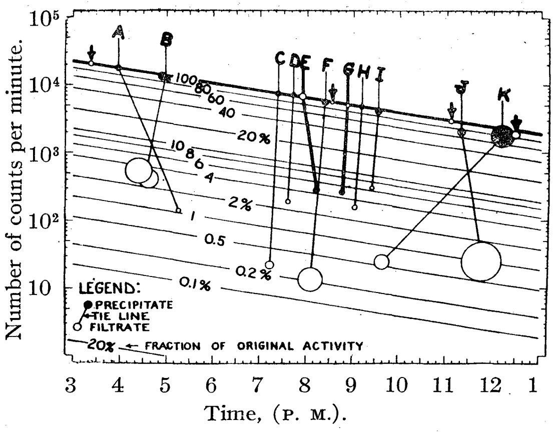

Fig. 1.—Complete record of radioactive measurements. The activities of the solutions obtained from the precipitates (blackened circles) and from the filtrates (plain circles). A very active filtrate indicates an exchange reaction. An inactive filtrate indicates the absence of exchange. Exchange reactions evident in Experiments E and G. In all other experiments no exchange took place. In experiment I the filtrate contained 6.7% of the original activity because of the use of an excess of marked manganous ion in the preparation of the manganese dioxide. The small activity of the filtrates in A, B, C, D, F, H, J and K was due to imperfect filtration.

It will be seen that in all experiments, but J, the sum of the activities of the filtrate and the precipitate was equal to the activity of the control solution, within the experimental accuracy of measuring the activity. In experiment J the deficiency was large, for some unexplained reason. Inspection of the results in experiment K and of Fig. 2 will show, however, that this slight uncer-

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[10] Olson, Libby, Long and Halford, THIS JOURNAL, **58**, 1313 1936).

tainty does not invalidate the conclusions to be drawn from experiment J.

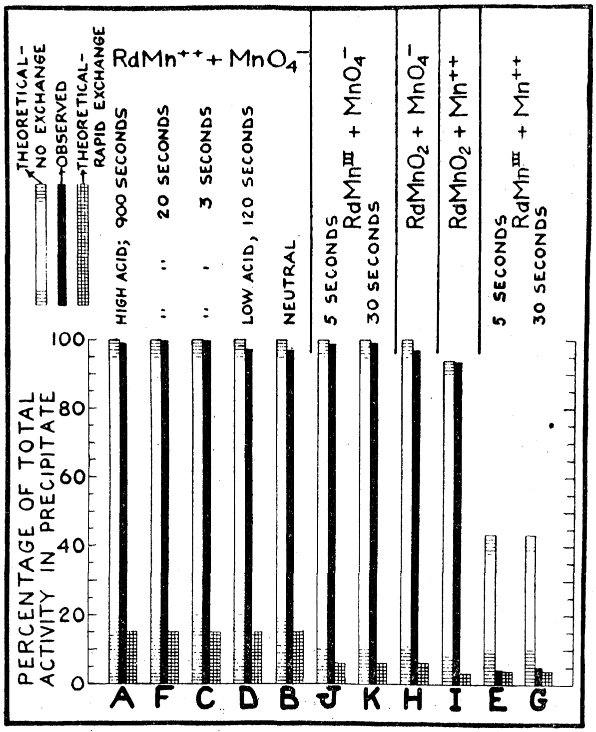

Fig. 2.—Observed activities of the precipitates (black bars) compared with the theoretical values for complete absence of exchange (shaded bars) and for complete exchange (cross-hatched bars). This diagram exhibits more clearly the complete exchange in a solution containing manganic complex and manganous ions (Experiments E and G) and the absence of exchange in the other nine mixtures.

Description of Individual Experiments

Experiments C, F, A, D, B. Marked Manganous and Permanganate Ions.—*Experiment C.*—(10.0 cc. of 0.02 *M* $KMnO_4$ + 1.0 cc. 1 *M* $HClO_4$) was added to (2.0 cc. 0.01 *M* $MnSO_4$ + 10 cc. H_2O). Three seconds later, with the solution still clear and violet, 10.0 cc. of 0.1 *M* NaOH was added. The manganese dioxide precipitated at once. Filtration started about two minutes later. 100% (±6%) of the original activity was found in the precipitate; 0.3% (±0.05%) in the filtrate. (The small amount of radioactivity found in this and in some of the other filtrates is probably not due to a slow exchange. The weight of the precipitated manganese dioxide did not exceed 4.4 mg. in any of the experiments. From visual observations, the writer is inclined to ascribe small activities of the filtrates to imperfect filtration.)

Experiment F.—The same mixture as in C quenched forty seconds after mixing. Just before quenching, the solution was still clear, but definitely reddish, because of the small amount of manganese dioxide formed; 100% (±8.5%) of the original activity found in the precipitate; 0.2% (±0.1%) in the filtrate.

Experiment A.—The same mixture as in C allowed to stand for fifteen minutes. By this time the spontaneous formation of manganese dioxide was practically complete, and it was unnecessary to add sodium hydroxide: 100% (±8%) of the original activity in the precipitate; 1% (±0.05%) in the filtrate.

Experiment D.—(10.0 cc. of 0.02 *M* $KMnO_4$ + 0.1 cc. 1 *M* $HClO_4$) was added to (2.0 cc. 0.01 *M* $MnSO_4$ + 10 cc. H_2O). In this experiment the initial acid concentration was one-tenth as large as in experiment C. The spontaneous formation of manganese dioxide was much faster. In three to four seconds the mixture was definitely red, and in a few more seconds it was opaque. No sodium hydroxide was necessary. Filtered five minutes after mixing: 100% (±6.5%) of the original activity in the precipitate; 3% (±0.18%) in the filtrate.

Experiment B.—The perchloric acid was omitted. The precipitation of manganese dioxide took place on mixing; filtered two minutes later. In this experiment the activities of the two solutions were measured twice: 95% (±6%) of the original activity in the precipitate; 3% (±0.3%) in the filtrate.

Experiments J and K Marked Manganic Oxalate Complex Ion and Permanganate Ion.—*Experiment J.*—Ten cc. of 0.002 *M* potassium permanganate was added to (2.0 cc. 0.01 *M* $^*MnSO_4$ + 10.0 cc. 0.5 *M* $H_2C_2O_4$). Manganic oxalate complex formed on mixing. The solution contained a slight excess of permanganate ion. Two seconds after mixing, 25.0 cc. of 0.02 *M* potassium permanganate was added. Five seconds later the following quenching mixture was added: (5 cc. 3 *M* NH_4OH + 10 cc. 0.5 *M* $CaCl_2$). (The calcium chloride was added to facilitate the decomposition of the manganic oxalate complex into manganese dioxide and manganous ion.) Filtered about two minutes later. In this experiment, and in experiment K, after treating the precipitate with the buffered hydrogen peroxide, it was necessary to carry out a second filtration, since calcium oxalate does not dissolve in the acetic acid buffer solution: 75% (±10%) of the original activity found in the precipitate; 1% (±1%) in the filtrate.

Experiment K.—The same as in J, except that the manganic complex-permanganate mixture was allowed to stand for thirty seconds before adding the quenching mixture: 80% (±24%) of the original activity found in the precipitate; 1% (±1%) in the filtrate.

Experiments E and G. Marked Manganic Oxalate Complex and Manganous Ions.—*Experiment E.*—(2.4 cc. 0.002 *M* $KMnO_4$ + 10 cc. H_2O) was added to (2.0 cc. 0.01 *M*$^*MnSO_4$ + 10.0 cc. 0.5 *M* $H_2C_2O_4$). Marked manganic oxalate complex formed on mixing. Two seconds later 25.0 cc. 0.01 *M* $MnSO_4$ was added. Five seconds later (5 cc. 3 *M* NH_4OH + 5 cc. 2.5 *M* $(NH_4)_2SO_4$) was added. Manganese dioxide precipitated at once; the manganous ion remained in solution. The mixture was filtered two minutes later: 105% (±8%) of the original activity found in the *filtrate;* 4.5% (±0.5%) in the precipitate.

Experiment G.—Procedure the same as in E, except that the quenching mixture was added thirty seconds, instead of five seconds, after the addition of the manganous sulfate: 95% (±7%) of the original activity was found in the filtrate; 5% (±0.25%) in the precipitate.

Experiments H and I. Marked Manganese Dioxide and Permanganate Ion. Marked Manganese Dioxide and Manganous Ion.—*Experiment H.*—(7.0 cc. 0.002 *M* $KMnO_4$ + 10 cc. H_2O) was added to 2.0 cc. 0.01 *M* $^*MnSO_4$. Manganese dioxide formed at once. In this case the excess of permanganate was used advisedly. Two minutes later 25.0 cc. of 0.02 *M* $KMnO_4$ was added. The mixture was shaken and filtered two minutes later: 100% (±6%) of the original activity was found in the precipitate; 3.3% (±0.6%) in the filtrate.

Experiment I.—(6.25 cc. 0.002 *M* $KMnO_4$ + 10 cc. H_2O) was added to 2.0 cc. 0.01 *M* $^*MnSO_4$. Manganese dioxide formed at once. Two minutes later 10.0 cc. 0.1 *M* $MnSO_4$ was added. The mixture was shaken and filtered two minutes later: 95% (±7%) of the original activity was found in the precipitate; 6.7% (±0.35%) in the filtrate.

Attention should be called to the fact that in the preparation of the manganese dioxide a slight excess of the marked manganous ion was used. This accounts for practically the entire activity of the filtrate. Assuming that there is no exchange, the theoretical distribution would be 93.76% in the precipitate and 6.24% in the filtrate.

Sample Calculations

In the following calculations all the amounts have been multiplied for the sake of convenience by the factor 10^6.

Experiments C, F, A, D, B.—The original solution contained 20 moles of marked manganous ion and 200 moles of permanganate ion. The final mixture contained 33.33 moles of manganese dioxide and 186.67 moles of permanganate ion in solution. If there were a rapid exchange between the manganous and permanganate states in the original solution, then the radioactivity of the two ultimate phases would have been proportional to the manganese content of each, namely, 15.1% in the precipitate and 84.9% in the filtrate. In the absence of any interchange, the precipitate should contain all the radioactive manganese.

Experiments E and G. Marked Manganic Oxalate Complex and Manganous Ions.—Subsequent experiments with ordinary manganese yielded the following information, essential for the calculation of the theoretical distribution of radioactivity. (a) In the instantaneous reaction in which manganic oxalate complex was formed, 10% of the oxidizing titer was lost through oxidation of oxalic acid. (b) After this initial reduction, the further reduction of manganic ion was extremely slow, both before and after the addition of the large amount of manganous ion.

The mechanism of the initial 10% reduction is not sufficiently well understood. For this reason it is impossible at present to decide whether the manganous ion formed in this process originated from the marked manganous ion, from the permanganate ion, or from both. The last assumption was made in carrying out the calculation of the theoretical distribution of activity. In other words, it was assumed that the oxidation of the oxalic acid took place *after* the instantaneous formation of trivalent manganese. It should be emphasized, however, that this uncertainty is only of secondary importance. It does not in any way invalidate the conclusions to be drawn from the experimental results, namely, that there is a rapid exchange between the bivalent and trivalent states. On the contrary, if it is assumed that the oxalic acid was oxidized by the permanganate only, the evidence for rapid exchange is strengthened, but only to a small extent.

The mixture was prepared from

$$4.8 \text{ moles } MnO_4^- + 20 \text{ moles } ^*Mn^{++}$$

On mixing, the solution contained the following substances

$$4.8\ Mn^{III} + 19.2\ ^*Mn^{III} + 0.8\ ^*Mn^{++}$$

After the 10% reduction, the mixture contained

$$4.32\ Mn^{III} + 17.28\ ^*Mn^{III} + 2.72\ ^*Mn^{++} + 0.48\ Mn^{++}$$

To this was added 250 moles of ordinary manganous ion. After precipitation, the mixture contained

$$2.16\ MnO_2 + 8.64\ ^*MnO_2 + 11.36\ ^*Mn^{++} + 252.64\ Mn^{++}$$

The preceding material balance was carried out on the assumption that there was no exchange between the bivalent and trivalent states. Under such conditions, the precipitate should contain 8.64/20.0, or 43.2% of the original activity.

On the other hand, if there is a complete exchange between the two valence states, the precipitate must contain only 10.80/274.8, or 3.93% of the original activity.

Discussion of the Experimental Results

The experimentally observed activities are shown in Fig. 1. The fraction of the original activity present in the precipitate and in the filtrate, respectively, can be read directly, with the use of the reference semi-logarithmic lines.

In Fig. 2 the same data are presented in the form of a bar diagram. Before plotting, each pair of activities was multiplied by the same factor, to normalize the total activity to 100%. In each case the observed value of the activity of the precipitate is flanked on both sides by the two theoretical values corresponding to complete exchange and to complete absence of exchange, respectively.

An inspection of the diagram will show that there was no exchange between the two valence states in the first nine experiments. In the last two experiments there was a complete exchange between the two valence states.

The evidence seems to be conclusive that the equilibrium postulated in equation (1) does not actually exist. It does not follow, however, that no other equilibrium exists between permanganate and manganous ions in the same solution. It is possible to postulate other equilibria which would not be in disagreement with the experimental results obtained in the present investigation. The following two will serve as illustrations

$$MnO_4^- + {}^*Mn^{++} = Mn^{VI} + {}^*Mn^{III} \text{ (rapid, reversible)} \quad (6)$$

$$\text{or } 2MnO_4^- + {}^*Mn^{++} = 2Mn^{VI} + {}^*Mn^{IV} \text{ (rapid, reversible)} \quad (7)$$

An inspection of the two equations will show that the radioactivity cannot spread from the bivalent to the permanganate state, provided there is no exchange between Mn^{VI} and Mn^{III}, or between Mn^{VI} and Mn^{IV}, respectively.

The rapid exchange between the manganous and manganic states can be explained easily with the use of the well-known equilibrium shown in equation (2). However, the observed exchange cannot be considered as additional evidence for such an equilibrium. The exchange may have been taking place through the operation of an entirely different reversible reaction, involving no quadrivalent manganese, but involving a direct transfer of an electron from one ion to another

$$^*Mn^{III} + Mn^{++} = {}^*Mn^{++} + Mn^{III} \quad (8)$$

The absence of exchange in experiment I (manganese dioxide and manganous ion) is probably due to the fact that only the surface atoms of the precipitate can be affected by the exchange reaction.

Acknowledgments.—The writer wishes to express his indebtedness to Dr. W. F. Libby, whose lecture on the general topic of Nuclear Chemistry suggested the method of attack used in this investigation, and who contributed liberally of his time in carrying out the radioactive measurements. The writer also wishes to express his gratitude to Professor E. O. Lawrence, who made this investigation possible, and to Dr. R. L. Thornton and Dr. A. H. Snell, who prepared the radioactive manganese.

Summary

1. Radioactive manganese was used as a "tracer" in a search for possible equilibria existing in solutions containing manganese in two valence states.

2. It was found that no exchange takes place in the following pair-systems: (a) permanganate ion–manganous ion; (b) permanganate ion–manganic oxalate ion; (c) permanganate ion–solid manganese dioxide; (d) solid manganese dioxide–manganous ion.

3. A rapid and complete exchange was found to take place in the system (e) manganic oxalate ion–manganous ion.

4. The absence of exchange in system (a) offers conclusive evidence against the existence of a rapidly established equilibrium between permanganate and manganous ions on one hand and some *one* substance of intermediate valence on the other.

5. The absence of exchange in system (a) cannot be taken as evidence against the existence of a rapidly established equilibrium between permanganate and manganous ion on one hand and *two* substances of intermediate valence on the other, provided there is no exchange between the latter two substances.

6. The rapid exchange in system (e) is in agreement with the known existence of an equilibrium between manganic oxalate ion, manganous ion and quadrivalent manganese. However, it may be due to yet another rapid reversible reaction involving the transfer of an electron from a manganous to a manganic ion.

7. The apparent absence of exchange in system (d) is probably due to the fact that only the surface atoms on the solid manganese dioxide can be affected by such an exchange.

8. Work on the mechanism of reduction of permanganate ion is to be continued.

SAN FRANCISCO, CALIF.

RECEIVED MAY 25, 1936

[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Rearrangement of Molecules in Plastic Monomolecular Films: Pressure–Area and Potential Relations for Polycyclic Compounds of the Five-Ring Series

BY WILLIAM D. HARKINS, EVERETT F. CARMAN AND HERMAN E. RIES

1. Introduction

Monomolecular films of certain compounds whose molecules contain five benzene rings have been found to exhibit a remarkable phenomenon. That is, a rapid rearrangement of the molecules occurs in the film in such a way that the pressure at the initial area almost disappears. Thus with betuline the initial or immediate pressure at a molecular area of 34.5 sq. Å. is 17 dynes per cm. while after this there is at this area an almost exponential fall of pressure with time to a practically constant value of 1.0 dyne. Nevertheless, a rapid compression to 33.5 sq. Å., or by about $^1/_{34}$ of the area, increases the pressure by 21 times to 21 dynes, or to 4 dynes more than the previous initial compression. At an area of 28 sq. Å. the initial pressure of 40 dynes falls to 5.5 dynes in thirty seconds, but on rapid compression to 26.2 sq. Å. rises to 50 dynes per cm.

The set of six polycyclic compounds was made available through the kindness of Professor Ruzicka. The molecules of these compounds contain a phenanthrene residue (Figs. 1 and 2) as did the *d*-pimaric acids (Fig. 3) investigated in this Laboratory by Harkins, Ries and Carman.[1] A comparison of the surface potentials and force–area relations of the monomolecular films formed by this series (Figs. 4, 5, 6) is of considerable value, since the compounds (supposedly) differ only in their polar substituents.

The writers had the privilege of discussing the proposed structures with Professor Ruzicka (August, 1935), who tentatively assigned the polar groups to the locations suggested in Fig. 1. These proposed structures have not been definitely established, as yet, particularly with reference to the location of some of the polar groups. This fact must be borne in mind throughout the following discussion, as to cite all the possibilities at each reference to structure is not practicable.

2. Apparatus and Procedure

The apparatus is essentially the same as that described by Harkins and Fischer[2] and modified by Harkins, Carman and Ries.[3] The improved method of determining "zero" or clean surface potentials as described by Harkins, Ries and Carman[1] has been used throughout these experiments.

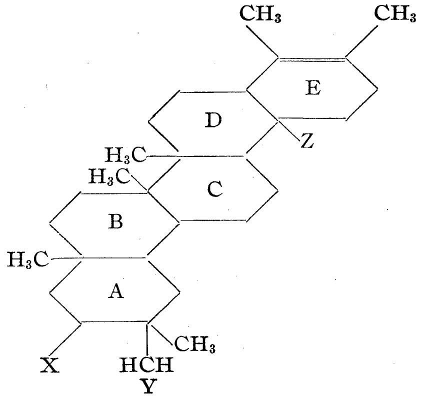

Fig. 1.—General structure of the five-ring compounds.

A modification in the older technique was made to obtain certain effects important in this investigation. As the area of the film was decreased, the torsion wire was turned simultaneously with the movement of the compression barrier. The pressure thus remained balanced during compression and instantaneous pressure readings were obtained. The compression barrier was moved at intervals of one minute and pressure readings taken immediately (unbroken lines) and then thirty seconds later (dotted lines; Figs. 4–6).

The compounds were dissolved in twice distilled chloroform and the films spread on 0.01 molal aqueous hydrochloric acid. The experiments were conducted at room temperature (24–29°) in a metal box covered with a thermal insulation.

3. Pressure–Area Relations

The pressure–area relations for these compounds are shown in Figs. 3–9 and Table I. The condensed films of these substances are of the solid type similar to those of stearic acid. This was demonstrated by the immobility of particles of lycopodium powder on their surface under a jet of air.

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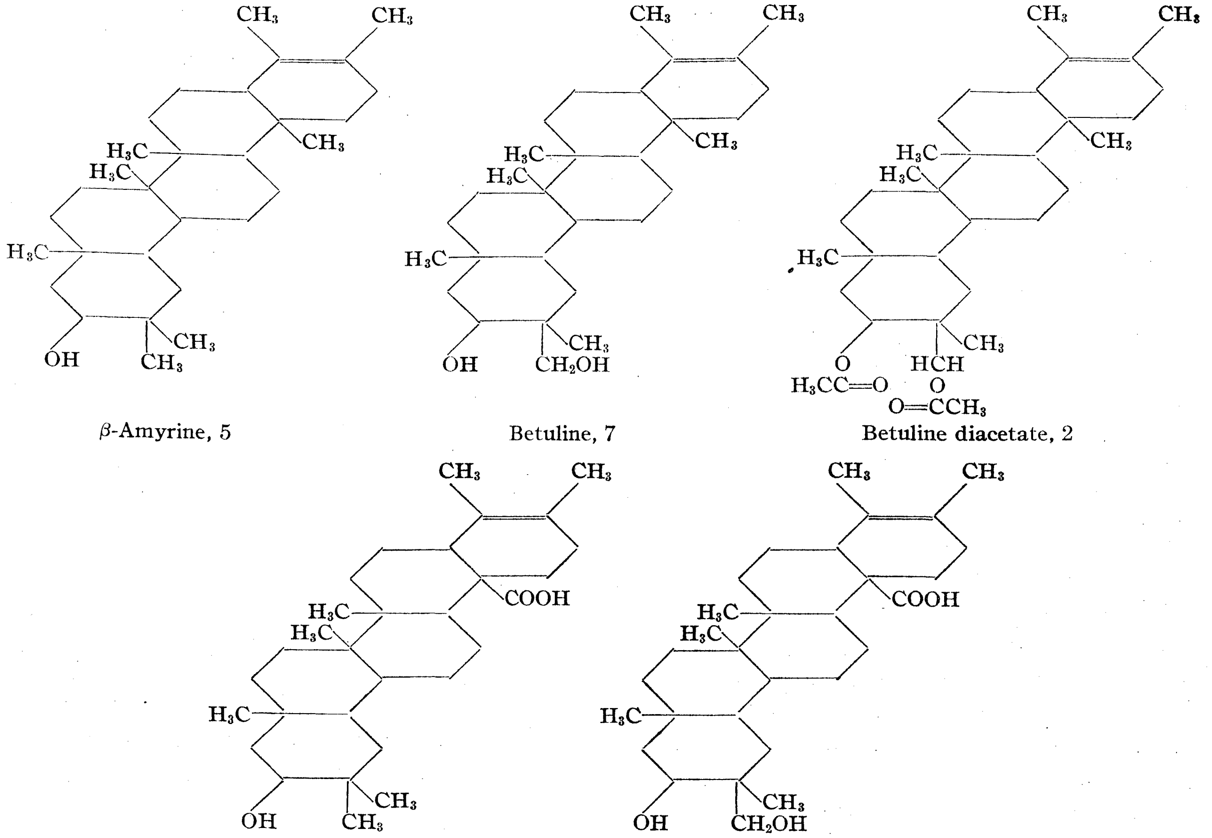
[1] Harkins, Ries and Carman, THIS JOURNAL, **57**, 2224 (1935).

[2] Harkins and Fischer, *J. Chem. Phys.*, **1**, 852 (1933).

[3] Harkins, Carman and Ries, *ibid.*, **3**, 692 (1935).



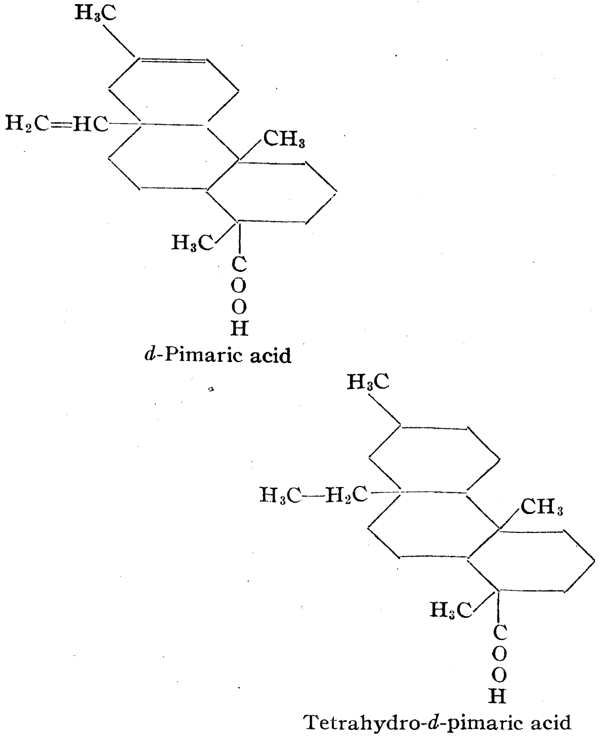
β-Amyrine, 5 Betuline, 7 Betuline diacetate, 2

Oleanolic acid, 3 Sumaresinolic acid, 4, or siaresinolic acid, 1

Fig. 2.—Structure of the five-ring compounds (the numbers refer to numbers on the figures).

The compressibility coefficients $\frac{(a_0 - a_1/a_0)}{f_1 - f_0}$, given in Table I are calculated from the slopes of the curves at pressures just below those of collapse. These coefficients range from 0.0033 to 0.0103 (stearic acid = 0.00763), and are normal for solid condensed films with perpendicular orientation of the molecules. The compressibility coefficient for tetrahydro *d*-pimaric acid, which has a three-ring structure, is greater than for any of the five-ring compounds, except betuline diacetate. This was to be expected, as pointed out by Harkins, Carman and Ries,[3] since the compressibility of films of vertically oriented molecules decreases with increasing length while that of horizontally oriented molecules is independent of the length. In betuline diacetate the high compressibility is related to the presence of the ester groups.

It may be noted here that at the lower portion of the curves, especially in the case of oleanolic, sumaresinolic and siaresinolic acids, each of which is supposed to contain a carboxyl group at Z in the upper part of the molecule (Fig. 1), the compressibilities coefficients are very much larger.



d-Pimaric acid

Tetrahydro-*d*-pimaric acid

Fig. 3.—Structure of the pimaric acids.

TABLE I

PRESSURE–AREA RELATIONS OF MONOMOLECULAR FILMS OF POLYCYCLIC COMPOUNDS OF THE FIVE-RING SERIES

INITIAL NON-CONTRACTED FILMS

Compounds	Mol. wt.	Density	Vol. of molecule, cu. Å.	Area per molecule at a film pressure $f = \theta$	$f = 10$	$f = \text{max.}$	Max. press. fm	t = Film thickness of film at a film pressure $f = 0$	$f = 10$	$f = \text{max.}$	Compressibility at $f = 0$
β-Amyrine	426.4	0.92	765	46.8	45.2	43.4	22.0	16.3	16.9	17 6	0.0033
Betuline	442.4	.92	792	37.2	37.4	26.4	49.8	21.3	21.2	(30.0)	.0059
Betuline diacetate	526.4	1.0	868	52.6	Collapse	47.6	9.2	16.5	Collapse	18.2	.0103
Oleanolic acid	456.4	0.94	801	55.4	56.6	43.0	47.8	14.5	14.1	18.6	.0047
Sumaresinolic acid	472.4	.92	846	51.0	51.0	43.0	44.8	16.6	16.6	19.7	.0035
Siaresinolic acid	472.4	.94	828	49.0	49.4	37.5	48.0	16.9	16.8	22.8	.0049
Tetrahydro-*d*-pimaric acid	306.3	1.0	506	52.3	48.8	47.1	14.7	9.70	10.4	10.7	.0068

CONTRACTED FILMS

Contracted curve								
β-Amyrine	See initial values							
Betuline	24.1	26.2	22.0	44.0	32.8	30.2	36.0	0.00198
Betuline diacetate	See initial values							
Oleanolic acid	47.2	47.0	43.0	29.6	17.0	17.1	18.6	.0030
Sumaresinolic acid	51.8	47.8	39.8	24.0	16.3	17.7	21.2	.00965
Siaresinolic acid	42.2	42.6	35.8	33.6	19.6	19.4	23.1	.0045
Tetrahydro-*d*-pimaric acid	See initial values							

It is interesting to compare the extrapolated areas per molecule at the collapse pressure. The areas for β-amyrine, oleanolic acid and sumaresinolic acid are approximately 43 sq. Å. Betuline gives a much smaller area of about 26 sq. Å. while tetrahydro-*d*-pimaric acid and betuline diacetate give larger areas of about 47 and 48 sq. Å., respectively.

There seems to be some relation between collapse pressure and the number and kind of polar groups in the molecule. Tetrahydro-*d*-pimaric acid with three rings and one carboxyl group has a collapse pressure of about 15.0 dynes per cm.; β-amyrine, which contains one hydroxyl group at X and a double bond in ring E has a higher collapse pressure of about 22 dynes per cm. Betuline, oleanolic acid and siaresinolic acid have collapse pressures of about 48 dynes per cm. while that of sumaresinolic acid is about 45 dynes per cm. All of these compounds which exhibit collapse pressures only slightly below 50 dynes, have either two or three polar groups beside the double bond in ring E (Fig. 1). The fact that the adhesion of the film for the substratum is greatly increased in these latter compounds is undoubtedly related to the addition of polar groups to the molecule. By comparing betuline with betuline diacetate the effect of changing from two hydroxyl to two acetyl groups is very clearly shown in their collapse pressures. Betuline has a collapse pressure of about 48 dynes per cm. while that of betuline diacetate is only 9 dynes per cm. This illustrates the effect of changing from a strongly to a weakly polar group.

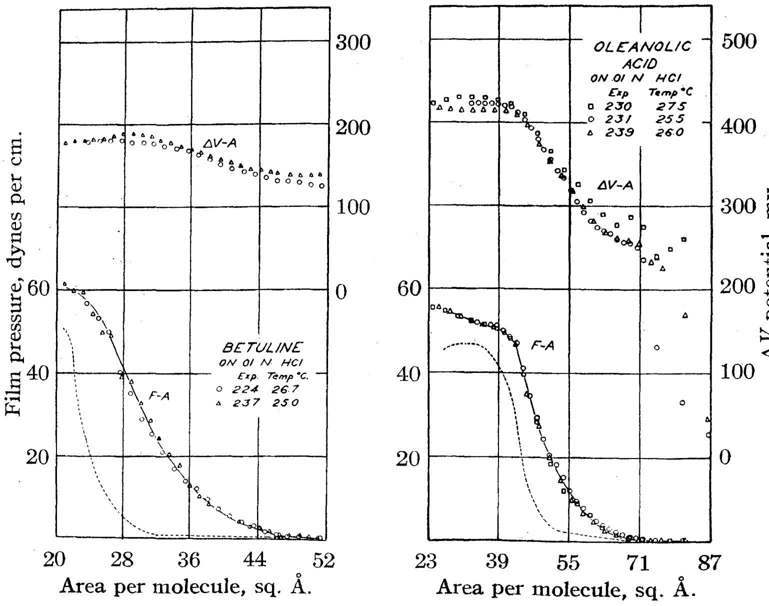


Fig. 4.

4. Molecular Rearrangement in the Films

It has been pointed out in the introduction that films of betuline exhibit a rapid rearrangement of the molecules such that the initial pressure, developed during a compression, almost entirely disappears at lower pressures, and largely disappears at higher pressures.

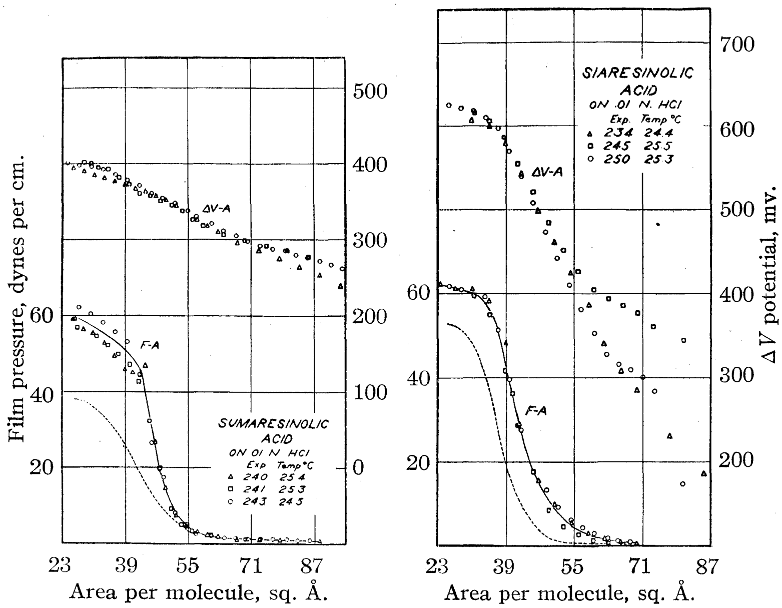


Fig. 5.

After a compression, the film shrinks for about thirty seconds, but the total decrease in area is small. If now the area is restored to its former larger value by the extremely small expansion necessary, the pressure is greatly reduced, as from 30 dynes to 1 dyne, or from 40 dynes to 5.5 dynes. The film is now under a lower pressure, and does not under this lower pressure undergo any further contraction in five minutes. However, if the pressure is kept at the higher value (as 40 dynes) for five minutes, and the area restored to the initial value at the end of five minutes, the pressure is found to be slightly lower than if the pressure had been reduced by adjusting the area at the end of thirty seconds.

Thus the rate of contraction of the film is higher at high than at low pressures. The shrinkage of the film produces a lowering of pressure, when the area is enlarged to the initial value, which is most extreme for betuline, is also great for oleanolic and siaresinolic acids, is large for sumaresinolic acid at high but not at low pressures, and appears with films of β-amyrine and of betuline diacetate only at the higher pressures (Figs. 4–6).

Thus the phenomenon of molecular readjustment and the resultant shrinkage of the film is very pronounced for those molecules of the five-ring type which have two highly polar groups attached to a single ring. These should be oriented toward the water. The removal of one of these groups, as in β-amyrine, or a change from hydroxyl to acetate groups, as in betuline diacetate, causes the phenomenon nearly to disappear. However, with β-amyrine on 0.02 molar hydrochloric acid Askew[4] found a marked contraction of the film up to an initial pressure of 15 dynes per cm.

When the pressure of a film of betuline was adjusted to 16 dynes every five minutes the area decreased in an hour by 18%, but at 1.0 dyne the decrease in area was only 4.5%. If the pressure is kept constant at 16 dynes, the decrease in area occurs more rapidly.

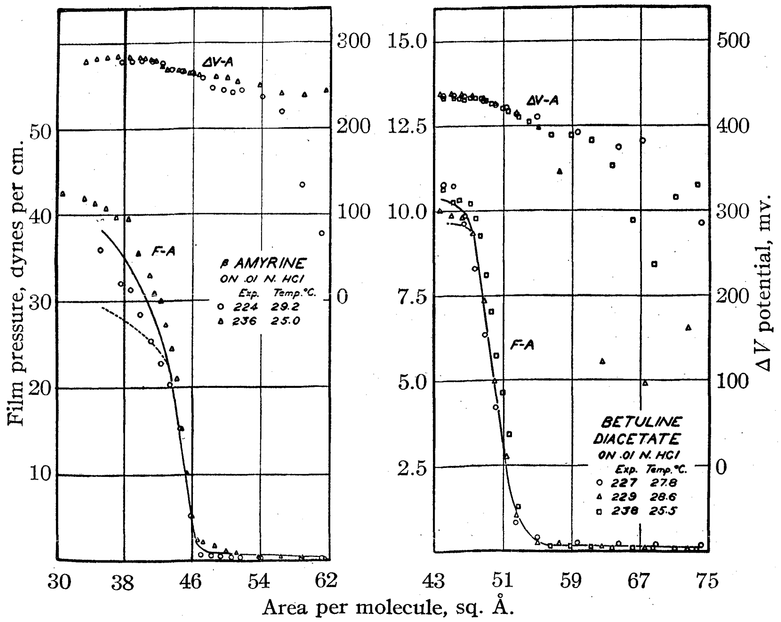


Fig. 6.

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(4) Askew, *Biochem. J.*, **29**, 472 (1935).

5. Molecular Dimensions and Orientation

Models of the five-ring compounds give a value of about 15 Å. as the length of the molecule, and indicate that the molecular area in a tightly packed film, without water present, should be of the order of 50 sq. Å. The values found at 8 dynes per cm. pressure are of this general order (Table I), with the exception of those for betuline, which seems to give a thickness of film which is anomalous, especially at the highest pressure (48.8 dynes/cm.). This indicates either that the film of this particular substance is not truly monomolecular, or that a part of the betuline has dissolved.

For the three-ring compound the model gives a molecular length of 10 Å., while the apparent film thicknesses are 9.7, 10.2 and 10.7; at zero (extrapolated), 8, and 14.7 dynes/cm., respectively.

These compounds are apparently oriented with the XY ring toward the water, and the presence of a carboxyl group at Z seems to increase the cohesion in the film.

6. Surface Potential Relations

The surface potential (ΔV) of a film composed of molecules of an organic substance is the difference between the contact potential of the aqueous surface and that of the surface when covered by the film. This is defined as positive when of the usual sign.

The data for the contact potentials of the six five-ring compounds are represented by the points of Figs. 4–6. As usual, the spread of the points at low pressures is due to non-homogeneity of the film: that is, islands of condensed film and the adjacent gaseous film are represented. In this region the highest values give the surface potential for the islands.

The shrinkage of the film produces very little effect upon the surface potential, so the data refer to either state.

The mean values for the surface potentials of the condensed films are given in Fig. 7. The surface potentials increase as the concentration in the film increases, that is, as the molecular area decreases, and most rapidly in the case of siaresinolic acid, though almost as rapidly for oleanolic acid.

The values of ΔV per molecule are represented by the values of m, where

$$m = \Delta V/n$$

in Fig. 8. Here n is the number of molecules in one sq. cm. of film. The values of $\mu = m/4\pi$ are also given in order to simplify a comparison with the results expressed by English workers. They assume that μ is the dipole moment of the molecules in the film, even although its values are commonly only one-tenth as large as the true dipole moments. It is recommended that the use of μ be discontinued, since it is the standard symbol for the dipole moment. The equation which has been used for the calculation of μ, is

$$\mu = \Delta V/4\pi n$$

This equation represents a parallel plate condenser with metallic plates, but with the dielectric constant (K) omitted. Even for this simple case the correct equation is $\Delta V = 4\pi\sigma d/K$ which they would write $\mu = \Delta VK/4\pi n$.

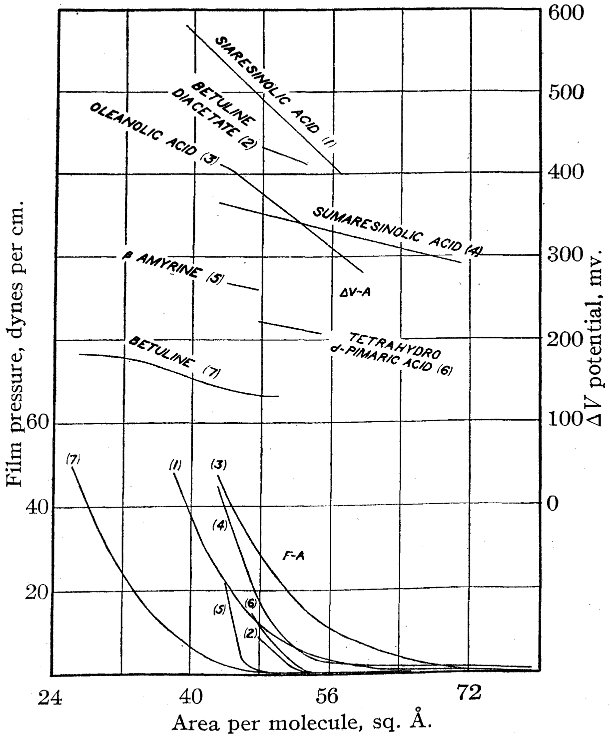

Fig. 7.

If an equation for a condenser could be applied to the case of a film, which is somewhat improbable, the value of μ would depend upon at least three dielectric constants, and the correct constant would not be 4π. It is preferable to use the value of m, which does not assume that the relation to the molecular dipole moments is known.

However, as a preliminary assumption it may be considered that the dipole moments of the molecules of the film contribute to the surface potential, although other factors are involved. It is apparent that the surface potential divided by the number of molecules (*m*) usually decreases slightly as the number of molecules per unit area increases. That is, though the surface potential (ΔV) increases with the concentration in the film, usually the contribution of each molecule to ΔV decreases with the concentration. With siaresinolic and oleanolic acids the variations are more complicated.

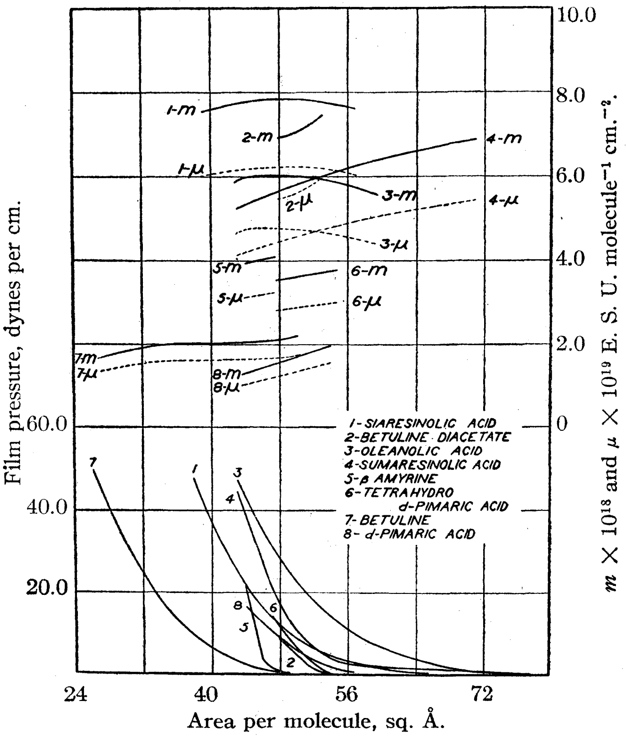

Fig. 8.

These relations are presented in a slightly different way in Table II, which gives the percentage increase in surface density and the corresponding percentage increase of surface potential for a specified range of surface density for the condensed film.

In general, the increase of surface density is more than sufficient to account for the increase of surface potential, but with oleanolic and siaresinolic acid the percentage increase of density is less than that of the potential.

Oleanolic acid is β-amyrine in which a hydrogen atom at Z is replaced by a carboxyl group. While with both compounds the surface potential for the condensed film is about 250 mv., the values for oleanolic acid rise to 415 mv. at 39 Å., while at the same molecular area for amyrine the surface potential is only 280 mv. Thus, when the molecules are closely packed the carboxyl group at Z increases the surface potential by 135 mv. or by about 50%.

The substitution of a hydroxyl group in one of the lower methyl groups (Y) of oleanolic acid to give siaresinolic acid increases the surface potential at low areas from 415 to 625 mv. However, a substitution of a hydroxyl group in the same position in β-amyrine to give betuline lowers the potential by 100 mv. Thus, exactly the same substitution at Y increases the potential by 200 mv. if the carboxyl group is present at Z, and lowers it by 100 mv. if it is not present.

Sumaresinolic acid, which is a stereoisomer of siaresinolic acid, shows widely different surface potential effects. Its potential range, 290 to 400 mv., is considerably lower than that of its isomer (400 to 625 mv.), and is fairly close to that of oleanolic acid, 280 to 430 mv. There is obviously a compensation of the polar groups in the sumaresinolic acid molecule, practically amounting to the complete neutralization of the hydroxyl (Y) group. The striking feature of its potential curve, however, is that the percentage increase of the potential is only 6.67% as compared with its surface density increase of 16.8%. The compensating effect of the dipoles evidently increases rapidly on compression.

The most pronounced compensating effect of the type discussed for sumaresinolic acid was observed for *d*-pimaric acid, by Harkins, Ries and Carman.[1] As shown in Table II, the surface density increases 16.8% while the surface poten-

TABLE II

THE VARIATION OF SURFACE POTENTIAL WITH SURFACE DENSITY

Compound	Surface potential range, total	Increase of surface density, %	Increase of surface potential, %
β-Amyrine	260–285	16.8	7.44
Betuline	130–190	16.8	14.7
Betuline diacetate	410–440	16.8	8.00
Oleanolic acid	280–430	16.8	21.3
Sumaresinolic acid	290–400	16.8	6.67
Siaresinolic acid	400–625	16.8	19.5
Tetrahydro-*d*-pimaric acid	205–225	16.8	8.8
d-Pimaric acid	110–80	16.8	−14.1

The percentage changes are calculated from the straight portions of the $\Delta V - A$ curves, not over the total range, thus the change of surface density of 16.8% corresponds to a decrease of area from 56 to 48 sq. Å. for each compound, except for betuline (40 to 34.3) and β-amyrine (48 to 41.1), since for these two compounds the $\Delta V - A$ curves were not linear in the region between 56 and 48 sq. Å.

tial decreases 14.1% though the saturated compound, tetrahydro-*d*-pimaric acid (one polar group), exhibits normal potential relations.

As mentioned above the magnitude of the potentials of β-amyrine and betuline indicates an electrically oppositional alignment of the two hydroxyl groups in the latter molecule. It is not uncommon for a second polar group to cause a lowering of the surface potential. Similar results were found by us for *d*-pimaric acid as mentioned above and by others for certain sterols.[5] However, too much weight should not be placed on this relationship in the particular case of betuline, since both its $F-A$ and $V-A$ curves are somewhat anomalous.

The high potential, 410–440 mv., of the comparatively weak film of betuline diacetate is of interest. The addition of the two acetate groups to the betuline molecule has apparently produced marked changes in the film.

The surface potentials of the condensed films vary over a large range, from 130 mv. for betuline to 630 mv. as the maximum for siaresinolic acid.

Summary

The solid monomolecular films of four of the six five-ring compounds considered in this paper have been found to give a behavior not previously exhibited, at least not in anything like this high degree. That is, if kept at constant area the pressure almost entirely disappears due to a shrinkage of the film. The behavior is more nearly analogous to that of a wax than to a crystalline solid. Thus for these films the initial pressure seems to be of much more significance than the final pressure. The initial pressures of all of the films and the surface potentials, are exhibited in Fig. 7, while the final pressures and the potentials are given in Fig. 9.

At film pressures of eight dynes per cm. the apparent thickness of the film varies from 14 to 17 Å. for the various compounds, which is about the thickness to be expected if molecules with five rings stand on end.

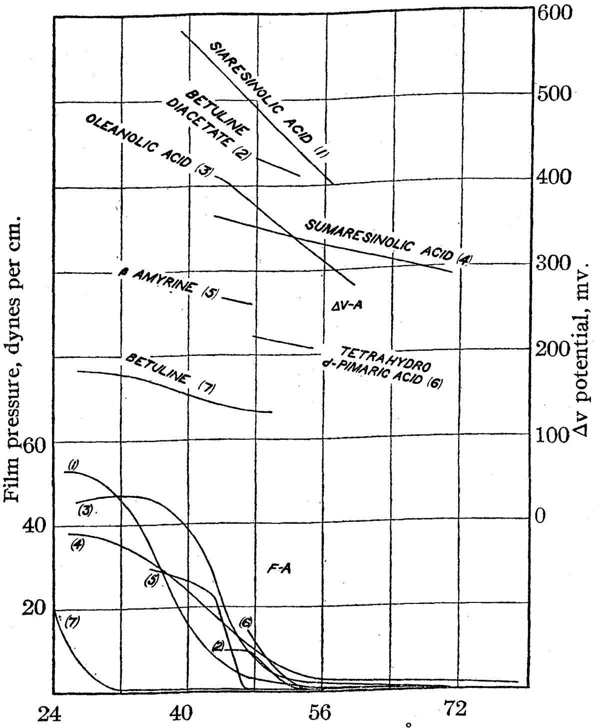

Fig. 9.

CHICAGO, ILLINOIS RECEIVED MAY 12, 1936

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[5] Adam, Askew and Danielli, *Biochem. J.*, **29**, 1786 (1935).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Derivatives of Tertiary Alcohols. Acid Phthalic Esters

BY W. A. FESSLER[1] AND R. L. SHRINER

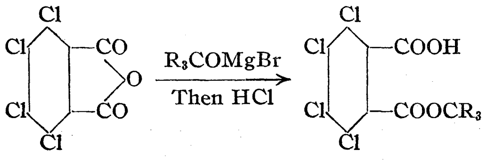
Many reagents are available for the preparation of derivatives of primary and secondary alcohols, but very few of these are applicable to tertiary alcohols. A few urethans and 3,5-dinitrobenzoates of *t*-butyl and *t*-amyl alcohols are reported.[2] The difficulties in obtaining derivatives of tertiary alcohols are due not only to the slowness with which they react, but also to the ease with which replacement of the hydroxyl or elimination of water takes place.

The preparation of solid esters of tertiary alcohols by using the tertiary alkoxymagnesium halide as one reactant seemed to offer a procedure which would avoid the dehydration reaction, since mild conditions could be used. The reaction of alkoxymagnesium halides with acid chlorides was first observed by Grignard[3] as a secondary reaction taking place when ethyl oxalyl chloride was treated with methylmagnesium iodide. Houben[4] later used the reaction with acid chlorides and anhydrides as a general method of esterification for primary and secondary alcohols. Recently Yabroff and Porter[5] prepared *t*-butyl phenylacetate by the action of *t*-butoxymagnesium bromide on phenylacetyl chloride.

In the present work, a study was made of the reaction between *t*-alkoxymagnesium halides and phthalic anhydride and three readily available substituted phthalic anhydrides. In order to determine the best conditions for the reaction and the most suitable anhydride, a series of preliminary experiments were carried out, using *t*-butoxymagnesium bromide prepared from *t*-butyl alcohol and ethylmagnesium bromide. Some of the runs are summarized in Table I.

The addition of dioxane increased the yield of the ester since it is a better solvent for the anhydrides than ether alone. Higher yields of the *t*-butyl ester were obtained at 50–55° than at lower or higher temperatures. The phthalic acid ester melts rather low and the esters of higher alcohols crystallized with difficulty. 3-Nitrophthalic anhydride gave crystalline esters, but the use of this anhydride may give rise to isomeric esters. It was found that ethoxymagnesium bromide reacted with 3-nitrophthalic anhydride to produce the 2-ethyl-3-nitro acid phthalate which melted at 156–158°, and was identical with that previously prepared by direct esterification.[6] It may, therefore, be assumed tentatively that the *t*-butoxymagnesium bromide produces the 2-*t*-butyl-3-nitro acid phthalate. No isomeric ester could be isolated, but it may have been lost during purification.

On the basis of the preliminary experiments, tetrachlorophthalic anhydride (I) seemed to be the most suitable since no isomeric esters are possible and the products crystallized more readily. Accordingly, it was used to prepare the tetrachlorophthalic acid esters (II) of the tertiary alcohols listed in Table II. This table also shows the best time and temperature for the reaction and indicates the best procedure for isolation.



I II

Examination of the data in Table II shows that the tetrachlorophthalic acid esters of tertiary alcohols are satisfactory solid derivatives which may be characterized by their decomposition points and neutral equivalents. Although the yields are not high, the reaction can be used satisfactorily when sufficient amounts of material are available.

The experimental conditions and method of isolation must be varied according to the molecular weight of the tertiary alcohol. For alcohols of low molecular weight a short reaction period at 50° is preferable, whereas the higher alcohols require a long time at a low temperature. The tetrachlorophthalic acid esters of alcohols below tri-*n*-propylcarbinol were soluble in aqueous alkalies, whereas the higher esters were insoluble. The neutral equivalents of these higher esters hence must be determined by titration in acetone solution.

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[1] Chemical Foundation Fellow in Organic Chemistry.

[2] Knoevenagel, *Ann.*, **297**, 148 (1897); Neuberg and Kansky, *Biochem. Z.*, **20**, 448 (1909); Reichstein, *Helv. Chim. Acta*, **9**, 799 (1926); Hoeke, Thesis, Leyden, 1934.

[3] Grignard, *Compt. rend.*, **136**, 1200 (1903).

[4] Houben, *Ber.*, **39**, 1736 (1906).

[5] Yabroff and Porter, THIS JOURNAL, **54**, 2453 (1932).

[6] Nicolet and Sacks, *ibid.*, **47**, 2348 (1925).

TABLE I

REACTION OF *t*-BUTOXYMAGNESIUM BROMIDE AND VARIOUS PHTHALIC ANHYDRIDES

Anhydride	Reaction solvent	Reaction Temp., °C.	Time, hr.	Dec. point	Yield of ester, %	Neut. equiv. Calcd.	Found
Phthalic	Ether	36	1	85.0–86.0 (melts)	17.5	222	220
Phthalic	Ether–dioxane	50–55	1	85.5–86.5 (melts)	42.8	222	221
3-Nitrophthalic	Ether–dioxane	50–55	1	145 dec.	54.3	267	267
Tetrabromophthalic	Ether	50–55	1	147 dec.	4.1	538	531
Tetrachlorophthalic	Ether–dioxane	50–55	1	142 dec.	54.2	360	360
Tetrachlorophthalic	Ether–dioxane	0	20	142 dec.	15.4	360	358

TABLE II

REACTION OF VARIOUS *t*-ALKOXYMAGNESIUM BROMIDES WITH TETRACHLOROPHTHALIC ANHYDRIDE

Alcohol	Reaction Temp., °C.	Time, hrs.	Yield, %	Dec. point, °C.	Neut. equiv. Calcd.	Found	Procedure[7]
t-Butyl	50–55	1	54.2	142	360	360	A
t-Amyl	50–55	1	38.4	126	374	372	A
Triethylcarbinol	25	2	66.0	145	402	398	A
Tri-*n*-propylcarbinol	0	10	54.3	138	444	443	B
Tri-*n*-butylcarbinol	0	10	36.2	112	486	482	B
Tri-*n*-amylcarbinol	0	20	47.0	102	528	529	B

The reaction with aryl carbinols was also studied. Diphenylcarbinol can be converted into the acid phthalate in 74% yields by use of the alkoxymagnesium bromide, whereas the direct reaction of diphenylcarbinol with phthalic anhydride gave only 18% yields of the ester.

All attempts to prepare acid phthalates of triphenylcarbinol (by varying the experimental conditions) have failed up to the present time.

Experimental

Tertiary Alkoxymagnesium Bromides.—A solution of 0.1 mole of the tertiary alcohol in 50 cc. of anhydrous ether was added dropwise to a vigorously stirred solution of 0.1 mole of ethylmagnesium bromide in 150 cc. of absolute ether in a flask equipped with a reflux condenser.

In the case of *t*-butyl alcohol a white precipitate appeared. With the higher alcohols no precipitate formed. The resulting solution or suspension was used in the following procedure.

In one run with *t*-butyl alcohol the precipitate was filtered, dried *in vacuo* and analyzed. The analysis showed that the precipitate was *t*-butoxymagnesium bromide containing some ether.

Anal. Calcd. for $C_4H_9OMgBr \cdot 0.5(C_2H_5)_2O$: Mg, 11.35; Br, 37.30. Found: Mg, 10.47, 10.57; Br, 35.81, 35.19. Atomic ratio: Mg:Br::1.00:1.02.

Phthalic Acid Esters.—To a vigorously stirred solution of 0.1 mole of the tertiary alkoxymagnesium bromide in 175 cc. of ether was slowly added 175 cc. of anhydrous dioxane (175 cc. of anhydrous ether was substituted on two occasions as noted in Table I). One-tenth mole of phthalic or the substituted phthalic anhydride was then introduced and the reaction flask surrounded by a bath to maintain a constant temperature. After the reaction mixture had been stirred at the temperature and for the time indicated in the tables, the contents of the flask was poured on 500 g. of ice and acidified with 125 cc. of 2 *N* hydrochloric acid. The unreacted anhydride was then filtered, after which the ether layer of the filtrate was separated and the water layer extracted once with a 75-cc. portion of ether. The combined ether layers were then washed with two 50-cc. portions of ice-cold water. Isolation of the acid ester was accomplished by one of two methods, depending upon whether or not it was soluble in a 5% solution of sodium hydroxide. It was found that the tetrachlorophthalic acid esters of the aliphatic alcohols above triethylcarbinol were insoluble in this solution.

Procedure A.—The ether layer was extracted with ice-cold, 5% sodium hydroxide, using a 100-cc. portion followed by a 25-cc. portion. The combined sodium hydroxide layers containing the sodium salt of the acid ester were acidified by slowly stirring in 6 *N* hydrochloric acid until addition of the acid caused no further precipitation. Acid esters separated by procedure A were, in each case, purified by recrystallization from a mixture of ether and low-boiling petroleum ether.

Procedure B.—The ether was evaporated from the ethereal solution of the acid ester by heating on a steam cone. The resultant mass was then placed in a vacuum desiccator over concentrated sulfuric acid for three days. At the end of this time most of the unreacted alcohol had been removed. Purification was completed by dissolving in acetone and precipitating by the addition of water. This was repeated three times, and the product washed with two 50-cc. portions of low-boiling petroleum ether chilled in solid carbon dioxide and acetone.

In each instance, a white amorphous precipitate was formed when dioxane was added to the solution of tertiary alkoxymagnesium bromide in the preparation of the acid ester. In one run with triethylcarbinol this precipitate was separated and found to contain a large and somewhat variable amount of $MgBr_2$ obtained by the effect of dioxane on the probable equilibrium in solution, $2ROMgBr \rightleftharpoons (RO)_2Mg + MgBr_2$.

The properties and neutral equivalents of the esters are recorded in Table II and the analyses in Table III.

Diphenylcarbinyl Acid Phthalate.—Treatment of diphenylcarbinol with ethylmagnesium bromide and subsequent reaction with phthalic anhydride produced this

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(7) See Experimental Part.

TABLE III

Compounds	Molecular formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
t-Butyl acid phthalate	$C_{12}H_{14}O_4$	64.83	6.35	64.60	6.30
t-Butyl acid 3-nitrophthalate	$C_{12}H_{13}O_6N$	53.91	4.90	53.88	4.88
t-Amyl acid 3-nitrophthalate	$C_{13}H_{15}O_6N$	55.49	5.38	55.22	5.06
t-Butyl acid tetrachlorophthalate	$C_{12}H_{10}O_4Cl_4$	39.98	2.80	39.65	3.05
t-Amyl acid tetrachlorophthalate	$C_{13}H_{12}O_4Cl_4$	41.69	3.23	41.58	3.12
Triethylcarbinyl acid tetrachlorophthalate	$C_{15}H_{16}O_4Cl_4$	44.75	4.01	44.47	3.95
Tri-*n*-propylcarbinyl acid tetrachlorophthalate	$C_{18}H_{22}O_4Cl_4$	48.62	4.99	48.49	5.03
Tri-*n*-butylcarbinyl acid tetrachlorophthalate	$C_{21}H_{28}O_4Cl_4$	51.82	5.67	51.64	5.60
Tri-*n*-amylcarbinyl acid tetrachlorophthalate	$C_{24}H_{34}O_4Cl_4$	54.54	6.49	54.41	6.85

ester in 74% yield. The reaction mixture was kept at 0° for twenty hours, and the acid ester separated by procedure A. The product melted at 164–165° and possessed a neutral equivalent of 333. Calcd. for $C_{21}H_{16}O_4$, 332.

By heating equimolar amounts of diphenylcarbinol with phthalic anhydride at 110° for fifteen hours, a yield of 18% of the diphenylcarbinyl acid phthalate resulted.

Summary

The reaction between *t*-alkoxymagnesium bromides and tetrachlorophthalic anhydride produces the *t*-alkyl acid tetrachlorophthalates in 36–66% yields. These solid esters may be characterized by their neutral equivalents and decomposition points.

The acid phthalate of diphenylcarbinol may be prepared in 74% yield by the reaction between phthalic anhydride and the alkoxymagnesium bromide.

URBANA, ILLINOIS RECEIVED MAY 14, 1936

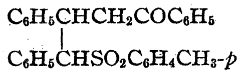
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS AND THE JOHN HARRISON LABORATORY OF CHEMISTRY AT THE UNIVERSITY OF PENNSYLVANIA]

The Michael Condensation. IV. The Active Methylene Group in Sulfones

BY RALPH CONNOR, C. L. FLEMING, JR., AND TEMPLE CLAYTON

Sulfones having the structure RCH_2SO_2R' (in which R is either aryl or another sulfone grouping) are of interest because the methylene group is attached to two activating groups, yet enolization is not possible unless sulfur expands its valence shell. Previous investigators[1] have shown that methylene disulfones form sodio derivatives and may be alkylated by methods similar to those used for the alkylation of 1,3-diketones and that benzyl phenyl sulfone forms a sodio derivative (but may not be alkylated). These are apparently the only characteristic reactions of the active methylene group which have previously been shown to apply to sulfones of this type.[2] This paper demonstrates the ability of benzyl *p*-tolyl sulfone to undergo the Michael condensation.

The product (I) obtained from the condensation of benzyl *p*-tolyl sulfone with benzalacetophenone



$$\begin{array}{l} C_6H_5CHCH_2COC_6H_5 \\ \quad | \\ C_6H_5CHSO_2C_6H_4CH_3\text{-}p \end{array} \qquad \text{(I)}$$

was present in two stereoisomeric forms, m. p. 139–141° and 197–197.5°. The total yield of the pure products was 26%; this does not represent the actual extent of the reaction, however, because of the losses encountered in the difficult separation of the isomers from each other and from unreacted benzyl *p*-tolyl sulfone.

The addition of benzyl *p*-tolyl sulfone to benzalacetophenone is similar to the behavior of the ketonic analog of the former[4] (desoxybenzoin). The analogy between the reactions of ketones and sulfones in the Michael condensation may be carried still further. Both dibenzoylmethane[5] and bis-(phenylsulfonyl)-methane do not condense with benzalacetophenone and both benzyl *p*-tolyl sulfone and desoxybenzoin fail to react with methyl cinnamate. However, the failure of

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[1] Shriner, Struck and Jorison, THIS JOURNAL, **52**, 2060 (1930).

[2] Aside from active methylene compounds, three other points of similarity may be noted[3] in the behavior of sulfones and their ketonic analogs: (1) the addition reactions of α,β-unsaturated sulfones, (2) the condensation of benzaldehyde with methyl *p*-tolyl sulfone and (3) the reaction of the Grignard reagent with sulfones to give magnesium derivatives similar to those obtained with certain ketones.

[3] Kohler and Potter, THIS JOURNAL, **57**, 1316 (1935).

[4] Knoevenagel and Schmidt, *Ann.*, **281**, 53 (1894).

[5] Connor and Andrews, THIS JOURNAL, **56**, 2713 (1934).

methyl *p*-tolyl sulfone to react with benzalacetophenone is in contrast to the behavior of acetophenone.[6]

Other typical reactions of the active methylene group were tested with these sulfones. The mercuric chloride test[7] for enolic substances was positive with bis-(phenylsulfonyl)-methane and negative with benzyl *p*-tolyl sulfone. All of the other reactions attempted (bis-(phenylsulfonyl)-methane and benzyl *p*-tolyl sulfone with benzaldehyde, *p*-chlorobenzaldehyde, selenium dioxide, nitrous acid and isoamyl nitrite in the presence of sodium ethoxide) were unsuccessful. In all cases the sulfones were recovered unchanged. While the usual caution in interpreting negative results must be observed, these data definitely form grounds for assuming a profound difference in the reactivity (if not in the nature of the reactions) of the methylene group in sulfones and in their ketonic analogs.

As regards the reactivity of benzyl *p*-tolyl sulfone in the Michael condensation and the reactivity of the disulfone with mercuric chloride, the choice between explanations assuming that the enol forms of the sulfones need not be involved or that sulfur may expand its valence shell,[8] is not clear. The former explanation agrees with the fact that it has been shown[5] that the reactivity of an addendum in the Michael condensation is not related to its tendency to enolize. However, the recognized ability of elements other than those of the first period to give transitory reaction intermediates and in some cases stable compounds with expanded valence shells, makes the latter explanation plausible.

Experimental Part

Condensation of Benzyl *p*-Tolyl Sulfone with Benzalacetophenone.—To a solution of 49.2 g. (0.2 mole) of benzyl *p*-tolyl sulfone[1] and 41.6 g. (0.2 mole) of benzalacetophenone in 1700 ml. of dry thiophene-free benzene was added a sodium methoxide solution prepared by dissolving 4.6 g. (0.2 gram atom) of sodium in 60 ml. of absolute methanol. Because of the formation of two liquid phases, the mixture was stirred with a mechanical stirrer. After a reaction period[9] of one week at room temperature 15 ml. of glacial acetic acid was added and the mixture washed with water to remove sodium acetate. The aqueous layer contained an emulsion; this layer, upon separation from the benzene gave, upon standing, 4.8 g. of product which upon recrystallization from benzene gave 2.2 g., m. p. 194–195° (corr.).

The benzene extracts were distilled until 1300 ml. of benzene had been removed. Upon cooling, 16.4 g. (m. p. 164–170°) of solid was obtained, which after recrystallization from benzene gave 9.8 g. melting at 197–197.5° (corr.).

Further concentration of the benzene extracts gave 14.1 g. (m. p. 134–136°) which, upon recrystallization from alcohol gave 11.3 g. of benzyl *p*-tolyl sulfone, m. p. 141–142° (corr.), which suffered no depression of the melting point when mixed with an authentic sample of benzyl *p*-tolyl sulfone.

All of the solvent was removed from the benzene extracts and ether added. The sulfones, which are quite insoluble in ether, are readily separated from benzalacetophenone in this manner. The ether-insoluble residue was washed with ether, giving 29.0 g., m. p. 104–111°, which, after seven recrystallizations from alcohol, gave 7.0 g., m. p. 139–141° (corr.). This product, when mixed with benzyl *p*-tolyl sulfone, gave a mixture melting at 111–113°.

The mother liquors from all the above recrystallizations were combined, concentrated and recrystallized many times from alcohol. The total yields of pure substances, including those mentioned above, finally isolated from the reaction were as follows. There was obtained 13.4 g. (14.7%) of the higher melting condensation product, m. p. 197–197.5° (corr.).

Anal. Calcd. for $C_{29}H_{26}O_3S$: S, 7.0. Found: S, 7.2, 7.2.

In addition to 11.3 g. (23%) of unreacted benzyl *p*-tolyl sulfone (m. p. 141–142°, corr.) there was obtained 10.3 g. (11.4%) of the lower melting isomer of the condensation product, m. p. 139–141° (corr.).

Anal. Calcd. for $C_{29}H_{26}O_3S$: S, 7.0. Found: S, 6.6.

The mother liquors from the crystallizations contained 10.4 g. of a mixture, m. p. 96–118°.

Other Reactions.—Under conditions similar to those described above, the reactions of benzyl *p*-tolyl sulfone and desoxybenzoin with methyl cinnamate, and of bis-(phenylsulfonyl)-methane[10] and methyl *p*-tolyl sulfone with benzalacetophenone were unsuccessful. Using conventional methods, the reactions of bis-(phenylsulfonyl)-methane and benzyl *p*-tolyl sulfone with benzaldehyde,[11] *p*-chlorobenzaldehyde,[11] selenium dioxide,[12] nitrous acid,[13] and isoamyl nitrite[14] (in the presence of sodium ethoxide) were tested. The recovery of unchanged sulfone was above 90% in the majority of the cases and was never below 75%.

Application of the mercuric chloride test[7] gave a positive result with bis-(phenylsulfonyl)-methane but was negative with benzyl *p*-tolyl sulfone.

Summary

The addition of benzyl *p*-tolyl sulfone to benzalacetophenone has been described and certain

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[6] Andrews and Connor, THIS JOURNAL, **57**, 895 (1935).

[7] Connor and Van Campen, *ibid.*, **58**, 1131 (1936).

[8] The consideration of the electronic structure of sulfones has been adequately discussed by others[1,3] in relationship to similar questions.

[9] Another run in which the reaction period was twenty-four hours gave similar results, but slightly lower yields of condensation products.

[10] Kohler and Tishler, THIS JOURNAL, **57**, 223 (1935).

[11] Tröger and Nolte, *J. prakt. Chem.*, **101**, 136 (1920).

[12] "Organic Syntheses," John Wiley and Sons, New York, 1935, Vol. XV, p. 67.

[13] *Ibid.*, p. 17.

[14] Tröger and Lux, *Arch. Pharm.*, **247**, 618 (1909).

similarities in the behavior of sulfones and ketones in the Michael condensation pointed out. The mercuric chloride test was positive with bis-(phenylsulfonyl)-methane but negative with benzyl *p*-tolyl sulfone. The other reactions of active methylene compounds tested were not successful with these sulfones.

PHILADELPHIA, PENNA. RECEIVED JUNE 3, 1936

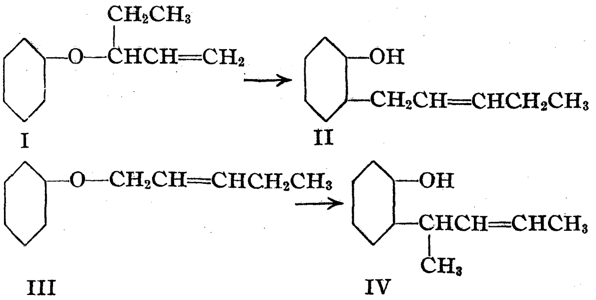
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Rearrangement of Phenyl Allyl Ethers[1]

BY WALTER M. LAUER AND WILLIAM F. FILBERT

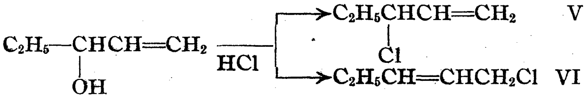
The results of Claisen's investigations dealing with the rearrangement of phenyl allyl ethers are well known. It is sufficient for our present purpose to recall that the migrating allyl group shows a preference for the ortho position and that the point of attachment of the allyl group in the cases hitherto investigated is shifted from the alpha to the gamma carbon atom. The rearrangement of a number of substituted phenyl allyl ethers has been examined,[2] but no study has been made of an isomeric pair of the type, $C_6H_5OCH(R)CH{=}CH_2$ and $C_6H_5OCH_2CH{=}CHR$. This omission presumably is due to the difficulty of obtaining the isomeric halides necessary for the usual synthesis of these ethers. Fortunately, however, Meisenheimer and Link[3] have shown that the action of hydrogen chloride on ethylvinylcarbinol leads to a mixture of $CH_3CH_2CHClCH{=}CH_2$ and $CH_3CH_2CH{=}CHCH_2Cl$, which may be separated by means of a careful fractional distillation. It was therefore considered not without interest to prepare such a pair of isomeric ethers and to study their rearrangement.

The ether I yielded the expected rearrangement product, II, but its isomer, III, quite unexpectedly, yielded IV.



The Isomeric Ethers

The two isomeric chlorides, 3-chloro-1-pentene and 1-chloro-2-pentene, were prepared by the action of gaseous hydrogen chloride upon ethylvinylcarbinol.



$$C_2H_5CH(OH)CH{=}CH_2 \xrightarrow{HCl} \begin{cases} C_2H_5CHClCH{=}CH_2 & \text{V} \\ C_2H_5CH{=}CHCH_2Cl & \text{VI} \end{cases}$$

The two isomeric ethers, I and II, were obtained from these chloropentenes by treatment with phenol and potassium carbonate in the presence of acetone. On account of the possibility of an alpha-gamma transposition, it was especially important to establish the structures of these ethers. This was accomplished by oxidation: I yielded α-phenoxybutyric acid, $C_6H_5OCH(C_2H_5)COOH$, whereas III under similar conditions gave phenoxyacetic acid, $C_6H_5OCH_2COOH$.

The preparation of *1-chloro-2-pentene* (VI) and *3-chloro-1-pentene* (V) was carried out as follows. Ninety-nine grams (1.15 moles) of freshly distilled ethylvinylcarbinol was saturated with dry hydrogen chloride at 0°. After standing for three hours in an ice box, the reaction mixture was again saturated at 0°. This process was then repeated after standing overnight. The total gain in weight was 62 g. Finally after standing for twenty-four hours in an ice box, the lower aqueous layer was separated and the mixed chlorides were placed over anhydrous potassium carbonate for two weeks. The mixture was filtered and then fractionally distilled using a 60-cm. Widmer column. Refractionation gave the following results: (1) $C_2H_5CHClCH{=}CH_2$, b. p. 50–50.2° (150 mm.), 42.1 g.; (2) intermediate, b. p. 50.2–62° (149 mm.), 2.1 g.; (3) $C_2H_5CH{=}CHCH_2Cl$, b. p. 62° (149 mm.) to 63.2° (146 mm.), 43.5 g.; (4) residue 3.7 g.

γ-Ethylallyl Phenyl Ether (III).—A mixture of 18.8 g. of phenol (0.2 mole), 20.9 g. of 1-chloro-2-pentene (0.2 mole), 29.0 g. (0.21 mole) of anhydrous potassium carbonate and 20 cc. of acetone, combined in the order named, was placed in a 200-cc. round-bottomed flask. The reaction mixture was refluxed on the steam-bath for eighteen hours, cooled, taken up in water and 25 cc. of ether added. After separating the aqueous layer, it was again extracted with ether. The combined ether extract was then shaken twice with 15–20 cc. of 20% sodium hydroxide. After drying

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[1] Abstract of a thesis submitted to the Graduate Faculty of the University of Minnesota by William F. Filbert for the degree of Doctor of Philosophy, August, 1934.

[2] For an excellent discussion see Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., Inc., N. Y., 1929, p. 214 *et seq.*; also Hurd *et al.*, THIS JOURNAL, **52**, 1700, 3356 (1930); **53**, 1068, 1917 (1931); **54**, 1648 (1932).

[3] Meisenheimer and Link, *Ann.*, **479**, 211 (1930).

the ether solution over magnesium sulfate, it was concentrated and then subjected to distillation at reduced pressure; yield 18.6 g. (57%); b. p. 118.6° (20 mm.); $d^{20}{}_{20}$ 0.9566. Analysis by use of the Grignard machine showed the presence of a negligibly small amount of active hydrogen.

α-Ethylallyl Phenyl Ether (I).—In a 500-cc. flask fitted with a condenser the reagents were placed in the following order and amounts: 28.2 g. of phenol (0.3 mole), 43.5 g. of anhydrous potassium carbonate (0.31 mole), 40 cc. of acetone, and 31.4 g. of 3-chloro-1-pentene (0.3 mole). After standing at room temperature for eighteen hours, the mixture was heated for nine hours and then allowed to stand overnight. Sufficient water to dissolve the precipitate was added and the solution was then extracted several times with ether. The combined ether extracts, after washing with two 25-cc. portions of 20% sodium hydroxide followed by 25 cc. of water, were dried over anhydrous magnesium sulfate. Distillation under reduced pressure using a Widmer column gave the following fractions: (1) chloropentene; (2) b. p. 103–115° (18.5 mm.); (3) b. p. 115–118° (18 mm.). Fraction 2 redistilled yielded 5.6 g. of α-ethylallyl phenyl ether, b. p. 92–93° (15 mm.); $d^{20}{}_{20}$ 0.9465. Likewise fraction 3 gave 9.9 g. of the isomer γ-ethylallyl phenyl ether; b. p. 116–117° (17 mm.); $d^{20}{}_{20}$ 0.9567.

Oxidation of the isomeric ethers was accomplished by means of potassium permanganate in aqueous acetone solution.

(a) **γ-Ethylallyl Phenyl Ether.**—One and two-tenths grams of III, dissolved in aqueous acetone, was treated with 3.2 g. of potassium permanganate dissolved in a small amount of water. After standing overnight, the solution became almost colorless. The reaction mixture was filtered and the solution acidified. About one-half of the solvent was then distilled off to remove most of the acetone. The solution was extracted twice with ether. The ether extract, washed with a small amount of water, then was extracted twice with a 5% solution of sodium carbonate. Acidification of the carbonate solution with dilute sulfuric acid precipitated 0.32 g. of phenoxyacetic acid; melting point and mixed melting point with an authentic specimen of phenoxyacetic acid 98–99.5°.

(b) **α-Ethylallyl Phenyl Ether.**—A 1-g. sample of (I) oxidized in the manner described in (a) yielded an oil which finally crystallized; melting point after two crystallizations from water 80–82°. α-Phenoxybutyric acid prepared according to the directions of Bischoff[4] did not cause any lowering of the melting point when mixed with this oxidation product.

The Rearrangement Products.—The convenient technique of Claisen, which involves heating of the ether in diethylaniline, was adopted after it had been shown that the same rearrangement products were obtained in the absence of diethylaniline. That α-ethylallyl phenyl ether (I) gave *o*-(γ-ethylallyl)-phenol (II) upon rearrangement is indicated by the fact that ozonolysis of the methyl ether of II led to the formation of propionaldehyde. The direct nuclear alkenylation of phenol with 1-chloro-2-pentene, VI, also gave a product which was identical with that obtained by the rearrangement of I. Apparently, this α-monosubstituted allyl phenyl ether follows the rearrangement pattern outlined by Claisen.

The rearrangement of 3-phenoxy-1-pentene (I) was carried out by boiling 5.6 g. of this ether with one-half its weight of diethylaniline in an atmosphere of carbon dioxide. The temperature of the boiling mixture rose from 201 to 225° in three and one-half hours. After cooling, the reaction mixture was taken up in ether and petroleum ether, extracted twice with dilute sulfuric acid to remove the amine, and then three times with 20% sodium hydroxide to remove the phenol. The alkaline solution was acidified with hydrochloric acid and extracted with three 15-cc. portions of ether. After drying with anhydrous magnesium sulfate, the ether solution was concentrated and the residue distilled at reduced pressure. About 1 cc. of higher boiling material remained; yield 4.7 g. (83%); b. p. 131–132.5° (16 mm.); $d^{20}{}_{20}$ 0.988.

The phenylurethan was prepared by the action of phenyl isocyanate on the phenol dissolved in petroleum ether, in the presence of potassium carbonate. After crystallization from petroleum ether and dilute methyl alcohol, it melted at 67–68°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.85; H, 6.81. Found: C, 76.65; H, 6.61.

The aryloxyacetic acid was prepared from 1 g. of the phenol by the method of Koelsch[5] giving 0.78 g. of *o*-(2-pentenyl)-phenoxyacetic acid. After crystallization from dilute methyl alcohol, it melted at 108.5–110°.

The methyl ether of the rearrangement product (II) was obtained in 88% yield by treating the phenol with methyl iodide in the presence of a methyl alcohol solution of sodium methoxide; b. p. 143–145° (35 mm.); $d^{20}{}_{20}$ 0.9586. *Ozonolysis* of this methyl ether was carried out using ethyl bromide as solvent. Decomposition of the ozonide was accomplished in a manner similar to that used by Whitmore.[6] The steam distillate contained some brown oil, which was probably a polymer of homoanisaldehyde; it failed to give a semicarbazone. The remainder of the steam distillate was treated with methone (dimethylhydroresorcinol).[7] The precipitated derivative, recrystallized once from alcohol, had a melting point of 120–165°. By washing with cold acetone, a small residue of formaldimethone was obtained. This could have resulted only by deep-seated decomposition of the molecule. The solution from which this mixture of derivatives had been filtered was treated with more methone. The precipitate was crystallized from alcohol, then carbon tetrachloride and finally from dilute acetone; colorless plates, m. p. 152.5–153°. A mixed melting point with propionaldimethone showed no depression.

Anal. Calcd. for $C_{19}H_{28}O_4$ (propionaldimethone): C, 71.2; H, 8.81. Found: C, 71.1; H, 8.62.

The residue from the steam distillation of the ozonide

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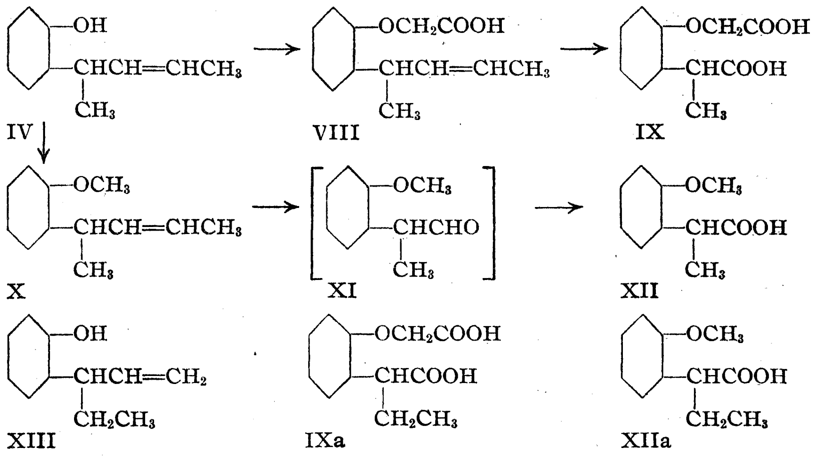
[4] Bischoff, *Ber.*, **33**, 931 (1900); see also Luchmann, *ibid.*, **29**, 1421 (1896).

[5] Koelsch, THIS JOURNAL, **53**, 304 (1931).

[6] Whitmore *et al.*, *ibid.*, **54**, 3711 (1932); **56**, 180 (1934).

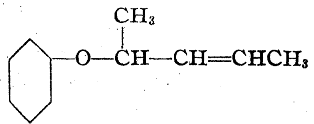
[7] Klein and Linser, *Mikrochemie*, Pregl Festschrift, 204 (1929).



was made alkaline, the precipitated zinc hydroxide filtered off, the filtrate acidified and then extracted with ether. Evaporation of the ether left an oil which finally solidified. This was dissolved in dilute sodium hydroxide and treated with charcoal. By acidification, extraction with ether and evaporation, there was obtained a solid, which when twice crystallized from water showed a melting point of 121–123°. This corresponds to the melting point of *o*-methoxyphenylacetic acid.

Direct nuclear alkylation of phenol with 1-chloro-2-pentene (VI) yielded a product which was identical with that obtained by the rearrangement of I. Sodium (4.6 g.) was dissolved in a solution of phenol (18.8 g.) in benzene (75 cc.). 1-Chloro-2-pentene (20.9 g.) in 25 cc. of benzene was then added and the mixture refluxed on the steam-bath for twelve hours. After standing for twenty-four hours the sodium chloride was dissolved in water, petroleum ether was added and the layers were separated. The petroleum ether–benzene solution was extracted with five portions of Claisen's alkali and then with one portion of water. The alkaline solution was then acidified and extracted with ether. After drying with magnesium sulfate, the ether solution was concentrated and the residue distilled at reduced pressure. A liquid (13.5 g.) boiling at 146°(29)–145° (21 mm.) was obtained. This gave an aryloxyacetic acid that was identical with the one already described.

The rearrangement of γ-ethylallyl phenyl ether (III) led to a product which is identical with that produced by the rearrangement of α,γ-dimethylallyl phenyl ether (VII).



VII

The structures of these isomeric ethers were also established by means of oxidation; VII yielded α-phenoxypropionic acid whereas III gave phenoxyacetic acid. That the rearrangement products of these isomeric ethers are identical is shown by the fact that they gave identical phenylurethans. Structure IV is assigned to this rearrangement product. The transformations outlined in the following diagram will make the reason for this choice clear.

The alternative structure XIII leads to IXa and XIIa, compounds differing in composition from IX and XII.

The rearrangement of γ-ethylallyl phenyl ether (III) was carried out in a small flask fitted with an air condenser. Eight and eight-tenths grams of the ether and one-half its weight of diethylaniline were heated to the boiling point in an atmosphere of carbon dioxide. The temperature rose from 220 to 235° in a period of one and three-quarter hours, after which no further increase of the boiling temperature was noted. After cooling the reaction mixture was taken up in petroleum ether and ether, the solution extracted twice with dilute sulfuric acid to remove the diethylaniline, then three times with 20% sodium hydroxide to remove the phenol. The alkaline solution was acidified with hydrochloric acid and extracted with ether. The ether solution, after drying over magnesium sulfate, was concentrated on the steam-bath and the residual oil distilled at reduced pressure; b. p. 125–127° (16 mm.); d^{20}_{20} 0.9915; yield 7.8 g. (88%).

The phenylurethan, recrystallized three times from petroleum ether and twice from dilute methyl alcohol, melted at 108.5–109.5°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.85; H, 6.81. Found: C, 76.80; H, 6.66.

The aryloxyacetic acid (VIII), crystallized from a benzene–petroleum ether mixture and twice from dilute methyl alcohol, melted at 128–130°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.87; H, 7.33. Found: C, 70.84; H, 7.44.

Oxidation of the Aryloxyacetic Acid (VIII ⟶ IX).—One gram of the aryloxyacetic acid was dissolved in 50 cc. of water containing enough acetone to form a homogeneous solution. To it was added, dropwise and with shaking, a solution of 2.7 g. of potassium permanganate in 100 cc. of water. It was necessary to cool the reaction mixture during the reaction. After standing overnight, the reaction mixture was filtered. The filtrate acidified with dilute sulfuric acid, was extracted with ether. The ether solution, dried over magnesium sulfate, was evaporated slowly. The residual oil was dissolved in benzene and crystallized from this solvent, m. p. 170–171°.

Anal. Calcd. for $C_{12}H_{14}O_5$(IXa): C, 60.5; H, 5.88. Calcd. for $C_{11}H_{12}O_5$(IX): C, 58.9; H, 5.38. Found: C, 59.02; H, 5.39.

Methylation of the Rearrangement Product (IV ⟶ X).—This conversion was brought about by means of (a) methyl iodide and sodium methoxide or (b) dimethyl sulfate. A typical experiment using methyl iodide will be described. To a cooled solution of sodium methoxide prepared in a 200-cc. round-bottomed flask from 0.96 g. of sodium and 30 cc. of methanol there was added 6.8 g. of the *o*-(α,γ-dimethylallyl)-phenol, IV, followed by 5.95 g. of methyl iodide. The reaction mixture was heated for four hours on the steam-bath and then allowed to stand overnight. The alcohol was removed by distillation. Enough water was added to dissolve the sodium iodide, and the oily layer was extracted with ether. The ethereal solution, after washing with dilute sodium hydroxide and drying over anhydrous sodium sulfate, was concentrated on the steam-bath. The residual oil was distilled at reduced pressure collecting the fraction boiling at 134–137° (35 mm.); practically all of it distilled in the range 135–136° (35 mm.) and almost no residue was left; yield 6.5 g. (88%); d^{20}_{20} 0.9633.

Ozonolysis of *o*-(α,γ-Dimethylallyl)-anisole (X).—Two different procedures were used. (a) The anisole (6.2 g.) was dissolved in 50 cc. of ethyl bromide and ozonized by passing a stream of ozonized oxygen (7.5% by weight of ozone) at the rate of 10.6 liters per hour, through the solution in a suitable absorption bottle immersed in an ice–salt mixture. After two and one-half hours (65% excess) the ozonization was discontinued and the solution allowed to stand overnight.

Decomposition was accomplished in a manner similar to that used by Whitmore.[6] The apparatus consisted of a 100-cc. separatory funnel attached by a rubber stopper to a small Claisen flask which contained 60 cc. of water, 2.3 g. of zinc dust, a trace of silver from silver nitrate and a few milligrams of hydroquinone. The distilling flask was attached to a condenser connected by an adapter to a suction flask which, in turn, was connected to a tube reaching to the bottom of a 50-cc. distilling flask containing 45 cc. of methone reagent. The solution of the ozonide was transferred to the separatory funnel and the ethyl bromide was removed as completely as possible by applying suction. A viscous yellow oil remained, which was dropped into the boiling water contained in the distilling flask. Slow distillation took place and a white precipitate appeared in the methone reagent. After all of the ozonide had been added, water was slowly dropped in while the distillation continued until about 75 cc. of distillate had been collected.

There separated, as the bottom layer of the distillate, an oil weighing 2.9 g. This was treated with semicarbazide hydrochloride in the usual way. After twenty-four hours the precipitate was filtered off, crystallized twice from 95% ethyl alcohol and once from 60% alcohol as white needles of m. p. 162.2–162.6°.

Anal. Calcd. for $C_{11}H_{15}O_2N_3$: C, 59.70; H, 6.84. $C_{12}H_{17}O_2N_3$: C, 61.28; H, 7.23. Found: C, 59.91, 60.19; H, 6.79, 6.85.

A mixed melting point with *o*-methoxypropiophenone semicarbazone (m. p. 154–156°) gave a lowering of 25°.

The semicarbazone isolated as a product of ozonolysis was heated on the steam-bath with a small amount of aqueous oxalic acid. The droplet of oil which separated after a few minutes, was washed by decantation with water. It was then treated with 2,4-dinitrophenylhydrazine according to the directions of Allen.[8] The precipitate, after crystallizing from 95% alcohol, melted at 123–125°.

Anal. Calcd. for $C_{16}H_{16}O_5N_4$: C, 55.79; H, 4.69. $C_{17}H_{18}O_5N_4$: C, 56.96; H, 5.07. Found: C, 55.9; H, 4.80.

The distillate was treated with methone solution after separation of the above-mentioned oil. The ether extract left an oil which partially crystallized on standing. The crystals, washed once with cold alcohol, melted at 184–186°. Mixed melting point with formaldimethone showed no depression. The solution in the methone trap after decomposition of the ozonide was filtered. The precipitate melted at 136–137.5°. When mixed with a sample of acetaldimethone of m. p. 139–140°, the melting point was 137–139°.

Decomposition of the ozonide therefore furnished evidence of the formation of formaldehyde, acetaldehyde and a carbonyl compound of composition $C_{10}H_{12}O_2$. The occurrence of formaldehyde along with acetaldehyde is perhaps indicative of deep-seated changes.[9]

(b) The procedure similar to that of Hahn and Wassmuth[10] was also used. The anisole (4.8 g.) was dissolved in 60 cc. of ethyl acetate and the ozonolysis was carried out at a temperature of −10 to −15° using a mixture of air and oxygen containing 1.4% ozone by weight. A 25% excess of ozone was used. After standing overnight, the ozonide solution was subjected to catalytic hydrogenation using 0.2 g. of a 5% palladium–calcium carbonate catalyst which had been reduced in 20 cc. of ethyl acetate. After no further pressure drop, it was assumed that the reduction of the ozonide had been accomplished, and the catalyst was removed by filtration. Water was then added and the ethyl acetate was removed under reduced pressure. Since we were not successful in obtaining satisfactory aldehyde derivatives at this stage, the small amount of oil which separated out was brought into solution with acetone and the solution was subjected to oxidation by the addition of an acetone solution of potassium permanganate. The precipitated manganese dioxide was separated by filtration, the filtrate concentrated to a volume of 15 cc., cooled, acidified with hydrochloric acid and extracted with ether. The ether extract yielded an oil which solidified on cooling. After crystallization with the addition of norite it melted at 100–101°.

Anal. Calcd. for $C_{10}H_{12}O_3$ (XII): C, 66.6; H, 6.72; OCH_3, 17.2. $C_{11}H_{14}O_3$ (XIIa): C, 68.0; H, 7.27; OCH_3, 16.0. Found: C, 66.7; H, 6.71; OCH_3, 17.45.

α,γ-Dimethylallyl phenyl ether (VII) was prepared in accordance with the directions of Claisen.[11] The structure of this compound was established by oxidation as follows. A 2-g. sample was dissolved in a small amount of aqueous acetone and to the solution was added a saturated potassium permanganate solution in 2% excess. The reaction mixture was cooled during the addition. After standing overnight, the manganese dioxide was filtered off and washed with water and acetone. The alkaline filtrate

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(8) C. F. H. Allen, THIS JOURNAL, **52**, 2955 (1930).

(9) See for example, Clemo and MacDonald, *J. Chem. Soc.*, 1294 (1935).

(10) Hahn and Wassmuth, *Ber.*, **67**, 696 (1934).

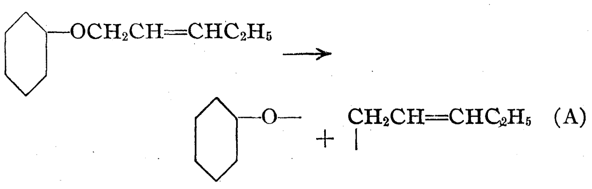
(11) L. Claisen *et al.*, *Z. angew. Chem.*, **36**, 478 (1923); *Ann.*, **442**, 210 (1925).

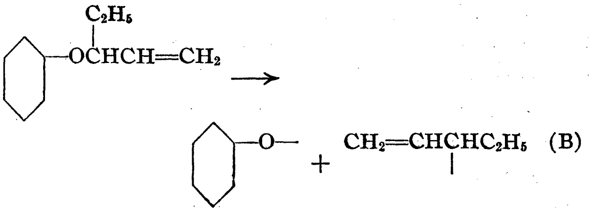
was concentrated to about 25 cc., cooled, extracted with ether, acidified with dilute sulfuric acid and allowed to stand. The solid obtained in this way was crystallized twice from water containing about 5% alcohol, using decolorizing carbon; m. p. 113–114°; yield 0.5 g. A sample of α-phenoxypropionic acid prepared from α-bromopropionic ester and sodium phenoxide according to the directions of Bischoff[4] melted at 114–115°. (Bischoff gives 115–116°, Saarbach 112–113°.) A mixed melting point with the acid obtained by the oxidation of the ether showed no depression.

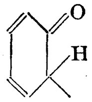
The rearrangement of this ether was carried out by boiling in diethylaniline in an atmosphere of carbon dioxide. The product (28% yield) boiled at 141–145° at 31 mm.

The phenylurethan of the rearrangement product was crystallized from petroleum ether, dilute methyl alcohol, petroleum ether and finally from dilute methyl alcohol, as colorless needles melting at 107–108.5° (Claisen gives 107–109°). The mixed melting point with the urethan of the phenol obtained by rearranging γ-ethylallyl phenyl ether was 108–109.5°.

The relation of the present results to the mechanism of the phenyl allyl ether rearrangement is not clear. It is evident, however, that the widely held formulation of Claisen must be modified. The view that rearrangement is preceded by dissociation





to yield fragments A and B, one of which isomerizes to the other before combination with  or its benzenoid isomer, leads to the prediction that the two isomeric ethers should give the same rearrangement product. The results of the present study, designed to test this hypothesis, are not in agreement with this prediction. Further work which is in progress has as its aim the accumulation of pertinent facts.

Summary

The three isomeric ethers, α-ethylallyl phenyl ether, γ-ethylallyl phenyl ether and α,γ-dimethylallyl phenyl ether have been rearranged and the structures of their rearrangement products were investigated. The first and third-named ethers rearrange in accordance with the pattern outlined by Claisen, but γ-ethylallyl phenyl ether does not, since it yields a rearrangement product identical with that obtained from α,γ-dimethylallyl phenyl ether.

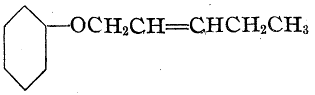
MINNEAPOLIS, MINN. RECEIVED MARCH 27, 1936

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

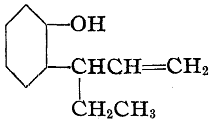
The Rearrangement of Phenyl Allyl Ethers. II. Phenyl Crotyl Ether

BY WALTER M. LAUER AND HERBERT E. UNGNADE

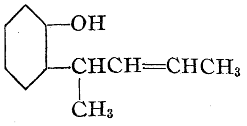
A recent study[1] of γ-ethylallyl phenyl ether (I) led to the conclusion that its rearrangement product was not the expected o-(α-ethylallyl)-phenol (II) but o-(α,γ-dimethylallyl)-phenol (III)



I



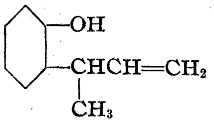
II



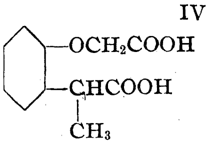
III

The present study was carried out in order to obtain further evidence for the structure assigned to this rearrangement product.

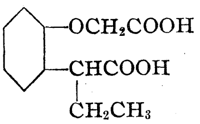
According to Claisen and Tietze[2] phenyl crotyl ether, $C_6H_5O—CH_2—CH=CHCH_3$, when rearranged by heat yields o-(α-methylallyl)-phenol (IV).



IV



V



VI

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[1] Lauer and Filbert, THIS JOURNAL, **58**, 1388 (1936).

[2] Claisen and Tietze, *Ber.*, **59**, 2344 (1926).

Consequently, oxidation of the aryloxyacetic acid derived from the rearrangement product of phenyl crotyl ether should yield the dibasic acid V. Such a series of transformations has already been described for the rearrangement product of γ-ethylallyl phenyl ether (I) and on the basis of its composition it was concluded that the structure of the dibasic acid was V rather than VI. The present work describes the rearrangement of phenyl crotyl ether and the conversion of its rearrangement product to the dibasic acid and demonstrates the fact that it is identical with the one previously obtained. This supplies additional evidence that III rather than II represents the correct structure for the rearrangement product of γ-ethylallyl phenyl ether.

The work of Claisen and Tietze[2] has shown that direct alkenylation of phenol with crotyl bromide leads to a product differing from that obtained by the indirect method which involves ether formation with subsequent rearrangement. The formation of the dibasic acid V here described incidentally furnishes independent confirmatory evidence pointing to IV, the accepted structure of the rearrangement product of phenyl crotyl ether.

Experimental

Methylvinylcarbinol was prepared by the action of methylmagnesium iodide on acrolein.

Crotyl bromide was obtained from methylvinylcarbinol by treatment with 45% hydrobromic acid according to the procedure of Claisen.[2,3] The directions of Claisen were followed for the preparation and rearrangement of *phenyl crotyl ether*. The rearrangement product was converted to the phenylurethan which melted at 88.5–89° (Claisen gives 89.5–90.5° as the melting point of this compound). The phenylurethan of the rearrangement product was analyzed.

Anal. Calcd. for $C_{17}H_{17}O_2N$: C, 76.38; H, 6.40. Found: C, 76.29; H, 6.45.

Oxidation of Phenyl Crotyl Ether.—Phenyl crotyl ether (1.2 g.) was dissolved in aqueous acetone. A concentrated aqueous solution containing 3.2 g. of potassium permanganate was added and the mixture allowed to stand overnight. The manganese dioxide was filtered off and the filtrate was then acidified with dilute sulfuric acid. The solution was concentrated to one-half its original volume and then subjected to extraction with ether. The ether extract was washed with water and then extracted with 5% sodium carbonate. Acidification of the carbonate solution followed by cooling yielded 0.32 g. of *phenoxyacetic* acid. The melting point and mixed melting point with an authentic sample of phenoxyacetic acid was 97–98°.

The aryloxyacetic acid of the rearrangement product was prepared in accordance with the method of Koelsch.[4] One gram of the *o*-(α-methylallyl)-phenol (IV) was mixed with 3.5 cc. of 33% sodium hydroxide. To this mixture 2.5 cc. of 50% monochloroacetic acid was added slowly with shaking. After heating in a test-tube on the steam-bath for one hour, the solution was acidified with dilute sulfuric acid. The mixture was then extracted with ether and the ether extract washed with water. The product was then extracted with dilute sodium carbonate and after acidification was crystallized from water; m. p. 120–120.5°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.87; H, 6.84. Found: C, 69.66; H, 6.74.

Oxidation of *o*-(α-Methylallyl)-phenoxyacetic Acid.—The oxidation was accomplished by dissolving the *o*-(α-methylallyl)-phenoxyacetic acid (1.033 g.) in 50 cc. of water containing sufficient acetone to form a homogeneous solution. Potassium permanganate (2.7 g. in 100 cc. water, *ca.* 8% excess) was added dropwise to the cooled solution and the reaction mixture allowed to stand overnight. After filtration, the filtrate was acidified with dilute sulfuric acid and extracted with one 50-cc. and two 25-cc. portions of ether. The combined ether extracts were dried over magnesium sulfate and then allowed to evaporate spontaneously. The residual oil insoluble in petroleum ether did not solidify at −15°. The oil, dissolved in benzene, was heated on the steam-bath for several hours. After standing overnight, the white crystalline product was collected; m. p. 170–171°; mixed with a sample of the product obtained[1] by the oxidation of *o*-(α,γ-dimethylallyl)-phenoxyacetic acid it melted at 170–171°.

Anal. Calcd. for $C_{11}H_{12}O_5$: C, 58.90; H, 5.40. Found: C, 59.16; H, 5.56.

Summary

Evidence is presented which confirms *o*-(α,γ-dimethylallyl)-phenol and *o*-(α-methylallyl)-phenol as the structures of the rearrangement products of γ-ethylallyl phenyl ether and γ-methylallyl phenyl ether, respectively.

MINNEAPOLIS, MINN. RECEIVED MARCH 27, 1936

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[3] Young and Winstein, THIS JOURNAL, **57**, 2013 (1935).

[4] Koelsch, *ibid.*, **53**, 304 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY, SCHOOL OF MEDICINE, UNIVERSITY OF MARYLAND]

Sugar Alcohols. V. Chemical Constitution and Sweet Taste[1]

BY C. JELLEFF CARR, FRANCES F. BECK AND JOHN C. KRANTZ, JR.

The relationship between chemical constitution and sweet taste has not been elucidated satisfactorily. In a series of investigations[2-5] on the metabolism of sugar alcohols and their anhydrides a large number of these substances were prepared and the authors decided to study the relationship between their chemical constitution and sweet taste. The relative sweet tastes of the simple sugars have been investigated repeatedly, although comparative studies of the sugar alcohols and their anhydrides have not been reported. McGuigan[6] suggests a relationship between intensity of sweet taste and the number of hydroxyl groups in the molecule. This series affords an excellent opportunity to test this hypothesis. In addition, the response of animals and microorganisms to the sugar alcohols is so strikingly different from their response to their anhydrides that this investigation was initiated.

Experimental

Substances of C. P. quality were employed. The mannitol and sorbitol were supplied by the Atlas Powder Co. of Wilmington, Del. The anhydrides were prepared in this Laboratory and their purity and identity established as has been described previously.[2-5,7]

The polygalitol was extracted from *Polygala Amara* by the method of Picard[8] and occurred as colorless crystals, m. p. 142°; $[\alpha]^{16}_{D} + 47.5$. All of the substances were dried in a desiccator for a period of several months and the threshold quantities represent anhydrous material.

Six carefully standardized individuals were used for the determinations and not more than three or four substances were tested on any one day. The threshold quantity of sucrose was determined before each test. After rinsing the mouth with water, 5 cc. of the standard solution was placed on the tongue which was brought in contact with the roof of the mouth and the sensation noted within half a minute. The minimal concentration just producing a sweet taste within one-half to one minute was considered the threshold quantity. Freshly distilled water was used in preparing all solutions. The average of the results for the sugar alcohols is shown in Table I and is compared with sucrose as a standard.

TABLE I

RELATIVE SWEETNESS OF THE SUGAR ALCOHOLS, SUCROSE TAKEN AS 100

Product	Carbon atoms number	OH groups number	Mol. wt.	Ratio
Sucrose	..	..	...	100
Ethylene glycol	2	2	62	130
Glycerol	3	3	92	108
i-Erythritol	4	4	122	238
Pentaerythritol	5	4	136	110
l-Arabitol	5	5	152	100
d-Mannitol	6	6	182	57
d,l-Sorbitol	6	6	182	54
i-Dulcitol	6	6	182	74
Inositol	6	6	180	50

Discussion

The results show no significant relationship between the number of carbon atoms or hydroxyl groups in the molecule and sweet taste. The anhydrides of several of these sugar alcohols, namely, ethylene oxide, epihydrin alcohol, mannitan, mannide, isomannide and dulcitan were devoid of a sweet taste and in most instances exhibited a decidedly bitter taste. It is of interest that these sugar alcohols are metabolized and produce gas with many members of the colon aerogenes group and their anhydrides do not.

Erythritan and polygalitol are the 1,4- and 1,5-anhydrides, respectively, of erythritol and mannitol. These substances possess a sweet taste and polygalitol produces gas and acid with many members of the colon aerogenes group of organisms.

There appears to be no relationship between spatial structure and sweet or bitter taste in this class of compounds. While α- and β-glucose have exactly the same degree of sweetness (ratio of 75), the derivatives of β-glucose are reported to be

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(1) The expense of this investigation was defrayed in part by a grant from the Committee on Therapeutics of the Council of Pharmacy and Chemistry of the American Medical Association.

(2) Carr, Musser, Schmidt and Krantz, *J. Biol. Chem.*, **102**, 721 (1933).

(3) Carr and Krantz, *ibid.*, **107**, 371 (1934).

(4) Krantz, Carr and Evans, *J. Pharmacy and Pharmacol.*, **8**, 213 (1935).

(5) Dozois, Hachtel, Carr and Krantz, *J. Bact.*, **30**, 189 (1935).

(6) McGuigan, "An Introduction to Chemical Pharmacology," P. Blakiston Sons, Philadelphia, Pa., 1921, pp. 28, 30.

(7) Dozois, Hachtel, Carr and Krantz, in press.

(8) Picard, *Bull. soc. chim. biol.*, **9**, 692 (1927).

uniformly more bitter than those of α-glucose.[9] The isomeric substances mannitol, sorbitol and dulcitol have approximately the same degree of sweetness while the two anhydrides mannide and isomannide are also of about the same degree of bitterness.

Summary

1. The removal of water from a sugar alcohol with the formation of the anhydride as a rule destroys the sweet taste of the former.

2. Erythritan, the first anhydride of erythritol, possesses a bitter taste in high concentrations but a sweet taste in threshold quantities.

3. Polygalitol, the 1,5-anhydride of mannitol, possesses a sweet taste in high concentration and an astringency in high dilution.

4. No relationship between the number of carbon atoms or hydroxyl groups in the molecule or the molecular weight or spatial configuration and sweet taste has been observed in this class of compounds.

BALTIMORE, MD. RECEIVED JUNE 9, 1936

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[9] Brigl and Scheyer, *Z. physiol. Chem.*, **160**, 214 (1926); *C. A.*, **21**, 418 (1927).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Some Derivatives of 1,3-Diketohydrindene

BY W. H. HUNTER AND E. C. YACKEL[1]

Degradation of 2-acyl-1,3-diketohydrindenes by hydrolysis cannot be carried out successfully, and although these substances are converted by oxidation into a monocarboxylic acid and phthalic acid, the reaction does not always proceed smoothly. In connection with studies on the nitration of acyl diketohydrindenes we have found that bromination in acetic acid offers a superior method of degradation, the triketone being cleaved into 2,2-dibromo-1,3-diketohydrindene and a monocarboxylic acid. For example, 2-benzoyl-1,3-diketohydrindene yields dibromodiketohydrindene and benzoic acid. It is noteworthy that this cleavage, otherwise quite similar to the haloform reaction,[2] takes place in the absence of alkalies.

By means of this reaction it has been found that the nitration of 2-benzoyl-1,3-diketohydrindene yields 2-*m*-nitrobenzoyl-1,3-diketohydrindene, since bromination of the product yields dibromodiketohydrindene and *m*-nitrobenzoic acid.

Although the products obtained are too unstable to withstand the hydrolyzing action of the nitrating mixture, it is noteworthy that the O-acetate of 2-carbethoxy-1,3-diketohydrindene may be obtained by the action of acetyl chloride on either the sodium or the silver salt of the diketo ester, while the O-benzoate may be obtained only from benzoyl chloride and the silver salt.[3] The use of the sodium salt in the latter instance gives rise to an as yet unidentified substance, which is not the isomeric C-benzoate.

Experimental

Cleavage of 2-Benzoyl-1,3-diketohydrindene.—A solution of the triketone[4] (3 g.) and bromine (6 g.) in acetic acid (60 ml.) is warmed on a water-bath for two hours. After the bromine color has disappeared the mixture is cooled and diluted. The crystalline product separating melts at 178–179° and is 2,2-dibromo-1,3-diketohydrindene.[5]

Anal. Calcd. for $C_9H_4O_2Br_2$: Br, 52.7. Found: Br, 52.3, 52.7.

Evaporation of the mother liquor yields benzoic acid, purified by sublimation and identified by nitration.

Nitration of 2-Benzoyl-1,3-diketohydrindene.—The triketone (5 g.) is dissolved in sulfuric acid (40 ml.) at −5°, and treated at this temperature with a mixture of fuming nitric acid (1.5 g.) in sulfuric acid. After thirty minutes the solution is poured onto ice. The solid is washed with water and with much hot alcohol and crystallized from chloroform. The product forms microscopic needles that melt with decomposition at 228–229°; yield 70%.

Anal. Calcd. for $C_{16}H_9O_5N$: N, 4.74. Found: N, 4.73, 4.65.

On bromination in acetic acid, the nitrotriketone yields dibromodiketohydrindene and *m*-nitrobenzoic acid, identified by mixed melting points.

Acetylation of Ethyl 1,3-Diketohydrindene-2-carboxylate.—The sodium salt of the diketo ester[6] may be purified by crystallization from water with the aid of charcoal, and

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[1] The work presented in this paper is taken from a thesis by E. C. Yackel presented to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Master of Science, October, 1929.—C. F. KOELSCH.

[2] *Cf.* Fuson, *Chem. Rev.*, **15**, 299 (1934).

[3] Hantzsch and Gajewski, *Ann.*, **392**, 306 (1912).

[4] Schwerin, *Ber.*, **27**, 106 (1894).

[5] Kronfeld, *ibid.*, **17**, 720 (1884).

[6] Wislicenus, *ibid.*, **20**, 594 (1887).

freed of water of hydration by drying at 170° for three hours. The silver salt, obtained by treatment of the sodium salt in aqueous solution with silver nitrate, separates directly without water of crystallization.

The reaction between the sodium salt (10 g.) and acetyl chloride (50 ml.) is completed by boiling the mixture for one hour. The sodium chloride is filtered off, the acetyl chloride is evaporated, and the residue (3.4 g.) is crystallized from ether. Similar treatment of the silver salt yields the same compound (mixed melting point) which forms yellow needles that melt at 77–78°.

Anal. Calcd. for $C_{14}H_{12}O_5$: C, 64.6; H, 4.6. Found: C, 64.7; H, 4.8.

Ethyl 3-acetoxyindone-2-carboxylate is readily hydrolyzed, even on exposure to atmospheric moisture, to 1,3-diketohydrindene.

Benzoylation of Ethyl 1,3-Diketohydrindene-2-carboxylate.—The reaction of the silver salt of the diketo ester with benzoyl chloride in benzene is completed by warming for one hour, and the product is crystallized from benzene and ether. In agreement with the description of Hantzsch and Gajewski,[3] the benzoate forms yellow crystals that melt at 146–148°.

The sodium salt of the diketo ester does not react with benzoyl chloride in boiling benzene. However, if the sodium salt (54 g.) is stirred with benzoyl chloride (60 g.) at 80° for five hours, a reaction takes place. Separated from the sodium chloride with ether and crystallized from benzene, the organic product forms large yellow prisms that melt at 140–141°.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.3; H, 4.1. Found: C, 69.4; H, 4.4.

The substance depresses the melting point of the benzoate. Treated with sodium ethoxide in alcohol it gives a red solution which becomes yellow on acidification. Benzoic acid may be sublimed from the tarry residue obtained by evaporating this solution.

Summary

Bromination is suggested as a method for cleaving 2-acyl derivatives of 1,3-diketohydrindene. Some reactions of 2-benzoyl diketohydrindene and of ethyl 1,3-diketohydrindene-2-carboxylate are described.

MINNEAPOLIS, MINN. RECEIVED JUNE 8, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Deuterium Exchange Equilibria in Solution and the Quinhydrone Electrode[1]

BY SAMUEL KORMAN AND VICTOR K. LA MER

Introduction

For the elucidation of the isotopic influence of deuterium upon various phenomena in heavy water (deuterium oxide), it is important to know with some degree of precision the magnitude of the equilibrium constants of the exchange processes set up between the protons and deutons in the solvent and solute molecules. For example, the interpretation of acid and base catalysis in D_2O–H_2O mixtures requires a knowledge of the distribution of deuterium and protium between the various substrate, catalyst (*e. g.*, H_3O^+ and D_3O^+) and solvent molecules.[2]

The measurement of the e. m. f. of galvanic cells involving D_2O furnishes a precise means of determining these exchange constants. To exclude the experimental complications and the theoretical uncertainties inherent in galvanic cells with liquid junction potentials, we have restricted our investigation to cells without transference. The experimental difficulties attendant upon the use of the deuterium gas electrode with small quantities of solution make an appropriate substitute highly desirable.

We have found that the quinhydrone electrode[3] establishes equilibrium quickly and is particularly well adapted for the micro technique necessary for heavy water studies. To this end, the following cells were investigated

(I) Pt, $Q\cdot QH_2/HCl\ (0.01\ M)$ in $H_2O/AgCl$, Ag

(II) Pt, $\{Q\cdot QH_2 + Q\cdot QD_2\}/HCl\text{-}DCl\ (0.01\ M)$ in $H_2O\text{-}D_2O/AgCl$, Ag

(III) Pt, $Q\cdot QH_2/\{HA(m_1) + NaA(m_2) + NaCl(m_3)\}$ in $H_2O/AgCl$, Ag

(IV) Pt, $Q\cdot QD_2/\{DA(m_1) + NaA(m_2) + NaCl(m_3)\}$ in $D_2O/AgCl$, Ag

where $Q\cdot QH_2$ and $Q\cdot QD_2$ represent light and heavy quinhydrone, and HA and DA are the light and heavy varieties of a weak acid.

For (I) and (II) the cell reactions may be written

(A) $2HCl\ (0.01\ M) + Q(H_2O) + 2Ag(s) = 2AgCl(s) + QH_2(H_2O);\ E_H$

(B) $2DCl\ (0.01\ M) + Q(D_2O) + 2Ag(s) = 2AgCl(s) + QD_2(D_2O);\ E_D$

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(1) From a thesis submitted by Samuel Korman in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

(2) Hamill and La Mer, *J. Chem. Phys.*, **4**, 294 (1936); **4**, 395 (1936); Urey and Teal, *Rev. Modern Phys.*, **7**, 34 (1935). For a discussion of the importance of exchange reactions see pp. 52, 59, 60.

(3) La Mer and Korman, THIS JOURNAL, **57**, 1510 (1935).

Subtracting (A) from (B)

$$\text{(C)}\quad 2DCl\ (0.01\ M) + QH_2(H_2O) + Q(D_2O) = 2HCl\ (0.01\ M) + QD_2(D_2O) + Q(H_2O);\ (E_D - E_H)$$

Measurements of the solubility of quinone in light and heavy water given below, permit (C) to be rewritten as

$$\text{(D)}\quad 2DCl\ (0.01\ M) + QH_2(H_2O) = 2HCl\ (0.01\ M) + QD_2(D_2O);\ (E_D - E_H)$$

Then

$$\text{(1)}\quad (E_D - E_H) = \frac{RT}{2F}\ln K,\ \text{where}\ K = \frac{(QD_2)\ (HCl)^2}{(QH_2)\ (DCl)^2}$$

From this fundamental exchange constant, by appropriate combination with values obtained from other sources, a number of important exchange equilibrium constants will be derived.

Furthermore, the data on cells (III) and (IV) can be used to obtain the ratio of dissociation constants of weak acids following the method of Harned and co-workers[4] who used the hydrogen electrode. To maintain precision using a micro method, we again substitute the quinhydrone electrode for the gas electrode. The cell reaction then becomes

$$\text{(E)}\quad 2AgCl(s) + QH_2 + 2NaA(m_2) = 2Ag(s) + 2HA(m_1) + 2NaCl(m_3) + Q$$

for which

$$\text{(2)}\quad E - E_0 = -(RT/F)\ \text{in}\ f_H f_{Cl} m_H m_{Cl}$$

where E_0 is the normal electrode potential of cell (I). Since

$$K_{HA} = f_H f_A m_H m_A / f_{HA} m_{HA}$$

we substitute for m_H in equation (2) and rewrite the expression

$$\text{(3)}\quad E - E_0 + \frac{RT}{F}\ln\frac{m_{HA}m_{Cl}}{m_A} = -\frac{RT}{F}\ln\frac{f_H f_{Cl} f_{HA}}{f_H f_A} - \frac{RT}{F}\ln K_{HA}$$

and a similar expression involving D_2O, QD_2, etc., for the deutero acid. The logarithm of the ratio of the activity coefficient products is zero at infinite dilution and varies but little from zero at low ionic strengths. The extrapolation of the right side of equation (3) plotted against ionic strength is linear at temperatures over 15° for ordinary water.[4] Since the dielectric constants of H_2O and D_2O are almost identical,[5] the same extrapolation will be valid in heavy water. Thus the values of K_{HA} and K_{DA} may differ, but their ratio will certainly remain constant to a very good approximation in the dilute range ($\sim \mu = 0.05$). We thus have a method for obtaining the ratios of dissociation constants of weak acids in heavy and light water, which have proved to be valuable in the interpretation of acid catalyzed reactions in heavy water.[2]

Experimental

Materials.—Quinhydrone,[6] constant boiling hydrochloric acid solution,[7] heavy water[8] and silver oxide[9] were prepared according to directions given previously. Acetic anhydride was purified by fractional distillation, while sodium acetate, sodium salicylate and sodium chloride were recrystallized from conductivity water. Salicylic acid was recrystallized from chloroform. Quinone was resublimed twice.

Apparatus.—The micro cell has been described by La Mer and Armbruster.[6] Their preliminary measurements established the reliability of the method as applied to the silver chloride electrode in heavy water, where the quantities of solution available for rinsing are severely limited. The vacuum technique for removing oxygen from the final cell solution, for rinsing the silver chloride electrodes. and for filling the cell, follows closely the method given by Harned and Wright.[10] The cell shown in Fig. 1 was of 4-cc. capacity. Space is provided for duplicate electrodes of each kind, and stopcocks arranged to separate the compartments for rinsing of the silver chloride electrodes.

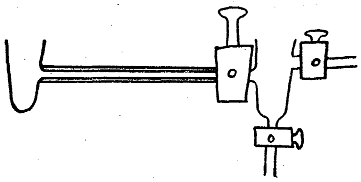

Fig. 1.—Diagram of cell.

Electrodes.—Reproducible quinhydrone electrodes were prepared by immersing several platinum spiral wires, carefully sealed in separate glass tubes filled with mercury contacts, in 0.01 *N* hydrochloric acid solution saturated with quinhydrone, and "short circuiting" them together for about a half hour.[11] They then agreed to within 0.03 millivolt. The electrodes were kept in cleaning solution[12] until another pair was required, whereupon they were rinsed thoroughly with distilled water.

The silver–silver chloride electrodes were the Type 2 described by Harned.[13] Several electrodes made simultaneously were washed repeatedly with distilled water, immersed in 0.01 *N* hydrochloric acid solution, and "shorted" together for twenty-four to thirty hours. They agreed to within 0.05 millivolt. The electrodes so prepared were protected against light.

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[4] Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932); **55**, 2179 (1933).

[5] Lewis, Olson and Maroney, *ibid.*, **55**, 4731 (1933); Müller, *Physik. Z.*, **35**, 1009–11 (1935); P. Abadie and G. Champetier, *Compt. rend.*, **200**, 1387 (1935).

[6] La Mer and Armbruster, THIS JOURNAL, **57**, 1510 (1935).

[7] Bonner and Titus, *ibid.*, **52**, 633 (1930).

[8] W. N. Baker and La Mer, *J. Chem. Phys.*, **3**, 406 (1935).

[9] Helferich and Klein, *Ann.*, **450**, 225 (1926).

[10] Harned and Wright, THIS JOURNAL, **55**, 4849 (1933).

[11] L. E. Baker, Thesis, Columbia University, 1922.

[12] Morgan, Lammert and Campbell, THIS JOURNAL, **53**, 454 (1931).

[13] Harned, *ibid.*, **51**, 416 (1929); Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

Preparation of Cell Solutions.—The limiting factor in the precision of the measurements is the accuracy with which the composition of the cell solution is known. In the preparation of the buffer solutions, the equivalent amounts of sodium chloride and the sodium salt of the weak acid were transferred from weighing bottles to a 50-cc. ground glass-stoppered flask containing the water sample.[14] The final concentration of the cell solution was corrected for the water lost in the evacuation process.

Characteristics of the Micro Cell.—Equilibrium was attained within from twenty to forty-five minutes at 25°, and was maintained to within 0.05 millivolt for two to four hours, followed by a slow drift to higher values, due probably to the formation of chlorohydroquinone. There is a definite lag in attainment of equilibrium when the temperature is raised, while equilibrium is reached almost immediately in proceeding from a higher to a lower temperature.

Results and Precision of the Measurements

Hydrochloric Acid Solutions.—E (0.01) in Table I is calculated on the basis of mols/55.3 mols D_2O-H_2O. Figure 2 is E (0.01) plotted against $N_{D_2O} = 9.377\ \Delta S - 1.01\ (\Delta S)^2$, where ΔS is the excess specific gravity of the solvent over ordinary water. The fourth column gives the average deviation from the mean, and the fifth column gives the precision measure for each experiment. This takes into account the deviation of the mean, the weighing error and the difference in electrodes. It will be seen that the average δ for this set of results does not exceed 0.06 millivolt, while the average deviation does not exceed 0.03 millivolt, a result which is about twice as precise as has been obtained with the hydrogen gas electrode, and ten times as precise as has been obtained with the deuterium gas electrode.[15] The precision with the weak acid solutions is about the same, and corresponds to that reported by Harned and Ehlers.[4]

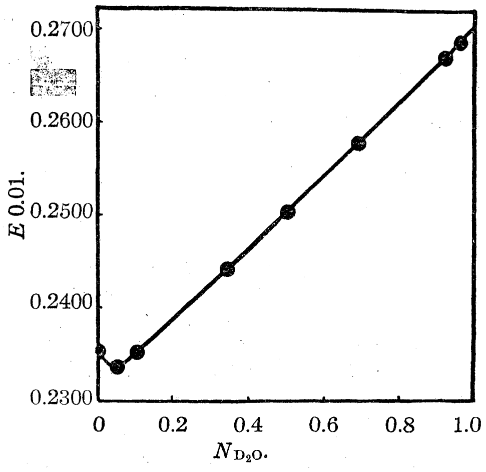

Fig. 2.—Quinhydrone electrode in heavy water.

TABLE I

DATA FOR CELLS (I) AND (II)

N_{D_2O}	Molality HCl (M/55.3 mols)	$-E_{obsd.}$	A. d., mv.	δ mv.	$-E_{0.01}$
0.0	0.011182	0.24122	0.01	0.05	0.23548
	.010855	.23963	.03	.08	.23541
.0515	.011263	.23960	.03	.07	.23349
	.013103	.24738	.02	.05	.23350
.1030[a]	.01010	.23605			.23555
	.01010	.23602			.23552
.3454	.014100	.26175	.01	.05	.24409
	.009139	.23957	.02	.06	.24419
.5109	.011913	.25915	.02	.06	.25016
	.010762	.25398	.02	.07	.25021
.6925	.009528	.25543	.05	.05	.25770
	.010470	.26022	.02	.06	.25766
.9240	.011524	.27414	.05	.02	.26685
	.011022	.27190	.04	.04	.26690
.9640	.011870	.27687	.03	.05	.26807
	.011878	.27694	.02	.07	.26812
(1.0000)					(.2700)

[a] The results, for N_{D_2O} = 0.1030, were obtained in 1934 by Dr. M. H. Armbruster in a preliminary investigation.

The curve in Fig. 2 has an unexpected but definite minimum at N_{D_2O} = 0.05, corresponding qualitatively to the flat minimum at N_{D_2O} = 0.6 for the cell $Pt,H_2\text{-}D_2/HCl\text{-}DCl$ in $H_2O\text{-}D_2O/AgCl,Ag$, studied by Abel, Bratu and Redlich.[15] These data appeared during the progress of our investigation. No discussion or claim was given concerning the presence of a minimum in the curve for the gas electrode. The experimental difficulties inherent in the deuterium gas electrode prevented these authors from obtaining the precision which we have obtained with the quinhydrone electrode. They mention, however, that as a result of the large value of the constant for the exchange reaction (No. V, Table II below), the concentration of deuterium gas at the electrode was greater than they had supposed at the time the measurements were made. It is likely that their data for mixtures of H_2O and D_2O represent steady state values rather than true equilibrium values with the bulk of the solution since the exchange reaction occurs only on the platinum black at the surface of the electrode. This surface equilibrum will determine the e. m. f., but the e. m. f. will be disturbed depending upon the rate of convection and diffusion of acid and water from the bulk of the solution in H_2O-D_2O mix-

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[14] For further details in the preparation of cell solutions, see W. N. Baker and V. K. La Mer, *J. Chem. Phys.*, **3**, 406 (1935).

[15] Abel, Bratu and Redlich, *Z. physik. Chem.*, **A173**, 353 (1935).

TABLE II

EXCHANGE EQUILIBRIA IN SOLUTION

No.	Process	$E^0 = (0.059/n) \log K$	K	Observer
I	$2DCl + QH_2 = 2HCl + QD_2$	0.0345	14.64	L. and K.
II	$QH_2 + D_2O = QD_2 + H_2O$		0.96	H. and L.
III	$2DCl + H_2O = 2HCl + D_2O$		15.30	I–II
IV	$2DCl + H_2(g) = 2HCl + D_2(g)$	.0034	1.30	A., B. and R.
V	$D_2(g) + H_2O = H_2(g) + D_2O$		11.80	III–IV
VI	$QH_2 + D_2(g) = QD_2 + H_2(g)$		11.26	I–IV
VII	$2H_2O + D_2(g) + 2NaOD = 2D_2O + H_2(g) + 2NaOH$	.0431	28.58	A., B. and R.
VIII	$H_2O + 2NaOD = D_2O + 2NaOH$		2.42	VII–V
IX	$HCl + NaOD = DCl + NaOH$		0.40	$^1/_2$ (VIII–III)
X	$2NaOD + H_2(g) = 2NaOH + D_2(g)$		.21	VII–2V
XI	$D^+ + OD^- + H_2O = H^+ + OH^- + D_2O$	.0233	6.13	$^1/_2$(VII + IV)

tures. The deuterium content of the gas phase was always greater than that determined by the exchange equilibrium set up on the surface of the electrode between the gaseous H_2–D_2 mixture and the HCl–DCl and the H_2O–D_2O. Since an excess of hydrogen in the cell solution occurred in all the intermediate mixtures which were used, Abel, Bratu and Redlich's measurements can be considered only as indicative of the presence and position of a minimum. Their value for pure D_2O and the pure deuterium gas electrode obtained by short extrapolation, however, should not be affected appreciably by any disturbance of the equilibrium mixtures.

The substitution of the quinhydrone electrode results not only in greater precision, but in contrast to the two-phase gas electrode, the exchange equilibria in cell (II), since they occur entirely in the cell solution, are homogeneous. This circumstance establishes our measurements in mixtures as true equilibrium values. Our results show conclusively that the e. m. f. curve of the quinhydrone electrode, when plotted against the D_2O content of the solvent, has a minimum value, which we may reasonably suppose will be true for the analogous deuterium electrode, although the position of the minima will be different.

Exchange Equilibrium Constants

K of equation (I) may now be evaluated, and may be combined with constants derived in a similar way from the data on the deuterium electrode,[15] and from the exchange reaction

$$\text{(F)}\quad QH_2 + D_2O = QD_2 + H_2O$$

studied by Hamill and La Mer.[16] Table II lists the values of the constants obtained in this way.

The value of the constant for No. V is in excellent agreement with the values which have been calculated from other data by use of the following equations[17]

$$\text{(G)}\quad H_2 + D_2 = 2HD;\ K_1 = (HD)^2/(H_2)(D_2) = 3.27$$

$$\text{(H)}\quad H_2O + D_2O = 2HDO;\quad K_2 = (HDO)^2/(H_2O)(D_2O) = 3.27$$

$$\text{(J)}\quad H_2O + HD(g) = HDO(l) + H_2(g);\ K_3'$$

$$\text{(L)}\quad H_2O(l) + D_2(g) = D_2O(l) + H_2(g);\quad K_4' = (D_2O)(H_2)/(H_2O)(D_2) = (K_3')^2K_1/K_2 = (K_3')^2$$

From Table II, $K_4' = 11.8$; therefore our value of $K_3' = (11.8)^{1/2} = 3.44$. The values of K_3' obtained from other sources are as follows.

TABLE III

VALUES OF K_3' AT 25°

K_3'	Catalyst	Observer
3.8	Pt black	Bonhoeffer and Rummel[18] Horiuti and Polanyi[19]
2.95	Pd black	Farkas and Farkas[20]
3.24	B. coli	Farkas, Farkas and Yudkin[21]
3.44	(e. m. f.)	La Mer and Korman
Av. 3.36		

The exchange constants listed in Table II may also be interpreted as ratios of dissociation constants. For example, process VI is the ratio for the dissociation equilibria

$$\text{(M)}\quad QH_2(s) = Q(s) + H_2(g);\quad K_{QH_2}$$

$$\text{(N)}\quad QD_2(s) = Q(s) + D_2(g)\quad K_{QD_2}$$

K_{QH_2} has the value $10^{-23.65}$.[22] Since $K_{QH_2}/K_{QD_2} = 11.26$, then $K_{QD_2} = 10^{-24.70}$. Processes I and XI, Table II, can be treated as ratios of dissociation constants for weak acids. If we assume that the activity of the chloride ion is the same in both

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[16] Hamill and La Mer, unpublished results; for an outline of the experimental method, see Hamill and Freudenberg, THIS JOURNAL, **57**, 1427 (1935).

[17] A. Farkas, "Light and Heavy Hydrogen," Cambridge Univ. Press, Cambridge, England, 1935, p. 182 ff.

[18] Bonhoeffer and Rummel, *Naturwiss.*, **22**, 45 (1934).

[19] Horiuti and Polanyi, *Nature*, **132**, 819 (1933); **133**, 142 (1934); **134**, 377 (1934).

[20] Farkas and Farkas, *Trans. Faraday Soc.*, **30**, 1071 (1934).

[21] Farkas, Farkas and Yudkin, *Proc. Roy. Soc.* (London), **B115**, 373 (1934).

[22] V. K. La Mer and L. E. Baker, THIS JOURNAL, **44**, 1954 (1922).

TABLE IV

DISSOCIATION CONSTANTS OF ACETIC AND SALICYLIC ACIDS

($\mu \cong 0.05$)

t, °C.	$-E_{\text{obsd.}}$	$-E_0$	Molality acid	Molality Na salt	Molality NaCl	K
			Salicylic Acid			
			$N_{D_2O} = 0$			
25.0	0.17189	0.47745	0.008304	0.021811	0.019379	0.98×10^{-3}
	.17222		.008321	.021855	.019416	0.96
	.18381		.010504	.019770	.021610	1.01
			$N_{D_2O} = 0.917$			
25.0	0.17095	0.50885	0.008748	0.023766	0.020657	0.26
	.16871		.008664	.021751	.021002	0.214
			$K_{HA}/K_{DA} = 4.09$			
			Acetic Acid			
			$N_{D_2O} = 0$			
12.5	0.07773	0.47906	0.008682	0.035988	0.0189991	1.79×10^{-5}
25.0	.05945	.47745	.008682	.035988	.0189991	1.85
37.5	.04020	.47679	.008682	.035988	.0189991	1.80
12.5	.09425		.017179	.036280	.019488	1.74
25.0	.07658		.017179	.036280	.019488	1.79
37.5	.05807		.017179	.036280	.019488	1.73
12.5	.08365		.010568	.035661	.019864	1.77
25.0	.06507		.010568	.035661	.019864	1.80
37.5	.04585		.010568	.035661	.019864	1.71
			$N_{D_2O} = 0.917$			
12.5	0.11661	0.51046	0.027605	0.043260	0.023060	0.754
25.0	.09242	.50885	.027605	.043260	.023060	.613
37.5	.07520	.50819	.027605	.043260	.023060	.634
12.5	.11301		.025765	.043571	.021463	.756
25.0	.08856		.025765	.043571	.021463	.611
37.5	.07125		.025765	.043571	.021463	.634

t, °C.	K_{HA}/K_{DA}
12.5	2.34
25.0	2.96
37.5	2.75

waters, No. I may be considered as the difference of the dibasic acid dissociations

(O) $QH_2 = Q^= + 2H^+$ (in H_2O); K_H
(P) $QD_2 = Q^= + 2D^+$ (in D_2O); K_D

where K_H, the average dissociation constant, equals $(K'K'')^{1/2} = [(1.75 \times 10^{-10})\ (4 \times 10^{-12})]^{1/2} = 2.64 \times 10^{-11}$ for ordinary water.[23] Log $(K_H/K_D) = 0.0345/0.05911 = 0.5837$, or $(K_H/K_D) = 3.84$. No. XI is the ratio of the acid dissociations

(Q) $H_2O = H^+ + OH^-$; $K_w(H_2O)$
(R) $D_2O = D^+ + OD^-$; $K_w(D_2O)$

and equals 6.13 at 25°.

Salicylic and Acetic Acid Solutions.—The data for cells (III) and (IV) for salicylic and acetic acids are given in Table IV, with the ratios K_{HA}/K_{DA}. To obtain this ratio for acetic acid at 12.5 and 37.5°, we employ the equation of Harned and Wright[10]

$$(4)\quad E_0 = -0.47745 + (91.02 \times 10^{-6})(\ -25) - (3.008 \times 10^{-6})(t-25)^2$$

In the absence of a similar equation for the corresponding heavy water cell, we have assumed that the coefficients for the temperature terms are the same for both waters. The E_0 values are given in Table IV. Figure 3 shows R log (K_{HAc}/K_{DAc}) plotted against $(1/T)$. The slope of the curve is a measure of the difference $(\Delta H_H - \Delta H_D)$ of the heats of dissociation between proto- and deutero-acetic acids. From these preliminary measurements, there appears to be a maximum in the curve. The indication that this quantity changes sign, as a function of temperature, suggests that the temperature coefficient of the dissociation constant of deutero-acetic acid be subjected to a more detailed investigation to eliminate the assump-

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[23] S. E. Sheppard, *Trans. Am. Electrochem. Soc.*, Preprint 39 (1921); La Mer and Parsons, *J. Biol. Chem.*, **57**, 613 (1923).

tion of equality of the temperature coefficients of the DCl and HCl cells.

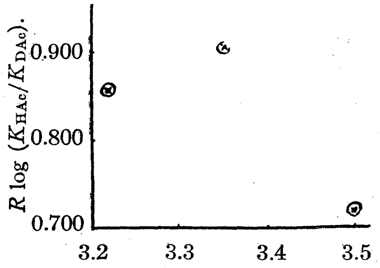

Fig. 3.—Dissociation constant of HAc and DAc.

The Solubility of Quinone, Hydroquinone and Deuteroquinone in H_2O and D_2O.—The errors in the determination of solubility in heavy water by ordinary analytical methods, *viz.*, titration, become greatly magnified when the quantity of solvent is severely limited, so it is scarcely feasible when dilution with ordinary water is undesirable. Furthermore, distillation of the solvent and weighing of the residue is not permissible with volatile substances like quinone.

Although the Zeiss interferometer has long been used for the accurate determination of the concentration of dilute solutions encountered in precision cryoscopic work, the capabilities of the instrument apparently have never been exploited for the precise determination of solubility on small samples. We present some illustrative data necessary for the interpretation of the e. m. f. results upon the quinhydrone electrode in heavy water.

The Method.—A Zeiss–Löwe–Haber portable liquid interferometer was employed. The description of this instrument and the principle upon which its use in determining concentrations of binary mixtures is based is given by Adams.[24]

Deuteroquinone was prepared by dissolving an excess of hydroquinone in 92% D_2O and separating by a vacuum distillation. The dry sample was kept in a vacuum desiccator.

About 5 g. of heavy water is weighed into a glass-stoppered 25-cc. flask and a quantity of solute just insufficient for saturation is added. About 0.15 cc. of the solution is sufficient for a reading in the interferometer when a special 10-mm. cell containing a 9-mm. glass block, producing a film of solution 1 mm. thick, is employed. Pure solvent is placed in the comparison chamber. For solutions more colored than saturated benzoquinone, 1 mm. is about the maximum thickness which will pass sufficient light.

If desired the aliquot may be returned to the flask with a micro-pipet. In any case the flask and solution remaining are reweighed, a small but accurately weighed additional quantity of solute dissolved and a new reading made with the interferometer. Finally, when a saturated solution has been produced, a considerable excess of solute is added. The solution is momentarily heated several degrees above 25°, and returned to the thermostat with constant swirling. Aliquots are removed at convenient (ten-minute) intervals, until an almost constant reading with the interferometer is obtained indicating an equilibrium state. The solution is then momentarily cooled below 25° and the procedure is repeated at convenient intervals. The average of the asymptotes of the two converging time–concentration curves is taken as the interferometer reading for the saturated solution. Obviously these observations can be repeated very readily upon the same sample if satisfactory results are not obtained at first.

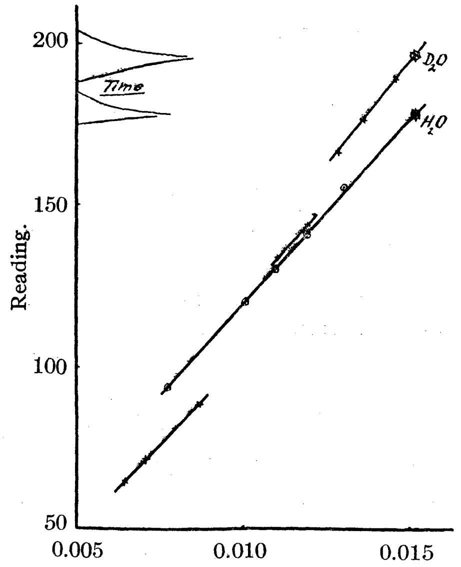

Fig. 4.—Solubility of quinone in H_2O and D_2O.

The tables and figures show that the interferometer readings are linearly proportional to the concentration at least near the saturation point, and that the intersection of the time–concentration asymptotes and the concentration calibration curve yield a value for the concentration of the saturated solution which is precise to about 0.1 mg. per g. of solvent. For a 5-g. sample this

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[24] L. H. Adams, THIS JOURNAL, **37**, 1181 (1915).

is approximately the error produced by evaporation during transfer of solute. Figure 4 shows the curves for quinone in light and heavy water; Fig. 5 those for hydroquinone in H_2O and for deuteroquinone in 99.8% D_2O.

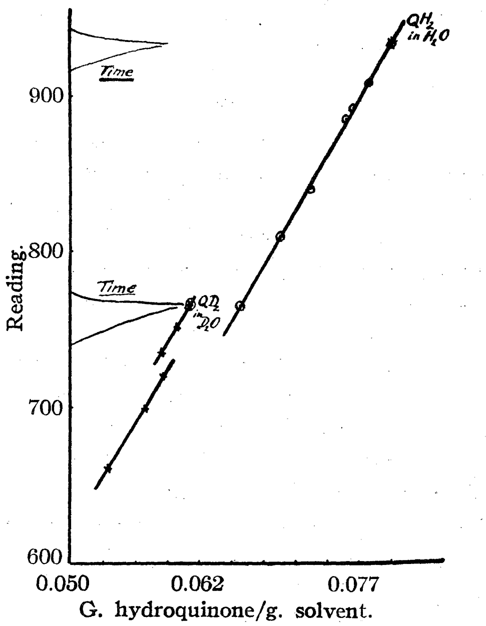

Fig. 5.—Solubility of hydroquinone in H_2O and D_2O.

TABLE V

SOLUBILITY OF QUINONE IN H_2O AND 99.8% D_2O

G. Q/g. H_2O	Reading, corr.	10^7 concn./ reading	G. Q/g. D_2O	Reading, corr.	10^8 concn./ reading
0.00774	94.0	823	0.00646	64.2	..
.01003	120.0	836	.00707	71.9	..
.01099	130.0	845	.00865	88.4	..
.01189	141.0	844	.01103	133.3	8275
.01298	155.7	834	.01191	143.9	8278
			.01282	166.3	7710
			.01353	176.4	7664
Av. for satd. soln.			.01451	189.7	7646
.0151	178.5		.0151	196.5	Av. s. soln.

TABLE VI

SOLUBILITY OF HYDROQUINONE IN H_2O AND DEUTEROQUINONE IN 99.8% D_2O

G. QH_2/g. H_2O	Reading, corr.	10^8 concn./ reading	G. QD_2/g. D_2O	Reading, corr.	10^8 concn./ reading
0.06583	765.3	8601	0.05336	661.7	8064
.06592	765.4	8613	.05696	699.9	8139
.06959	809.1	8597	.05861	721.0	8128
.07261	840.0	8644	.05861	735.8	7965
.07589	885.2	8573	.05991	752.1	7967
.07649	892.1	8574			
.07793	908.9	8574	Av. for satd. soln.		
.0802	934.0	Av. satd. soln.	.0611	765.9	

TABLE VII

SOLUBILITY OF QUINONE, HYDROQUINONE AND DEUTEROQUINONE AT 25°

	G./g. H_2O	G./g. D_2O	Mole/ mole H_2O	Mole/ mole D_2O	Mole ratio of soly. H_2O/ D_2O
Quinone	0.0151	0.0151	0.0025	0.0028	0.900
Hydroquinone	.0802	....	.0131	....	....
Deuteroquinone	....	.0611	....	.0109	1.204

Dissociation Constants of Weak Acids in H_2O–D_2O Mixtures.—The preliminary experiments with acetic and salicylic acids in 91.7% D_2O have established the feasibility of the microtechnique and the quinhydrone electrode in heavy water, as a method for determining dissociation constants of light and heavy acid mixtures. To extrapolate the dissociation constant obtained in H_2O–D_2O mixtures to pure D_2O, we define a constant for weak acid solutions in H_2O–D_2O mixtures by summing the various activities stoichiometrically[25]

$$K_{\text{H,D}} \equiv \frac{[(\text{H}^+) + (\text{D}^+)]\ (\text{A}^-)}{[(\text{HA}) + (\text{DA})]}$$

The fractions of deuterium ion and undissociated deutero-acid are

$$F_{\text{D}^+} \equiv \frac{(\text{D}^+)}{(\text{H}^+) + (\text{D}^+)};\quad F_{\text{DA}} \equiv \frac{(\text{DA})}{(\text{HA}) + (\text{DA})}$$

Then

$$K_{\text{H,D}} = \frac{[(\text{D}^+)/F_{\text{D}^+}]\ (\text{A}^-)}{[(\text{DA})/F_{\text{DA}}]} = K_{\text{DA}}\frac{F_{\text{DA}}}{F_{\text{D}^+}}$$

To evaluate the fractions at various values of $N_{\text{D}_2\text{O}}$, we utilize the constants for the exchange equilibria

$$\text{(S)}\quad \text{HA} + \text{HDO} = \text{DA} + \text{H}_2\text{O};\quad K = \frac{K_{\text{HA}}}{K_{\text{DA}}} \times \frac{1}{7.1}$$

$$\text{(T)}\quad \text{D}^+ + \text{H}_2\text{O} = \text{H}^+ + \text{HDO};\quad K = (15.3 \times 3.27)^{1/2} = 7.1$$

By so doing, we take account of the essential exchanges which must be postulated for H_2O–D_2O, HA–DA mixtures. Then

$$\frac{K_{\text{H,D}}}{K_{\text{HA}}} = \frac{K_{\text{DA}}}{K_{\text{HA}}}\left[\frac{1 + 7.1\,\dfrac{(\text{H}_2\text{O})}{(\text{HDO})}}{1 + 7.1\,\dfrac{K_{\text{DA}}(\text{H}_2\text{O})}{K_{\text{HA}}(\text{HDO})}}\right] \tag{5}$$

The water ratios may be calculated from the equilibrium

$$\text{(U)}\quad \text{H}_2\text{O} + \text{D}_2\text{O} = 2\text{HDO};\quad K = 3.27$$

If, then, we stipulate a value for $K_{\text{HA}}/K_{\text{DA}}$, we may determine the behavior of the constant $K_{\text{H,D}}$ over the range of H_2O–D_2O concentrations. The values for $K_{\text{H,D}}/K_{\text{HA}}$ given in equation (5) are

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(25) Abel, Bratu and Redlich (ref. 15) have employed a similar definition for the ion product of water in mixtures.

plotted in Fig. 6 as a function of K_{DA}/K_{HA}. It will be noted that the extrapolation is practically linear above 90% D_2O for most ratios. Since measurements must frequently be made in D_2O concentrations less than 100%, a reasonably accurate value for pure D_2O should be obtained by a method of successive approximations. Thus $K_{HA}/K_{H,D} = 2.96$ for acetic acid in 92% D_2O becomes $K_{HA}/K_{DA} = 3.3$ for pure D_2O. Since for most acids so far investigated this ratio lies between 3 and 6, the above method justifies our belief that extrapolations of $K_{H,D}$ from measurements over 90% D_2O are fairly reliable.

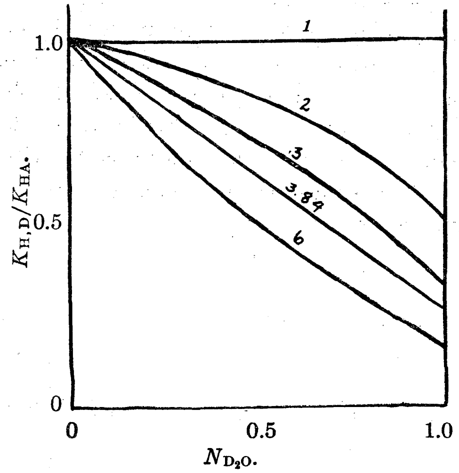

Fig. 6.—Dissociation constant, ratios in H_2O–D_2O mixtures.

Halpern[26] has predicted that K_{HA}/K_{DA}, the ratio of the dissociation constants of a weak acid in pure H_2O and pure D_2O, should increase as K_H decreases. Our studies upon hydroquinone and acetic acid, together with the ratio of the water constants, indicate that this prediction is probably correct. The somewhat anomalous ratio for salicylic acid will serve to indicate that certain conditions must be satisfied before a rigorous comparison of weak acids can be attempted. The constitution of the anion must not be affected by the change of solvent medium for H_2O to D_2O. A complicating factor may be introduced by the exchange of protium and deuterium atoms at points in the acid molecule other than those corresponding to the measured ionization. Thus, the exchange which occurs in the hydroxyl group of the salicylate ion may effectively alter the character of the ion, depending upon the isotopic composition of the medium.

Summary

The free energy changes for a number of important deuterium exchange reactions in aqueous solution have been investigated, using the quinhydrone, silver chloride–silver electrodes and a semi-microtechnique on hydrochloric acid and weak acid buffer systems. The dissociation constants of the weak acids salicylic, acetic, hydroquinone and water in light and 92% heavy water have been measured. With the exception of salicylic acid, the ratio of these dissociation constants in light and heavy water decreases as the constant increases. An equation has been developed which affords a controlled extrapolation of this ratio to 100% D_2O from a single measurement above 90% D_2O.

The quinhydrone electrode yields reliable results of greater precision than have been obtained with the deuterium gas electrode. The superiority of the quinhydrone electrode is due not only to the simplicity of manipulation, but to the fact that the equilibrium between the proto- and deutero-forms of quinhydrone, of water and of acid is established promptly in a homogeneous solution. With the gas electrode the exchange reactions are established only at the surface of the electrode, which equilibrium can be disturbed by convection and diffusion from the bulk of the solution, if the gas has been generated by the complete decomposition of a portion of the water employed.

The temperature coefficients of the e. m. f. indicate that the difference in the heats of ionization of the proto- and deutero-acetic acids may change sign in the neighborhood of 25°.

The solubilities of quinone, hydroquinone and deuteroquinone in small quantities of light and heavy water, necessary for the interpretation of the e. m. f. data, have been determined precisely by an interferometer method. Hydroquinone is 20% more soluble on a mole ratio basis than deuteroquinone at 25°, whereas quinone suffers no change in solubility.

NEW YORK, N. Y. RECEIVED JUNE 6, 1936

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[26] Halpern, *J. Chem. Phys.*, **3**, 456 (1935). Halpern's treatment can have the status only of an approximate theory, since he consciously omits a detailed consideration of the specific contributions of moments of inertia, mass ratios and interaction effects, leaving the contribution of the vibrational frequencies of the proton and deuton bonds as the only significant factor in determining the ratio.

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Photochemical Studies. XXIII. The Photochemical Decomposition of Acetone Vapor near 1900 Å. A Comparison with the Decomposition at Longer Wave Lengths

BY JOHN P. HOWE[1] AND W. ALBERT NOYES, JR.

Acetone, in common with other ketones and aldehydes, exhibits an absorption region beginning at wave lengths somewhat longer than 3000 Å. and extending down to about 2200 Å. On the long wave end some structure has been noted[2] and fluorescence has been observed in this region.[3] Whether or not fluorescence is excited by wave lengths below those for which discrete structure is obtained seems to be the object of some disagreement.[4]

It seems generally agreed that the main products of photochemical decomposition in this near ultraviolet region of the spectrum are carbon monoxide and ethane, although small amounts of other substances may be formed.[4a,5] The quantum yield is a function of wave length, increasing slightly as the wave length is decreased. While the general aspects of the photochemical decomposition of acetone in this region of the spectrum seem quite well established, experiments have not been carried out over a sufficient range of intensities, pressures of acetone and pressures of foreign gas to make it possible to present a mechanism free from criticism.

Recently the ultraviolet absorption spectrum of acetone has been investigated.[2c] In addition to the absorption region near 3000 Å., one additional region is susceptible of investigation with apparatus made of quartz. This region consists of discrete bands extending from about 1995 to about 1820 Å., probably overlaid with a faint continuum. Manning[6] has developed a method of gas analysis applicable to the products of acetone decomposition and studied the gases produced upon illuminating acetone vapor with polychromatic radiation transmitted by fluorite.

A complete understanding of the photochemistry of acetone can be based only on a thorough study of as many different excited states as possible over a wide range of experimental conditions. It is for this reason that the present investigation at wave lengths near 1900 Å. was carried out. A consistent picture of the results is possible.

I. Experimental Procedure and Results

The following primary processes and subsequent steps are possible in any dissociation such as that of acetone (I represents quanta absorbed per second, A represents an acetone molecule, A_1 represents an excited acetone molecule, D represents dissociation products, M represents a molecule of foreign gas):

Reaction	Rate	
$A + h\nu = D;$	I_1	(1)
$A + h\nu = A_1;$	I_2	(2)
$A_1 = A + h\nu_1;$	$k_1\ (A_1)$	(3)
$A_1 = A_2;$	$k_2\ (A_1)$	(4)
$A_1 = D;$	$k_3\ (A_1)$	(5)
$A_1 + A = 2A;$	$k_4\ (A_1)(A)$	(6)
$A_1 + A = D + A;$	$k_5\ (A_1)(A)$	(7)
$A_1 + M = A + M_1;$	$k_6\ (A_1)(M)$	(8)
$A_1 + M = D + M;$	$k_7\ (A_1)(M)$	(9)

If it can be shown that the dissociation products, D, do not react with each other to reform acetone, the quantum yield, ϕ, is found to be

$$\phi = (I_1/(I_1 + I_2)) + (I_2/(I_1 + I_2))(k_3 + k_5(A) + k_7(M))/ (k_1 + k_2 + k_3 + (k_4 + k_5)(A) + (k_6 + k_7)(M)) \quad (10)$$

providing the molecule A_2 either does not dissociate or has a very long life. The quantities in parentheses may be expressed either in pressure units or in numbers of molecules per cubic centimeter.

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(1) Jesse Metcalf Fellow, 1935–1936.

(2) This structure seems to have been observed first by Herzberg, see (a) Scheibe, Povenz and Linström, *Z. physik. Chem.*, **B20**, 297 (1933), for mention. It has been confirmed subsequently by other workers: (b) Crone and Norrish, *Nature*, **132**, 241 (1933); (c) Noyes, Duncan and Manning, *J. Chem. Phys.*, **2**, 717 (1934).

(3) Norrish, *Nature*, **133**, 837 (1934).

(4) (a) Damon and Daniels, THIS JOURNAL, **55**, 2363 (1933); (b) Fisk and Noyes [*J. Chem. Phys.*, **2**, 654 (1934)] have studied the fluorescence excited by monochromatic 3130 Å. radiation of mercury. They found the fluorescence to follow a Stern–Volmer mechanism at the pressures used (50 to 190 mm.). They did not investigate the effect of wave length. Recently Mr. Fisk and one of us (J. P. H.) using a crystal quartz monochromator and a quartz capillary arc have observed fluorescence to be produced by all of the mercury lines from 3130 to 2536 Å., but apparently not by the weak lines at still shorter wave lengths. These results are in agreement with those of Damon and Daniels.

(5) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1456 (1934).

(6) Manning, THIS JOURNAL, **56**, 2589 (1934). Monochromatic radiation was not used in Manning's experiments and moreover no attempt was made to remove mercury resonance radiation. In the present article it is shown that the effect of the latter is quite appreciable, particularly at low acetone pressure. Also Duncan [*J. Chem. Phys.*, **3**, 131 (1935)] has shown that acetone absorbs strongly still shorter wave lengths which would be transmitted by fluorite. In view of these facts the results of Manning, which generally showed relatively large amounts of hydrogen to be produced, should not be viewed as being in disagreement with the results reported in the present article.

The detailed description of the effect of radiation on the acetone molecule involves, therefore, the proof that the dissociation products do not reunite to give acetone, decision as to whether step (1) or step (2) or both must be considered, the evaluation of the constants k_1–k_7 and decision as to the nature of the molecule, A_2.

(a) The Nature of the Absorption Process.—The source of radiation used in these experiments was a spark between slowly revolving aluminum disks excited by two 1-kva. 25,000-volt transformers connected in parallel. The method of focal isolation was used to obtain monochromatic radiation and the purity of the radiation was tested spectroscopically using a small fluorite prism spectrograph. The following lines were transmitted with sufficient intensity to be photographed: 1854.7, 1858.2, 1862.5, 1862.9, 1930.3, 1935.2, 1989.8. The following bands lie near these exciting lines (intensities in parentheses):[2c] 1866.7 (3), 1868.9 (6), 1870.3 (3), 1872.4 (6), 1921.1 (4), 1923.0 (3), 1925.3 (3), 1926.4 (3), 1927.2 (4), 1938.9 (6), 1939.8 (6), 1941.1 (6), 1942.1 (6), 1943.9 (6). Only bands lying within 10 Å. of an exciting line have been listed. These bands have quite sharp edges, indicating the possibility that rotational structure might be observed with sufficient resolution. No bands lie very close to the group of lines 1854.7–1862.9; moreover these lines are relatively weak from the source due to the absorption by quartz and by the relatively long air path. The 1989.9 line falls in a region in which acetone is quite transparent. Most of the absorption must be due to the two lines at 1930.3 and 1935.2 Å.

In addition to the above lines this type of spark emits a faint continuum which cannot be ignored since it leads to some excitation of mercury vapor to the 2^1P_1 state through absorption of the 1849 Å. line. After this effect was discovered a chamber practically free from air circulation and containing mercury vapor was inserted between the second lens and the reaction vessel. This produced a noticeable decrease in the amount of decomposition at low acetone pressures and the evidence indicated convincingly that this error was removed in this way. The absorption coefficient of the 1849 line by mercury vapor is exceedingly high and even a temperature of −77° does not remove mercury vapor well enough to prevent practically complete absorption in the path length used.

Since absorption takes place in a banded region overlaid with a faint continuum, the spectroscopic evidence might indicate that both equations (1) and (2) should be considered. However, as will be shown, the data indicate that a molecule with a relatively long life is produced and that hence equation (1) may be omitted from consideration.

The fraction of the radiation absorbed by the acetone was determined by means of a photoelectric cell with quartz envelope. The following equation using two absorption coefficients was found to be obeyed (see Table I).

$$I/I_0 = 0.868 \exp. (-0.975P) + 0.132(1 - 0.0114P) \quad (11)$$

(I = transmitted intensity, I_0 = incident intensity, P is pressure in millimeters. The path length was 7.5 cm.)

TABLE I

ABSORPTION OF RADIATION BY ACETONE VAPOR

Pressure, mm.	I/I_0 calcd.	I/I_0 obsd.
0.295	0.786	0.791
.583	.627	.642
1.14	.422	.434
1.82	.281	.255
3.80	.149	.160
5.00	.132	.137
8.60	.122	.117
12.8	.113	.115
19.3	.103	.103

(b) Fluorescence.—A fluorescence cell was constructed with a window so placed that any fluorescence could be observed at right angles to the incident beam. Scattered and reflected radiation was reduced by tapering the ends of the tube and painting the entire cell except the windows with black paint. No visible fluorescence could be observed and attempts to produce blackening of ultraviolet sensitive plates gave negative results.[4b] If fluorescence exists it must either be very weak or the emitted radiation must lie in a region of the spectrum which could not be detected by the methods used.

(c) The Determination of Quantum Yields.—As shown by Manning[6] at low acetone pressures (below 0.03 mm.) approximately one molecule of carbon monoxide is produced per molecule of acetone disappearing (the average ratio was 1.03). In the present experiments no hydrogen was found and at low acetone pressures, as shown in Table II, carbon monoxide constituted very nearly 50% of the gases produced during decomposition. There seems to be no doubt, therefore, that the decomposition proceeds almost solely by the reaction

$$(CH_3)_2CO = C_2H_6 + CO \qquad (12)$$

At higher acetone pressures some of the ethane seems to dissolve in the acetone upon condensation with liquid air, as found by Norrish and coworkers.[5] The number of molecules of acetone disappearing is based, therefore, on an analysis for carbon monoxide.[6]

TABLE II

PERCENTAGE OF CARBON MONOXIDE IN REACTION PRODUCTS

Pressure of acetone, mm.	Total pressure of products, mm.	Carbon monoxide pressure, mm.	Carbon monoxide in products, %
1.80	0.0223	0.0110	49.8
1.78	.0210	.0102	48.7
8.35	.0191	.0098	51.3
		Average	49.9

For determinations of the absolute values of the quantum yield a hydrogen bromide actinometer was used. For this the production of one molecule of hydrogen (uncondensed by liquid air) per absorbed quantum was assumed.[7] The hydrogen bromide cell was about 15 cm. in length and pressures of hydrogen bromide of 10 to 15 mm. were employed. Under these conditions over 99% of the radiation was absorbed by the actinometer.

The hydrogen bromide cell was placed directly in back of the cell containing the acetone vapor, one window (of fused quartz sealed to the actinometer vessel) being in common between the two cells. The transmission of this window was measured subsequently after cutting off the end of the cell. The hydrogen bromide cell was made entirely of quartz and no wax was present in this system. The crystal quartz front window of the acetone cell was attached with picein wax.

In making a run the acetone was frozen with liquid air and the hydrogen bromide decomposition determined, a photoelectric cell being used to detect any variations in the over-all intensity of the spark. The acetone was then vaporized and the decomposition of the hydrogen bromide again determined. Corrections were made for variation in intensity between the two parts of the experiment. For this purpose the ultraviolet intensity was assumed to vary directly with the over-all intensity of the spark. This is not strictly true, but since intensity variations were always small the error introduced by the assumption would be negligible.

Table III presents the absolute values of the quantum yield as determined with the hydrogen bromide actinometer.

TABLE III

ABSOLUTE QUANTUM YIELDS OF ACETONE DECOMPOSITION

Acetone pressure, mm.	Time, min.	Quanta absorbed $\times 10^{-17}$	Molecules of CO produced $\times 10^{-17}$	Incident quanta per sec. $\times 10^{-13}$	Quantum yield, ϕ	Quantum yield, calcd. eq. (15)
6.00	120	2.19	1.163	4.19	0.53	0.57
2.20	38	0.605	0.361	4.87	.60	.61
2.20	60	1.57	.873	7.51	.56	.61
3.2	60	2.11	1.28	8.93	.61	.60
11.1	60	2.60	1.44	9.39	.56	.54
25.1	30	2.45	1.25	15.9	.51	.52

The complete determination of the mechanism of the decomposition involves the evaluation of the constants k_4–k_7. Quantum yields must be determined, therefore, with some precision over a wide range of experimental conditions and for this purpose the hydrogen bromide actinometer is not suitable. In particular the actinometer method lacks accuracy when the pressure of acetone is low and the percentage of the radiation absorbed small.

Relative quantum yields were obtained using a photoelectric cell to measure the incident intensity and calculating the amount of absorbed radiation from equation (11). A quantum yield of 0.55 at a pressure of 9.32 mm. (the average value at the average pressure in Table III) was assumed for the purpose of converting the relative quantum yields into absolute values. Table IV gives the values of the quantum yield obtained in this way.

TABLE IV

RELATIVE QUANTUM YIELDS OF ACETONE DECOMPOSITION

Acetone pressure, mm.	Intensity (arbitrary units)	Fraction absorbed	Pressure of CO, mm.	Time, min.	Quantum yield, ϕ	Quantum yield, calcd. eq. (15)
0.210	8.69	0.160	0.0072	180	0.66	0.64
.224	11.63	.169	.0094	180	.61	.64
.445	9.14	.296	.0092	120	.64	.64
1.07	10.19	.545	.0120	80	.62	.62
2.27	8.12	.784	.0102	60	.61	.61
4.20	1.59	.848	.00783	224	.59	.59
4.71	6.62	.858	.0086	60	.58	.58
4.73	8.85	.858	.0113	60	.57	.58
8.35	7.86	.873	.0097	60	.54	.56
8.35	7.70	.873	.0099	60	.56	.56
16.5	6.96	.894	.0088	60	.54	.53
20.4	11.38	.898	.0141	60	.53	.52
20.4	9.19	.898	.0115	60	.53	.52
52.3	9.35	.947	.0144	75	.50	.50
52.3	10.02	.947	.0159	90	.46	.50

(d) The Effects of Added Gases.—The constants k_6 and k_7 will be expected to vary from one

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[7] Warburg, *Sitzber. preuss. Akad. Wiss.*, 314 (1916).

added gas to another. Three different gases were used: carbon dioxide, nitrogen and ethane. The experimental difficulties were least with the carbon dioxide which could be condensed with liquid air completely enough to permit easy removal of the decomposition products of acetone. This difficulty was particularly great with nitrogen and frequent circulation of the gases through the liquid air trap was necessary to remove all of the acetone vapor. Within experimental error none of these gases absorbed the radiation used. There is some slight possibility of decomposition of the ethane and carbon dioxide sensitized in some way by the acetone.

Table V shows the results obtained with added gases.

TABLE V

EFFECT OF ADDED GASES ON QUANTUM YIELD OF ACETONE DECOMPOSITION

Acetone pressure, mm.	Foreign gas pressure, mm.	Quantum yield	Quantum yield without added gas	Added gas
1.82	9.8	0.81	0.61	Carbon dioxide
1.81	9.8	.85	.61	
1.72	18.4	.88	.62	
2.12	2.23	.69	.61	Nitrogen
2.12	3.78	.81	.61	
2.34	7.38	.74	.61	Ethane
2.32	7.13	.75	.61	
2.30	12.30	.80	.61	

(e) The Effect of Excited Mercury.—The presence of excited mercury raised the apparent quantum yield as shown in Table VI. It is evident from the results that solid carbon dioxide–chloroform mixtures do not remove mercury vapor completely enough to prevent this effect.

TABLE VI

EFFECT OF EXCITED MERCURY ON APPARENT QUANTUM YIELD

Acetone pressure, mm.	Apparent quantum yield	Quantum yield, calcd. eq. (15)	Remarks
1.51	0.73	0.62	Resonance radiation present
0.155	.72	.65	Trap in CO_2–$CHCl_3$
.124	.88	.65	
.134	.81	.65	
20.4	.53		Resonance radiation present
20.4	.53		Resonance radiation removed
9.9	.55	.55	Resonance radiation present

It is quite obvious from the results in Table VI that at high acetone pressures the fraction of the reaction due to excited mercury is too small to be significant. This is not true, as would be expected, at low pressures.

II. Discussion of Results

It is important first to show that the dissociation products do not react with each other to reform acetone. Two lines of evidence may be brought to bear on this point. (1) In Table III it is seen that the incident intensity was varied by a factor of nearly four and in Table IV the maximum variation is somewhat over seven-fold. In neither table is any significant variation of quantum yield with intensity apparent, whereas if a homogeneous gas phase recombination reaction were taking place the quantum yield should decrease as the intensity increases. (2) Methyl groups do not react with carbon monoxide, at least with any rapidity, when the carbon monoxide pressure is low and the temperature about 25°.[8] This means that if two methyl groups and normal carbon monoxide are produced almost simultaneously, as Norrish suggests at longer wave lengths,[5] the reverse reaction may be neglected. There still remains some slight possibility of a wall recombination between free radicals of the type of CH_3CO and CH_3. However, CH_3CO is probably not very stable and in the thermal decomposition of acetone its recombination with methyl groups does not seem to be important.[9] The evidence against free radical recombination is, therefore, not conclusive but is about as good as one can ever obtain in a photochemical reaction.

In arriving at an equation which will express the quantum yield as a function of the various variables, it is necessary to decide whether the quantum yield approaches unity at zero pressure. Experiments were carried out at pressures down to 0.2 mm. and at this pressure the yield is far from one. Experimental difficulties prevented the execution of precise experiments at still lower pressures. However, it may be stated definitely that the mechanism outlined in equations (2) to (9) inclusive will lead to a quantum yield of unity at zero pressure only if equations (3) and (4) are omitted. The omission of both of these equations results in disagreement between the quantum yield expression and the data, whereas the inclu-

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[8] Some experiments were carried out by one of us (W. A. N., Jr.) in which lead tetramethyl was illuminated by radiation from a zinc spark in the presence of carbon monoxide. A two per cent. acetone solution used as a color filter effectively removed any radiation which would be absorbed by acetone vapor. Leighton and Mortensen [THIS JOURNAL, **58**, 448 (1936)] have shown that methyl groups are produced when lead tetramethyl is illuminated. No significant reaction between methyl groups and carbon monoxide could be detected.

[9] Rice and Herzfeld, *ibid.*, **56**, 286 (1934).

sion of either one or both makes an agreement possible providing the molecule A_2 is of such a nature that it is always deactivated before dissociating.

We seem forced to one of the following conclusions: (1) fluorescence is emitted; (2) the primarily excited state A_1 changes into another state (or states) without collision, this reaction being necessarily reversible by the principle of microscopic reversibility; (3) the reaction products (especially CO) exert an unexpectedly large effect in deactivating excited acetone molecules; (4) the molecule A_2, for some reason, is stable or is always deactivated without dissociating.

These possibilities will be discussed in order.

(1) Omitting equation (4) and in the absence of foreign gases the quantum yield becomes

$$\phi = (k_3 + k_5(\mathrm{A}))/(k_1 + k_3 + (k_4 + k_5)(\mathrm{A})) \quad (13)$$

If it is assumed that collisions must produce either deactivation or dissociation, $(k_4 + k_5)$ must represent the total number of collisions per excited acetone molecule per second at unit pressure (1 mm.). This number of collisions at 25° is

$$z = 4.78 \times 10^{21}\sigma_1^2 = 1.2 \times 10^7 \quad (14)$$

if σ_1 (the distance between centers at closest approach) is taken as 5×10^{-8} cm.[10] If the quantum yield is 0.65 at zero pressure, the following values of the constants in equation (13) are obtained: $k_1 = 2.56 \times 10^7$; $k_3 = 4.74 \times 10^7$; $k_4 = 0.59 \times 10^7$; $k_5 = 0.61 \times 10^7$. With these values equation (13) fits the quantum yield well within experimental error.

It is now possible to show that 27% of the absorbed quanta should be reëmitted as fluorescence at 1 mm. pressure and about 8% at 10 mm. Since the fraction of the radiation reëmitted decreases with pressure whereas the amount of radiation absorbed per unit path length increases there will be an optimum pressure for observing the phenomenon. With the incident intensities available the intensity of the fluorescent radiation would not exceed the limit of visibility by a wide margin even if all of the fluorescence occurred in the visible spectrum. A lack of visual observation is not adequate proof of the absence of fluorescence. However, the intensity should be high enough to affect a photographic plate with exposures of thirty to sixty minutes providing the plate is sensitive to the wave lengths reëmitted. If fluorescence exists the failure to observe it must be ascribed to this cause, although the plates used should be sensitive to the region from 6000 to 1800 Å.

The question of the existence of fluorescence therefore must be left open.

(2) The introduction of two or more states which may change into each other reversibly without loss of energy makes it possible to derive an equation which will fit the data and still give a quantum yield of unity at zero pressure. The complete evaluation of all of the constants in such an equation is impossible from any experimental data, although conclusions may be drawn with regard to the values of certain ones. The rate of change of A_1 into A_2 and *vice versa* must proceed much more rapidly (at least 100 times) than the spontaneous dissociation of either one and the constant for spontaneous dissociation of the one of longest mean life must be twenty to one hundred times smaller than the number of collisions per second at unit pressure. This means that the mean life must be of the order of 10^{-5} to 10^{-6} sec., although this figure could be reduced somewhat by using a different collision diameter. Obviously any mechanism which will fit the experimental data and still permit the quantum yield to be unity at zero pressure must involve states with long lives.

(3) The reaction products may exert a deactivating effect on excited acetone molecules. However, ethane raises the quantum yield, so that the responsibility would have to be placed on the carbon monoxide. The decomposition was never allowed to proceed very far and the carbon monoxide pressure was usually not greater than 0.01 mm. at the end of an experiment. While fairly good resonance might be expected with carbon monoxide, here again either a long mean life for excited acetone or unreasonably large collision diameters would have to be used to fit the facts.

(4) If the molecule A_2 is stable and does not change back into A_1, the following equation (similar to (13)) is obtained

$$\phi = (k_3 + k_5(\mathrm{A}))/(k_2 + k_3 + k_4(\mathrm{A}) + k_5(\mathrm{A})) \quad (15)$$

The numerical values of the constants will be the same as for equation (13) except that k_2 will replace k_1. The calculated values in Tables III and IV were obtained from equation (15).

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(10) The various radii used in this discussion are as follows: acetone 2.5×10^{-8} cm., carbon dioxide 1.83×10^{-8} cm., nitrogen 1.58×10^{-8} cm., ethane 2.0×10^{-8} cm. These are estimated from tables and from interatomic distances and are admittedly very crude values. The results should be taken as verifying one of the general pictures presented to explain the experimental facts rather than as signifying an exact numerical agreement.

From the constants for either equation (13) or equation (15) the mean life of the excited acetone molecule is found to be 1.4×10^{-8} second, which is large enough so that a discrete spectrum should be observed.

The theoretical difficulties involved in introducing a metastable molecule of long life will be considered in the next section. However, since either equation (13) or equation (15) fits the experimental data over the range of observations, they will be used in discussing the effects of added gases.

One observes that the effect of added gases is in each case to cause an increase in the quantum yield. By taking into account the constants already evaluated one finds for the ratio of quantum yield with added gas to that without

$$\phi/\phi_0 = \frac{1 + k_7 P_2/(k_5(8.13 + P_1))}{1 + (k_6 + k_7)P_2/(k_4 + k_5)(6.1 + P_1)} \quad (16)$$

where ϕ is the quantum yield at foreign gas pressure of P_2 mm. and acetone pressure of P_1 mm., while ϕ_0 is the quantum yield when $P_2 = 0$. $(k_6 + k_7)$ will be the number of collisions per excited acetone molecule per second at unit pressure of added gas. An examination of the data in Table V reveals the fact that k_6 seems to be small compared to k_7. If one assumes $k_6 = 0$, the following equations are obtained (radii are given in Ref. 10): for carbon dioxide

$$\phi/\phi_0 = (1 + 1.62P_2/(8.13 + P_1))/(1 + 0.79P_2/(6.1 + P_1)) \quad (17)$$

For nitrogen

$$\phi/\phi_0 = (1 + 1.68P_2/(8.13 + P_1))/(1 + 0.82P_2/(6.1 + P_1)) \quad (18)$$

For ethane

$$\phi/\phi_0 = (1 + 2.00P_2/(8.13 + P_1))/(1 + 0.98P_2/(6.1 + P_1)) \quad (19)$$

Table VII shows the applicability of equations (17), (18) and (19) to the data of Table V.

TABLE VII

COMPARISON OF OBSERVED WITH CALCULATED EFFECTS OF FOREIGN GASES

Acetone pressure, mm.	Foreign gas pressure, mm.	ϕ/ϕ_0 obsd.	ϕ/ϕ_0 calcd.	Foreign gas
1.82	9.8	1.33	1.31	CO_2
1.81	9.8	1.39	1.31	
1.75	18.4	1.42	1.41	
2.12	2.23	1.13	1.12	N_2
2.12	3.78	1.33	1.18	
2.34	7.38	1.21	1.30	C_2H_6
2.32	7.18	1.23	1.30	
2.30	12.30	1.31	1.39	

With the exception of one run the agreement between observed and calculated values is satisfactory in the cases of carbon dioxide and nitrogen, thus indicating that practically every collision between an excited acetone molecule and a molecule of these gases leads to dissociation. For ethane the observed values are always lower than the calculated values. Agreement may either be obtained by using 3.4×10^{-8} cm. as the value of σ or by assuming that approximately 10% of the collisions lead to deactivation. In reality the two points of view do not differ materially, since the efficiency factor and the radius cannot be calculated separately. Ethane does possess some bonds similar to those in acetone and hence one should expect a better chance of resonance upon collision than with the other two gases. The fact that ethane is less efficient in producing dissociation than either carbon dioxide or nitrogen agrees with prediction.

III. Theoretical Discussion

As has been shown in the preceding section, many of the aspects of the photochemical decomposition of acetone in the neighborhood of 1900 Å. may be explained on the basis of a simple kinetic picture. The chief difficulty is connected with the fact that the quantum yield, in the apparent absence of fluorescence, does not rise to unity at zero pressure. Several explanations of this fact are possible. There remains the problem of correlating the spectroscopic and photochemical data for the two regions so far investigated.

Mulliken[11] has studied the various electronic states of ketones and aldehydes. The symmetry of the acetone molecule may be taken as C_{2v}, the same as formaldehyde, if the rotation of the methyls is considered. The normal state cannot be formed from two methyl groups and carbon monoxide in its ground ($^1\Sigma$) state. There are several reasons for believing that this is so: (1) the value of ω_e for normal carbon monoxide[12] is 2167.4 cm.$^{-1}$ which does not correspond to the frequency of about 1700 cm.$^{-1}$ observed for all molecules containing the carbonyl group;[13] (2) the carbon–oxygen distance in carbon monoxide corresponds most nearly to that of a triple bond and the electronic configuration of this molecule may best be described in this way.[14] One would

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(11) Mulliken, *J. Chem. Phys.*, **3**, 564 (1935).

(12) Jevons, "Report on Band Spectra of Diatomic Molecules," The Physical Society, London, 1932, p. 286.

(13) See Hibben, *Chem. Rev.*, **18**, 41 (1936).

(14) See Mulliken, *ibid.*, **9**, 373 (1931).

expect a system of two methyl groups and normal carbon monoxide to be repulsive.

The only state of carbon monoxide which has a value of ω_e approximately corresponding to that of the Raman frequency of the carbonyl group is $a^3\Pi$ with a frequency of 1739.3.[12] If this state is split into C_{2v} symmetry by bringing up two methyl groups one can arrive at Mulliken's configuration for the acetone molecule.

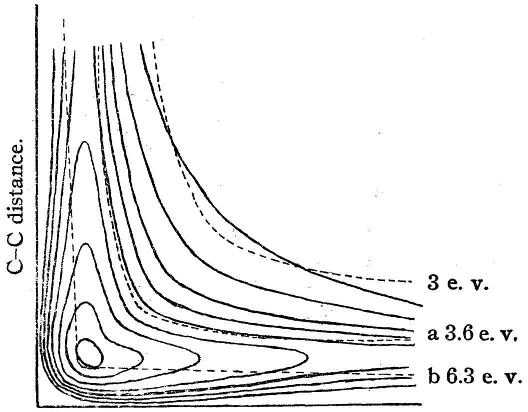

Fig. 1.

Excited states of the acetone molecule must exist which would separate adiabatically into other states of carbon monoxide and normal methyl groups, since the absorption is concerned mainly with electrons in the carbonyl group. Thus there is an excited electronic state of carbon monoxide with $\omega_e = 1182$,[15] which lies 7.13 electron volts above the ground state. Several observers have found upper state frequency differences in aldehyde and ketone absorption corresponding to 1180 to 1200 cm.$^{-1}$ [2c] in the absorption region around 3000 Å. In the bands between 1800 and 2000 Å., strong bands separated by 1049 and 1194 cm.$^{-1}$ were found and one of these frequencies is probably a carbon–oxygen frequency. The corresponding state of carbon monoxide is less definite here because no ω_e value is given for the $d^3\Pi$ state.

There are too many degrees of freedom in the acetone molecule to permit a diagram in two dimensions to represent them all. However, one may, for purposes of discussion, hold the energies in the carbonyl group and in the methyl groups constant and furthermore keep the angle between the carbon–carbon bonds constant. With these restrictions it is possible to represent the acetone molecule by a contour map after the method of Eyring[16] (Fig. 1). The two carbon–carbon distances are represented by ordinates and abscissas and energy differences are represented by contours. These diagrams may be made only semi-quantitatively since all of the necessary facts for the complete description of the acetone molecule are not known. The stable configuration of acetone will be represented by a point at the bottom of the valley and on the line bisecting the angle between the x and y axes. If Fig. 1 represents the surface for the first excited state of acetone, then the dotted lines may be taken to represent the repulsive state formed from normal $^1\Sigma$ carbon monoxide and two normal methyl groups. Since this state is assumed to be repulsive the surface representing it must be rising fairly steeply and will touch the surface for the upper state (at about 4.1 electron volts) at a point lying on the line bisecting the angle between the x and y axes. From the upper state, therefore, the easiest way of egress would lead to the simultaneous splitting off of two methyl groups as postulated by Norrish.[5] However, since the "point" of intersection is in reality a "surface" when one considers all degrees of freedom, there should be some chance of splitting off one methyl group alone, although the "pass" over which the molecule would have to go would be somewhat higher than for the other process. It is easily seen that thermal dissociation should occur with the splitting off of one methyl group as postulated by Rice and Herzfeld.[9] The heat of activation for this process should be the heat of dissociation of the carbon–carbon bond less the energy contained in the various degrees of freedom of the molecule; 70,000 calories is the value chosen by Rice and Herzfeld.[9]

Figure 2 is a vertical cross section cutting across all of the energy levels, keeping both the angle between the carbon–carbon bonds constant and the two carbon–carbon distances equal to each other. This diagram resembles that of a diatomic molecule, but it should be kept in mind that many more degrees of freedom are involved. From spectroscopic information, known heats of dissociation and the photochemical facts one can deduce the vertical distances quite accurately. The manners in which the various curves inter-

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(15) *Cf.* Ref. 12. Henri [*Compt. rend.*, **199**, 849 (1934)] has assigned the states of the carbonyl group in much the same way as that indicated here.

(16) Eyring, *Naturwissenschaften*, **18**, 914 (1930); Eyring and Polanyi, *Z. physik. Chem.*, **12B**, 279 (1931).

sect are in agreement with these facts, but the horizontal distances are schematic.

I represents the normal state of acetone and II the upper state for the bands near 3000 Å. Fluorescence should be most strong on the long wave end of this band system. There are two reasons for drawing the upper curve displaced horizontally with respect to the curve of the ground state: (1) the maximum intensity of absorption is displaced toward short wave lengths from the band chosen as the (0,0) band.[2c] (2) The maximum intensity of fluorescence is in the green. The curves are drawn to account semi-quantitatively for these facts. Dissociation takes place by a transition from II to the repulsive state IV, but there should be some chance of fluorescence in the entire region.

In discussing the near ultraviolet region of the spectrum it must be emphasized that a consistent explanation of the published results is impossible. It has been shown that practically all of the absorbed energy may be accounted for[4b] by (1) fluorescence, (2) dissociation, (3) deactivation by collision. In order to arrive at this balance it was assumed that the dissociation followed equation (5). However, it has been shown that the quantum yield probably decreases with pressure at 3130 Å.[4a] A mechanism fitting these facts may be derived by assuming that $k_3 = 0$ and that dissociation of an activated molecule occurs only upon collision. Thus it is seen that the relatively small amount of fluorescence is incompatible with a quantum yield approaching zero at zero pressure. To explain some of the facts in this region Norrish[5] has introduced the idea of "degradation to heat," which is equivalent to postulating a molecule formed spontaneously from the originally activated molecule, but incapable of dissociation in a time even considerably greater than the time between collisions. It is seen that a difficulty seems to exist in the near ultraviolet similar to that encountered at 1900 Å., but the experimental data, particularly in the former region, are not accurate enough at present so that one is justified in stating whether the difficulties are apparent or real.

Curve III represents the upper state for the spectral region discussed in the present article. Curve IV must lie fairly close to curve III so that there is a fairly high probability of transition to the repulsive state. In general the transition must occur after a period of time longer than that required for one rotation (between 10^{-10} and 10^{-11} sec.) or the bands would not appear to have sharp edges at low pressures. The mean life of about 10^{-8} second is not in disagreement with this statement. It may be pointed out that the perturbation caused by a collision would be of the right nature to cause a transition to the repulsive level.

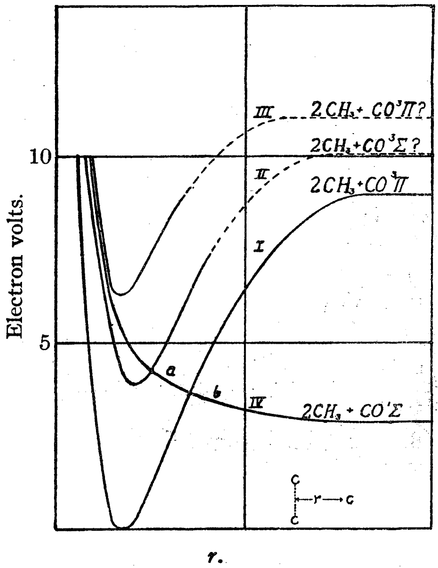

Fig. 2.

Since many of the photochemical facts seem to require the assumption of a state of long life formed spontaneously from the initially excited state, some speculation concerning this matter is in order.

At a first glance one might expect that once a molecule had transferred to the repulsive state IV its lifetime would be less than one period of vibration, about 10^{-13} sec. However, curve IV will not be continuous, but both I and IV will be broken at their intersection, the two upper parts and the two lower parts joining, respectively, to form two new continuous curves.[17] The probability of transition from the upper to the lower of these two new curves may be small enough to increase the mean life of the excited molecules by a large factor. Of course the proper selection rules must be obeyed for a perturbation of this type to occur. Whether or not the mean life would be long enough to account for the photochemical results is an open question, although so many different configurations may be assumed by the molecule that this is not impossible.

Once the molecule is on curve I there will be the

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[17] *Cf.* Eyring and Stearn, *J. Chem. Phys.*, **3**, 778 (1935).

possibility of dissociation into CH_3CO and CH_3. Damon and Daniels[4a] do note a decrease in quantum yield at high intensities. Most of the known facts for the 3000 Å. region may be explained by assuming a recombination reaction between CH_3CO and CH_3 which takes place largely on the walls but partially in the gas phase. Thus the yield may be made to approach zero at zero pressure even though the fluorescence is small. Dissociation would follow collision, supporting the increase in yield with pressure,[4a] and might be partially into 2 CH_3 and CO and partially into CH_3CO and CH_3. The chief arguments against this explanation are: (1) the supposed instability of the CH_3CO radical;[9] (2) the fact that the photochemical formation of diketones has not been observed.

Any CH_3CO radical produced by the dissociation of a molecule excited in the 1900 Å. region would possess so much energy that it should spontaneously dissociate. It seems very unlikely, therefore, that a recombination reaction can be responsible for the low yield in this part of the spectrum.

At least one other repulsive surface must exist, namely, that between normal carbon monoxide and normal ethane. However, ethane can be produced in one step only if the angle between the carbon–carbon bonds is varied and hence this surface cannot be represented on the diagrams. Moreover, there will be steric effects which will prevent transitions to this state from being very probable.

Certain relationships to the pictures for formaldehyde, acetaldehyde and methyl ethyl ketone may be stated. In formaldehyde there will be no steric effect to prevent transition to the repulsive surface formed by normal hydrogen and normal carbon monoxide and the observed quantum yield is unity.[18] A molecule with sufficient energy might dissociate in other ways. The methane–carbon monoxide surface must be important in acetaldehyde, since the steric effect would be considerably less than in acetone.[19] However, some decomposition in this case must be by way of the methyl–carbon monoxide–hydrogen atom surface since free radicals have been detected to some extent in this case. In methyl ethyl ketone several other repulsive surfaces must intervene and several products are observed upon illumination.

In conclusion the authors wish to express their appreciation to the Chemistry Department of the Johns Hopkins University for the loan of the rotating spark gap.

Summary

1. The quantum yield of acetone decomposition with approximately monochromatic radiation from the aluminum spark about 1900 Å. has been investigated. It is (a) independent of intensity over quite wide limits; (b) dependent upon acetone pressure, increasing at low pressures, the limiting value appearing to be about 0.65; (c) increases with the addition of nitrogen and carbon dioxide and to a lesser extent with the addition of ethane; (d) is apparently increased by the action of excited mercury unless precautions are taken to avoid this error.

2. No fluorescence could be detected.

3. Some difficulty is encountered in explaining the low quantum yield at low pressures, but otherwise the facts fit a simple kinetic picture.

4. The photochemical decomposition of acetone near 3000 Å., the decomposition near 1900 Å. and the various facts of spectroscopy and fluorescence may mostly be correlated with the use of potential energy surfaces.

PROVIDENCE, R. I. RECEIVED JUNE 1, 1936

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[18] Norrish and Kirkbride, *J. Chem. Soc.*, 1518 (1932).

[19] See Norrish, *Trans. Faraday Soc.*, **30**, 107 (1934).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, RHODE ISLAND STATE COLLEGE]

The Solubility of Thorium in Mercury[1]

BY W. GEORGE PARKS AND GEORGE E. PRIME

Very few alloys of thorium have been prepared. The only reference in the literature to a thorium amalgam is the work of Kettembeil,[2] who was unable to prepare an amalgam by the electrolysis of an aqueous solution of a thorium salt using a mercury cathode. Insoluble basic compounds were always formed during the electrolysis. This investigation was undertaken to see whether an amalgam could be prepared and, if so, what its possibilities are for use in galvanic cells to determine the thermodynamic properties of tetravalent thorium salts.

Experimental

Mercury.—Redistilled mercury was stirred under a dilute nitric acid–mercurous nitrate solution for three days. It was then redistilled three times in a slow current of air (15 mm.) by the Hulett[3] method, and finally under high vacuum.

Thorium.—Crystalline thorium prepared by the electrolysis of fused thorium chloride was kindly supplied by the Kemet Laboratories, Cleveland, Ohio. This metal analyzed 99.75% Th, by the oxalate method.[4] It contained small amounts of thorium oxide, silicon, iron and chromium due to the method of preparation. However, the amounts present are negligible for our purpose. It should be pointed out that very pure metallic thorium entirely free from thorium oxide has never been prepared; commercial samples rarely analyze better than 98.50%.[5] The samples for analysis were first fused with potassium bisulfate because when the metal is treated with acids, either singly or in combination, considerable oxide is formed which does not dissolve even in concentrated acids.[6]

Thorium Salts.—The best grade of C. P. thorium chloride, nitrate and sulfate were secured from Kahlbaum and were not further purified.

The preparation of a thorium amalgam was attempted by two methods. (1) Weighed quantities of thorium and mercury were heated together at 400° in small transparent fused quartz tubes for approximately eight hours. A higher temperature, although desirable, could not be employed due to shattering of the tubes. Furthermore, at elevated temperatures the thorium attacked the quartz badly. (2) An extensive series of experiments was carried out to determine the conditions under which an amalgam could be prepared electrolytically. These experiments included: electrolysis of thorium nitrate, sulfate and chloride in aqueous solution; $Th(NO_3)_4$ and $ThCl_4$ in 95% ethyl alcohol, and $ThCl_4$ in 12 N hydrochloric acid. Both the test-tube and H-type cell vessel were employed using a mercury cathode. The mercury was stirred slowly during all experiments. The concentration of salts, current density, length of time electrolyzed, temperature and acidity were varied over a wide range. The results may be summarized as follows: in all aqueous solutions insoluble basic salts were formed causing the current to decrease gradually with no detectable amalgam formation. In the alcoholic solutions, the purpose of which was an attempt to prevent the formation of the basic compounds, no amalgam could be formed. The basic compounds still precipitated. The only electrolysis which appeared to have some degree of success was carried out in a saturated solution of thorium tetrachloride in 12 N hydrochloric acid. A current of 0.5–1.0 amp. sq. cm. was passed through the solution for twenty-four hours. The H-cell was cooled continuously by running water.

The amalgams prepared by either method were placed in an oil-bath at 25 ± 0.01° and shaken for several days. The liquid mercury saturated with thorium was then separated for analysis by means of the special filter pipet previously described.[7] The analysis of mercury saturated with thorium offers very serious difficulties on account of the large quantity of mercury and relatively small quantity of thorium present. None of the ordinary methods of separation were found applicable. For example, no reagent could be found that would precipitate one without precipitating the other. It was found that hydrochloric acid would not react completely with the amalgam in the ordinary manner. The potassium permanganate oxidation method of Irvin and Russel[8] did not give satisfactory results. The distillation method also proved useless for quantitative work. The method finally adopted, although not entirely satisfactory, at least gives the order of magnitude of the solubility. For a more exact value an electrometric instead of a chemical method will have to be employed.

The samples to be analyzed were weighed carefully and then exposed to the atmosphere for at least two weeks in order that the thorium might separate from the mercury. This procedure has been found to be satisfactory for the separation of lanthanum and aluminum amalgams.[9] After standing the two weeks an excess of standard 0.5 N hydrochloric acid was added and after shaking well the excess acid was determined by titration with standard carbonate-free sodium hydroxide using phenol red as an indicator. The sodium hydroxide was standardized against Bureau of Standards potassium acid phthalate. The analytical weights and burets employed were calibrated and corrections applied where necessary.

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[1] Abstracted from a thesis submitted by George E. Prime to the faculty of Rhode Island State College in partial fulfilment of the requirements for the degree of Master of Science.

[2] Kettembeil, *Z. anorg. Chem.*, **38**, 217 (1903).

[3] Hulett, *Phys. Rev.*, **21**, 388 (1905); *ibid.*, **33**, 307 (1911).

[4] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York City, Vol. I, 1925, p. 524.

[5] Marsden and Rentschler, *Ind. Eng. Chem.*, **19**, 97 (1927).

[6] Driggs and Lilliendahl, *ibid.*, **22**, 1302 (1930).

[7] W. G. Parks and Campanella, *J. Phys. Chem.*, **40**, 333 (1936).

[8] Irvin and Russel, *J. Chem. Soc.*, 30, 891 (1932).

[9] Müller, *Monatsh.*, **53**, 215 (1929); Audrieth, Jukkola, Meints and Hopkins, THIS JOURNAL, **53**, 1805 (1931).

Results and Discussion

The solubility of thorium in mercury at 25° is summarized in Table I. The data given represent the average of three determinations on five different amalgams. The second and fourth amalgams were prepared by method (1) while the others were prepared by method (2). The atomic per cent. was calculated from the weight per cent. by the graphical method of Ölander.[10]

TABLE I

THE SOLUBILITY OF THORIUM IN MERCURY AT 25°

Weight, %	Atomic, %
0.0158	0.0140
.0157	.0139
.0156	.0138
.0145	.0128
.0154 ± 0.0005	.0136

There are many factors which must be considered in the determination of the solubility of a sparingly soluble metal in mercury. The solubility may or may not be a definite quantity. Some metals like copper and zinc or lead[11] are known to form aggregates not only with themselves but also with mercury. This means that until the particle size in the amalgam has been determined the term solubility must be a loose one. A method other than filtration must be found for determining a homogeneous phase. Furthermore, we are not absolutely certain that all the thorium separates from the mercury on standing two weeks in contact with the atmosphere. The reproducibility of our results, however, leads us to place confidence in them. The amount of mercury that dissolves when the hydrochloric acid is added was found to be negligible at the concentration employed.

These data may be interpreted in terms of internal pressures and the metallic solution theory of Hildebrand.[12] The mutual solubility of thorium and mercury should follow from their position in the table of internal pressures provided that there is no compound formation. The physical constants necessary for calculating the internal pressure of thorium are not accurately known. However, if we adopt the method of Gilfillan and Bent[13] thorium is placed next to tin in the table given by Hildebrand, Hogness and Taylor.[14] This position indicates a large difference in the internal pressure of thorium and mercury and is in fair accord with the solubility found in this investigation. Joyner[15] found the solubility of tin in mercury to be 1.24 atomic per cent. at 25.4°. The mutual solubility of thorium and tin has not been determined.

According to the relationship between the melting point of a metal and its solubility in mercury as developed by Tammann and Hinnüber[16] our results are too high. However, this relationship is only an approximation. Considering all factors which enter into a problem such as this, we feel that our results indicate a very low solubility with our value as a maximum. This low solubility together with the difficulty of preparation leads to the conclusion that this amalgam is unsatisfactory for precise e. m. f. measurements. Further work on the amalgamation of thorium is in progress.

KINGSTON, R. I.

RECEIVED JUNE 9, 1936

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[10] Ölander, *Ind. Eng. Chem., Anal. Ed.*, **4**, 438 (1932).

[11] Chuiko, *Ukrain. Khem. Zhur.*, **6**, No. 5-6, Sci. Part, 229 (1931).

[12] Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, 1936, p. 174 *et seq.*

[13] Gilfillan and Bent, THIS JOURNAL, **56**, 1661 (1934).

[14] Hildebrand, Hogness and Taylor, *ibid.*, **45**, 2830 (1923).

[15] Joyner, *J. Chem. Soc.*, **99**, 195 (1911).

[16] Tammann and Hinnüber, *Z. anorg. allgem. Chem.*, **160**, 249 (1927).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, HOLY CROSS COLLEGE]

Identification of Phenolic Ethers as Picrates

BY O. L. BARIL AND G. A. MEGRDICHIAN

The derivatives most frequently employed in the identification of phenolic ethers are those obtained by bromination, nitration and oxidation. The instructions for the preparation of these derivatives are variable, and the original article must be consulted for each individual ether. The products obtained vary from a mono- to a trinitro derivative, and from a mono- to a pentabromo derivative. In many cases, mixtures are obtained. The oxidation of ethers is limited to those containing a side-chain, and the length of the side-chain cannot be determined by this method.

The picrates of phenolic ethers have never been fully studied as a means of identification. In our study of the picrates of phenolic ethers, we arrived at a uniform method of procedure, whereby any phenolic ether can be identified from its picrate. These picrates can be precipitated conveniently, their forms are quite diverse and characteristic and were found to be constant after repeating the crystallization.

Experimental

All phenolic ethers used were Eastman pure, excepting the *p*-nitrophenyl benzyl ether which was prepared in our laboratory. Chemically pure

PICRATES OF CERTAIN PHENOLIC ETHERS

Ether	Color	Crystalline structure	M. p., °C.	Nitrogen, % Calcd.	Found
Anethole[a,b]	Orange-red	Long needles	69–70	11.14	11.60
Anisole[a]	Bright yellow	Tabular crystals	79–81	12.46	12.62
Benzyl	Orange-yellow	Prism clusters	77–78	9.83	9.91
Benzyl methyl	Cream	Square plates	115–116	11.96	11.99
n-Butyl phenyl[a]	Light yellow	Hexagonal plates	110–112	11.08	11.79
Catechol diethyl[a]	Red-brown	Rhombic crystals	69–71	10.63	10.76
o-Tolyl methyl	Light yellow	Short prisms	118–119.5	11.96	11.82
m-Tolyl methyl	Orange-yellow	Medium prisms	113–114	11.96	11.44
p-Tolyl methyl	Yellow-orange	Long prisms	88–89	11.96	12.32
o-Tolyl ethyl	Light yellow	Short prisms	117.5–118.5	11.57	11.23
m-Tolyl ethyl	Orange-yellow	Medium prisms	114–115	11.57	11.44
p-Tolyl ethyl	Yellow-orange	Long prisms	110–111	11.57	11.90
Eugenol	Brown-red	Long blades	62–63	10.68	10.45
Eugenol methyl	Red-brown	Rhombic crystals	114–115	10.32	10.97
Iso-eugenol[a]	Dark red	Silky needle clusters	46–47.5	10.68	10.71
Iso-eugenol methyl[c]	Very dark red	Slender rods	42–45	10.32	10.82
Guaiacol[a,d]	Orange-red	Short stout needles	88–89	11.89	11.42
Hydroquinone monomethyl	Orange-yellow	Long flat needles	43–44	11.89	11.96
Hydroquinone dimethyl[a]	Orange-red	Long blades	47–48	11.44	11.50
α-Naphthyl methyl	Yellow-orange	Silky needle clusters	127–127.5	10.85	10.25
β-Naphthyl methyl	Yellow	Fine needle clusters	113–113.5	10.85	10.48
α-Naphthyl ethyl	Yellow-orange	Fine needle clusters	107–108	10.47	10.63
β-Naphthyl ethyl	Orange-yellow	Fine needle clusters	99–100.5	10.47	10.58
p-Nitrophenyl benzyl	Very light yellow	Thin rectangular plates	84–84.5	12.23	12.16
Phenetole[a]	Very light yellow	Square plates	91–92	11.96	12.01
Phenyl	Yellow	Prisms	108–110	10.52	10.70
Pyrogallol trimethyl	Yellow	Thin rhombic plates	78.5–80	10.57	10.34
Resorcinol monomethyl[a]	Orange	Long blades	68–69.5	11.89	12.28
Resorcinol dimethyl[a]	Yellow-orange	Tetragonal needles	56–58	11.44	11.86
Resorcinol monoethyl	Red	Rhombic needles	105–106	11.44	10.98
Resorcinol diethyl	Brown-yellow	Long slender rods	108–109	10.63	10.94
Safrole	Orange-red	Long blades	104–105.5	10.74	10.62
Iso-safrole	Dark red	Thick needle clusters	74–75	10.74	10.89
Triphenylcarbinol methyl	Light yellow	Cubes	90–91	8.35	8.70
Veratrole[e]	Red-orange	Six-sided prisms	56–57.5	11.44	11.13

[a] Unstable on exposure to air. [b] Beilstein, Vol. VI, 4th ed., 1923, p. 568. [c] *Ibid.*, p. 956. [d] *Ibid.*, p. 770. [e] *Ibid.*, p. 771.

picric acid was dried in an oven at 100° for six hours. One millimole of the phenolic ether was dissolved in 10 cc. of warm chloroform. One millimole of picric acid plus 5% in excess (0.241 g.) was dissolved in 10 cc. of warm chloroform. The chloroform solution of the phenolic ether was then poured into the picric acid solution while stirring the mixture. This mixture was then set aside and allowed to crystallize in a 100-cc. beaker. The picrate was recrystallized from the smallest amount of warm chloroform. The form or habit of the crystals was then determined by means of a binocular microscope using a magnification of about seven.

The picrates of the four phenolic ethers found in the literature were reported by the investigators as being equimolecular addition products. Melting points were determined by the method of Mulliken[1] in which a thermometer calibrated by the Bureau of Standards was employed. All temperatures given are uncorrected. In the determination of nitrogen, Campbell and Gray's[2] modification of the Dumas method was used.

Discussion of Results

The molecular composition of all the picrates was found to be of the general type 1:1. All the stable picrates of the phenolic ethers can be prepared and recrystallized from 95% ethyl alcohol. The melting points of the picrates thus prepared correspond exactly to the melting points of the picrates prepared from chloroform. The instability of the unstable picrates is manifested by a loss of color upon exposure to air, a rise in melting point, and the amorphous form of the residual picric acid. The melting points of all the unstable picrates must be taken as soon after crystallization as possible, unless kept in a sealed container.

Anethole picrate is decomposed by ethyl alcohol, and the anethole polymerizes to di-anethole in the hot alcohol. The picrates of eugenol, iso-eugenol, eugenol methyl ether and iso-eugenol methyl ether form astatic liquid crystals from ethyl alcohol. The use of methyl alcohol as a solvent prevents this, but several days are required for crystallization. The picrates of anisole, phenetole and *n*-butyl phenyl ether are all decomposed by ethyl alcohol. Methyl alcohol prevents this to a certain extent. The picrates of the isomeric ethers are all darker, and possess lower melting points than the picrates of the normal ethers. The picrates of the α-naphthyl ethers are darker and possess higher melting points than the picrates of the β-naphthyl ethers.

The preparation and recrystallization of all the unstable picrates of phenolic ethers is possible through the use of chloroform as a solvent, thereby affording a general and uniform method of procedure in the preparation of all the picrates of the phenolic ethers. As optical crystallographic data are very important in the final identification of an organic compound, it is hoped to be able to report on the refractive indices of these picrates in a future communication.

Summary

1. The picrates of thirty-five phenolic ethers have been prepared and were found to be suitable derivatives for identification purposes.

2. The procedure is uniform and requires no special degree of skill.

3. The picrates are highly crystalline solids, easily purified and possessing sharp melting points.

WORCESTER, MASS. RECEIVED MAY 15, 1936

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[1] Mulliken, "Identification of Pure Organic Compounds," Vol. I, John Wiley & Sons, Inc., New York City, 1904, p. 218.

[2] Campbell and Gray, *J. Soc. Chem. Ind.*, **49**, 447 (1930).

[CONTRIBUTION NO. 31 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Reduction of Nitroguanidine. VI. Promoter Action of Platinic Chloride on Raney Nickel Catalyst

BY EUGENE LIEBER AND G. B. L. SMITH

Introduction

While investigating the effect of small amounts of impurities on the activity of the Raney nickel catalyst for the hydrogenation of nitroguanidine,[1] the further results of which will be reported in another paper, it was found that platinic chloride had a very marked enhancing action.

Nickel catalysts have been rather extensively studied with respect to the promoter action obtained when foreign substances are introduced into the catalyst mass and are summarized by Ellis.[2] Combinations of the platinum and nickel group catalysts have received attention as well as platinum and palladium deposited on other metals.[3] Of these Ginsberg and Ivanov[3e] have prepared active catalysts by adding *in situ* solutions of platinum or palladium chloride (the latter as Na_2PdCl_4) to powdered non-catalytically active metals. More recently, Delépine and Horeau[4] have described the enhancement of the activity of Raney nickel catalyst by platinum deposited from a solution of "alkaline platino-chloride" on the Raney nickel. The enhanced activity was manifested (for the reduction of ethyl acetoacetate) only after the addition of alkali.

In the hydrogenation of nitroguanidine it was observed that the addition of small quantities of platinic chloride very greatly increased the rate of reduction. It was in general found that this effect could be extended with even more marked results to other organic types. Table I summarizes these results, the details of which are given in the experimental section.

TABLE I

ADDITION OF PLATINIC CHLORIDE TO RANEY NICKEL

Hydrogen acceptor	Absorption rate, ml. H_2/min. Raney Ni	Raney Ni + $PtCl_4$
Nitroguanidine	28.4	51.4
Castor oil	35.8	125.8
Linseed oil	24.4	67.0
Nitrobenzene	18.4	165.6
Benzaldehyde	10.2	67.6

Experimental

Method.—The catalytic hydrogenations were carried out at one atmosphere pressure and at room temperature; the general procedure was the same as used previously.[1] The test mixtures were as follows: 5.2 g. (0.05 mole) of nitroguanidine, suspended in water as a solvent, 2.5 g. (or multiple of that quantity) of Raney nickel catalyst or non-catalytic metal powder. Just prior to the beginning of the hydrogenations, varying volumes of an aqueous solution of platinic chloride were added. The hydrogen adsorption rates were followed for a period of thirty minutes.

Concentration of Platinic Chloride.—Keeping the ratio of catalyst to hydrogen acceptor constant, the concentration of platinic chloride was varied from 0.034 to 0.680 g. (0.1 to 2.0 millimoles) per 100 ml. of solvent. The results are summarized graphically in Fig. 1.

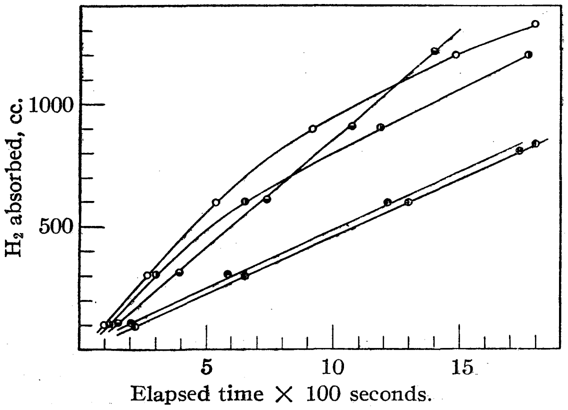

Fig. 1.—Variation in $PtCl_4$ concentration: ◓ Raney; ○ Raney + 2 millimoles $PtCl_4$; ◑ Raney + 1 millimole $PtCl_4$; ◒ Raney + 0.25 millimole $PtCl_4$; ◐ Raney + 0.13 millimole $PtCl_4$.

Variation in Catalyst Mass.—In this series of experiments the concentration of platinic chloride was maintained at 0.075 g. (0.25 millimole) per 100 ml. of solvent and the ratio of catalyst to nitroguanidine was varied from 0.25 to 1.0. It was found here that the greatest effect was with the smallest ratio of catalyst to nitroguanidine. The effect of adding 0.25 millimole of platinic chloride (48 mg. of platinum) to 0.50 g. of Raney nickel catalyst per gram of nitroguanidine gives a rate of hydrogenation equal to that obtained when the ratio of catalyst to nitroguanidine is 1.12.

The Reaction between Raney Nickel Catalyst and Platinic Chloride.—Certain facts concerning the promoter action of platinic chloride on Raney nickel catalyst are

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[1] Lieber and Smith, THIS JOURNAL, **57**, 2479 (1935).

[2] Ellis, "Hydrogenation of Organic Substances," 3d ed., D. Van Nostrand Co., New York, 1930.

[3] (a) Dewar and Liebmann, U. S. Patent 1,268,692 (1918); (b) Ueno, *J. Chem. Ind.* (*Tokyo*), **21**, 898 (1918); (c) Paal and Wendisch, *Ber.*, **56**, 4011 (1913); (d) Paal and Karl, *ibid.*, **56**, 3069 (1913); (e) Ginsberg and Ivanov, *J. Russ. Phys.-Chem. Soc.*, **62**, 1991 (1930).

[4] Delépine and Horeau, *Compt. rend.*, **201**, 1301 (1935); see *C. A.*, **30**, 1776 (1936). This paper came to the attention of the authors after this article was prepared for publication but before submission to the Editor.

revealed in the following experiments. Absorption of hydrogen in ml. of hydrogen in thirty minutes by 5.2 g. of nitroguanidine in 100 ml. of water and the catalyst (a) 1 millimole (0.337 g.) of platinic chloride alone, (b) an amount of Adams platinum oxide catalyst equal to 0.337 g. of platinic chloride, (c) a mixture of 2.5 g. of Raney nickel and platinum oxide equal to 0.337 g. of platinic chloride, (d) 2.5 g. of Raney nickel catalyst and (e) 2.5 g. of Raney nickel and 0.337 g. of platinic chloride, are (a) 0, (b) 537, (c) 796, (d) 851 and (e) 1222. These data indicate that platinic chloride is without activity and that the addition of Adams catalyst in an amount equal to the platinic chloride does not increase the activity of Raney nickel.

Thirty-four hundredths gram of platinic chloride was added to a suspension of 2.5 g. of Raney nickel catalyst in 100 ml. of water and the mixture was allowed to stand with occasional shaking for forty-five minutes. The mixture became opalescent during the first few minutes of contact but on standing the colloidal material settled and a clear green supernatant solution resulted. The clear solution was decanted, the remaining "catalyst" mass was washed several times by decantation, and the combined solutions were diluted to a volume of 200 ml. The nickel was determined in aliquot portions by weighing as nickel dimethylglyoxime: found 0.23, 0.25 g.; calcd. on the basis of equation

$$3Ni + PtCl_6^{=} + 2H^+ \longrightarrow Pt + 3Ni^{++} + H_2 + 6Cl^- \quad (I)$$

0.20 g. The solution was strongly acid and contained *no platinum.* The catalyst mass treated as described above had an activity *no greater* than the ordinary Raney nickel catalyst without platinum.

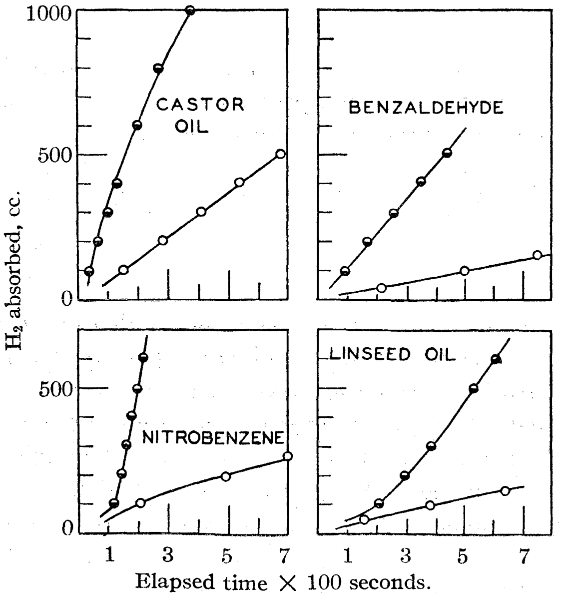

Fig. 2.—Promoted hydrogenations: ○ Raney nickel; ◒ promoted Raney nickel.

In order to determine the possible effect of the several components present the following experiments were performed. In each case 5.2 g. of nitroguanidine was suspended in 100 ml. of water.

	Catalyst	Adsorption ml. H_2/min.
1	2.5 g. Raney nickel	28.4
2	2.5 g. Raney nickel and 0.34 g. $PtCl_4$ added just before start of reduction	51.4
3	0.34 g. of $PtCl_4$ deposited as Pt on 2.5 g. Raney nickel and catalyst mass washed free of ions	29.0
4	As (3) with addition of 3 millimoles of nickel as Ni^{++}	22.7
5	As (3) with addition of 2 millimoles of HCl	26.6
6	2.5 g. of Raney nickel with 2 millimoles of HCl	5.4
7	2.5 g. of Raney nickel with 1 millimole of Ni^{++}	9.1

The addition of alkali (potassium hydroxide) sufficient to neutralize the acidity, produced in catalyst (2) above, decreased its activity 50–60%.

The nickel catalyst, which consists of nickel dispersed on kieselguhr, was prepared according to the method of Adkins and Cramer[5] and was tested for its catalytic activity with and without the addition of platinic chloride. There was no promotor action due to platinic chloride.

Platinic Chloride and Non-Catalytic Metal Powders.—The non-catalytic metal powders tested comprised Raney alloy (50% nickel), iron, aluminum and tungsten, using 0.337 g. (1 millimole) of platinic chloride the absorption rates obtained in ml. of H_2 per minute were 15.4, 8.0, 13.9 and 0.0, respectively. Using 0.075 g. (0.25 millimole) of platinic chloride with non-catalytic Raney alloy and catalytic Raney nickel the hydrogen absorption rates were 3.0 and 51.4 ml. of H_2 per minute, respectively.

Platinic Chloride Promotor Action on the Hydrogenation of Castor Oil, Nitrobenzene, Benzaldehyde and Linseed Oil.—In this series of experiments the solvent was 100 ml. of 95% ethanol; 0.25 g. of Raney nickel per gram of hydrogen acceptor (except for raw linseed oil where 0.1 g. of Raney nickel per gram of material was used) and 0.075 g. (0.25 millimole) of platinic chloride added just prior to the start of the reduction. The quantities of substances hydrogenated were 25 g. of castor oil, 25 g. of linseed oil, 12.5 g. of nitrobenzene and 10.5 g. of benzaldehyde. The reductions were carried out first with Raney nickel alone and then Raney nickel with platinic chloride. The data are summarized in Fig. 2 and Table I.

Discussion of Results

The action of platinic chloride on Raney nickel catalyst is open to several interpretations. It may be defined as a promoter action based upon the definition of Pease and Taylor[6] as the "activation of a catalyst by a small quantity of a relatively active substance." The examination of the reaction between platinic chloride and Raney nickel shows that we are dealing with reaction (I) and it is possible that the observed rates of hydrogenation are the result of the simultaneous activity of nickel and platinum. However, this re-

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[5] Adkins and Cramer, THIS JOURNAL, **52**, 4349 (1930).

[6] Pease and Taylor, *J. Phys. Chem.*, **24**, 241 (1920).

action apparently must take place during the reduction with hydrogen, *i. e.*, the promotor effect is manifested when platinic chloride is added just before the hydrogenation is started. The interpretation of the results is further complicated by the fact that in adding platinic chloride, poisons for the nickel catalyst are added, although it should be pointed out that using non-catalytically active metals, or completely plating out the platinum and removing the poisons resulted in completely reduced activity. Further, the type of catalytically active nickel appears to be a factor. On a weight basis, reduced nickel on kieselguhr is hundreds of times as active as is Raney nickel,[7] however, addition of platinic chloride to such a catalyst under the same conditions as Raney catalyst (temperature, pressure of hydrogen and ratio of catalyst to hydrogen acceptor) had no effect on its activity.

On the other hand, however, the effect is not limited to the hydrogenation of a single substance (nitroguanidine), as is often the case in promoter catalysis. It has, indeed, been applied even more successfully to the hydrogenation of castor oil, linseed oil, nitrobenzene and benzaldehyde.

The application of the Raney nickel–platinic chloride catalyst to the hydrogenation of various types of organic compounds, as well as a more detailed investigation of the effects involved particularly with respect to other noble metal salts, is in progress in this Laboratory and will be reported in a subsequent paper.

Summary

Small amounts of platinic chloride added to Raney nickel catalyst immediately before the beginning of the hydrogenation have a definite and pronounced enhancing action which is not limited to the hydrogenation of nitroguanidine but is apparently applicable to the reduction of many types of organic compounds.

BROOKLYN, NEW YORK RECEIVED MARCH 26, 1936

(7) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

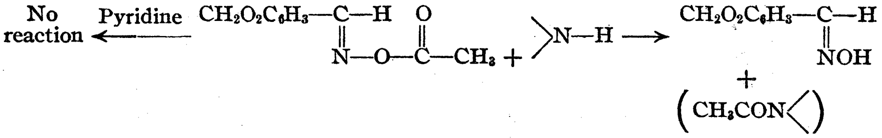
The Reactions of Aldoxime Derivatives with Bases. III. The Reactions of Geometrically Isomeric Acetyl-3,4-methylenedioxybenzaldoximes with Certain Amines

BY CHARLES R. HAUSER AND EARL JORDAN[1]

In continuation of our investigations[2] of the reactions of acyl-aldoximes with bases, a study has been made of the reactions of the two isomers of acetyl-3,4-methylenedioxybenzaldoxime with certain primary, secondary and tertiary amines.

It has been found that when the α-isomer is dissolved in *n*-butylamine, aniline, piperidine or diethylamine, and allowed to stand for a short time, it is converted into the corresponding α-aldoxime in yields of 90–99%; apparently these reactions are quantitative. On the other hand, the acetyl-α-aldoxime may be heated in pyridine solution at 97–100° for an hour and then recovered practically unchanged; also, it is relatively stable in triethylamine solution. The yields of aldoxime and recovered acetyl-α-aldoxime are given in Table I.

The reaction of acetyl-α-3,4-methylenedioxybenzaldoxime with a primary or secondary amine may be represented as an aminolysis,[3] thus[4]



$$\text{No reaction} \xleftarrow{\text{Pyridine}} \begin{array}{l} CH_2O_2C_6H_3—\underset{\|}{C}—H \quad \overset{O}{\underset{}{\|}} \\ \qquad\qquad\quad N—O—C—CH_3 \end{array} + \;>N—H \longrightarrow \begin{array}{c} CH_2O_2C_6H_3—C—H \\ \| \\ NOH \\ + \\ \left(CH_3CON\!<\right) \end{array}$$

The tertiary amines have no hydrogen atom attached to nitrogen and consequently are not capable of bringing about this reaction. The other possible decomposition, the elimination of acetic acid from the acetyl-α-aldoxime to form nitrile,[5] might occur very slowly in triethylamine solution at the boiling point of the

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(1) This is from a portion of a thesis presented by Earl Jordan in partial fulfilment of the requirements for the Ph.D. degree at Duke University.

(2) See (a) Hauser and Sullivan, THIS JOURNAL, **55**, 4611 (1933); (b) Hauser and Jordan, *ibid.*, **57**, 2450 (1935); (c) Hauser, Jordan and O'Conner, *ibid.*, **57**, 2456 (1935).

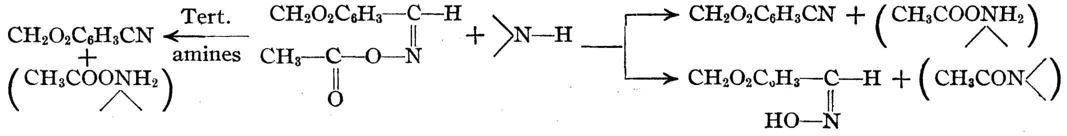
(3) This reaction is analogous to an ammonolysis of an ester; it is possible that the primary or secondary amine attacks the carbonyl group of the acetate, perhaps forming an intermediate addition compound which decomposes to form aldoxime and amide; the latter, however, has not been isolated.

(4) For references to evidence that α-aldoximes have the *syn* configuration, see note 2b.

(5) Although the acetyl-β-aldoxime in the presence of a base eliminates acetic acid to form nitrile much more readily than the α-isomer, it is possible for the latter, under certain conditions, to form nitrile or the corresponding acid; see reference 2b.

amine,[6] but this reaction does not occur in pyridine solution, at least not to an appreciable extent within an hour even at 97–100°.

The reactions of acetyl-β-3,4-methylenedioxybenzaldoxime with amines have been carried out under several different sets of conditions. In general, with primary or secondary amines this isomer gives partly nitrile by elimination of acetic acid, and partly the corresponding β-aldoxime presumably by aminolysis;[3] but with tertiary amines it gives only nitrile. These reactions may be represented as follows



The yields of nitrile and aldoxime obtained from the acetyl-β-aldoxime with a primary or secondary amine depend upon the relative rates of the two competing reactions. Similar to the reactions with alkali,[2b] an elevation of temperature accelerates the elimination of acetic acid to form nitrile more than the aminolysis to form oxime; also, these reactions are apparently dependent upon the basic strength of the amine used. In Table II are given the yields of products obtained by adding the acetyl-β-aldoxime in small portions to *n*-butylamine and to the much weaker base, aniline, at various temperatures. It can be seen that with *n*-butylamine the acetyl-β-aldoxime gives, below 0°, practically only oxime, between 20 and 45°, both oxime and nitrile; but at 78°, apparently only nitrile, no oxime being isolated at this temperature. With aniline at 25–30°, the acetyl-β-aldoxime gives apparently only oxime, and even at 97–100° this is the main product, the yield of nitrile being only 11%.

The difference in degree of reactivity of acetyl-α-, and acetyl-β-3,4-methylenedioxybenzaldoximes with various amines should be pointed out. Whereas the α-isomer merely dissolves in the amines listed in Table I without generating a noticeable amount of heat, the acetyl-β-aldoxime reacts vigorously with *n*-butylamine, piperidine, and diethylamine. When a few cubic centimeters of these amines are added, in 1-cc. portions, to gram samples of the acetyl-β-aldoxime, the reaction mixtures become hot immediately, producing high yields of nitrile and no appreciable amounts of oxime; however, when the relatively weak base, aniline, is added to the acetyl-β-aldoxime in a similar manner, the latter dissolves without a noticeable rise of temperature, giving a high yield of oxime and no appreciable amount of nitrile. The yields of products obtained with these primary and secondary amines under these conditions are given in Table III. In this table are included also the yields of nitrile obtained with the tertiary amines, pyridine and triethylamine; with the latter the reaction mixture becomes warm. The formation of nitrile from the acetyl-β-aldoxime and these tertiary amines is presumably quantitative over a considerable range of temperatures.

The yields of products obtained from the reactions of the acetyl-β-aldoxime with 1 *M* solutions of certain amines in water and in dioxane and with ammonia solutions, at 0 or 30°, are given in Table IV. It can be seen that with *n*-butylamine or piperidine both nitrile and oxime are obtained; in the reaction with aqueous piperidine the yield of nitrile is greater, and that of oxime correspondingly smaller at 30°, than at 0°.

It should be noted that with pyridine even in the presence of water the acetyl-β-aldoxime apparently gives only nitrile, whereas with triethylamine and water a small yield of oxime is obtained in addition to nitrile. In the latter case the formation of oxime presumably is due to the presence of hydroxyl ions since no oxime is found when the reaction is carried out in anhydrous dioxane solution; the concentration of hydroxyl ions in aqueous pyridine is apparently too small to produce an appreciable amount of hydrolysis before the acetyl-β-aldoxime is completely converted to nitrile.

Hantzsch[7] has previously reported that acetyl-β-aldoximes were decomposed by ammonium hydroxide to form β-aldoximes. We have found that with aqueous or alcoholic ammonia both nitrile and oxime are obtained except when the reaction is carried out at 0°; at this temperature with concentrated ammonia only oxime has been isolated.

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[6] It can be seen from Table I that the melting point of the recovered product is somewhat lower than that of the pure acetyl-α-aldoxime.

[7] Hantzsch, *Ber.*, **24**, 20 (1891).

TABLE I

PERCENTAGE YIELDS OF PRODUCTS FROM ACETYL-α-3,4-METHYLENEDIOXYBENZALDOXIME AND CERTAIN PRIMARY, SECONDARY AND TERTIARY AMINES

Amine		Oxime % yield	Oxime M. p., °C.[a]	Recovered acetyl deriv. % yield	Recovered acetyl deriv. M. p., °C.[a]
Primary					
n-Butylamine		91	108–110		
Aniline		98	108–110		
Secondary					
Piperidine		90	110		
Diethylamine		99	110		
Tertiary					
Pyridine	At 25°			92	105
	At 97–100°[b]			96	104–105
Triethylamine	At 25°			96	104–105
	At 89°[b]			99	95–97

[a] The melting points of these products were raised by recrystallization to those reported in the literature: for the α-aldoxime, 110°; for the acetyl-α-aldoxime, 105°. [b] This solution was heated for one hour.

TABLE II

PERCENTAGE YIELDS OF PRODUCTS FROM ACETYL-β-3,4-METHYLENEDIOXYBENZALDOXIME WITH *n*-BUTYLAMINE AND WITH ANILINE AT VARIOUS TEMPERATURES

Amine	Temp., °C.	Nitrile % yield	Nitrile M. p., °C.[a]	Oxime % yield	Oxime M. p., °C.[a]
n-Butylamine	−10– −5	5	92–93	90	144
	20–30	15	92–93	81	140–141
	25–45[b]	29	93–94	59	142–143
	78 (b. p.)	94	93–94		
Aniline	25–30			92	145–146
	97–100	11[c]	93–94	82	109–110[d]

[a] The melting points of these products were raised by recrystallization to those reported in the literature: for nitrile, 94–95°; for β-aldoxime, 146°. [b] In this case 5 cc. of *n*-butylamine was added all at one time to 1 g. of the acetyl-β-aldoxime; the heat of the reaction caused the temperature of the solution to rise from 25 to 45°. [c] In this case the nitrile might have been produced by a thermal decomposition of the acetyl-β-aldoxime. [d] In this case the β-aldoxime had changed to the α-isomer (m. p. 110°).

TABLE III

PERCENTAGE YIELDS OF PRODUCTS OBTAINED BY ADDING A FEW CUBIC CENTIMETERS OF VARIOUS AMINES IN ONE-CUBIC CENTIMETER PORTIONS TO GRAM SAMPLES OF ACETYL-β-3,4-METHYLENEDIOXYBENZALDOXIME

Amine	Nitrile % yield	Nitrile M. p., °C.[a]	Oxime % yield	Oxime M. p., °C.[a]
Primary				
n-Butylamine[b]	99	91–93		
Aniline			92	145–146
Secondary				
Piperidine[b]	99	92–94		
Diethylamine[b]	92	93–94		
Tertiary				
Pyridine	99	92–94		
Triethylamine	95	94–95		

[a] The melting points of these products were raised by recrystallization to those reported in the literature: for nitrile 94–95°; for β-aldoxime 146°. [b] The reactions with these amines were vigorous, generating considerable heat.

TABLE IV

PERCENTAGE YIELDS OF PRODUCTS FROM ACETYL-β-3,4-METHYLENEDIOXYBENZALDOXIME WITH 1 *M* SOLUTIONS OF CERTAIN AMINES IN WATER, DIOXANE AND AMMONIA

Amine	Solvent	Temp., °C.	Nitrile % yield	Nitrile M. p., °C.[a]	Oxime % yield	Oxime M. p., °C.[a]
n-Butylamine	Water	30	46	90–92	48	105–107[b]
n-Butylamine	Dioxane	30	42	93–95	56	143–144
Piperidine	Water	0	32	89–91	65	138–140
Piperidine	Water	30	63	92–94	28	110[b]
Piperidine	Dioxane	30	73	93–95	17	143–144
Pyridine	Water	30	99	94–95		
Triethylamine	Water	30	72	92–94	16	120–123
Triethylamine	Dioxane	30	97	93–95		
Ammonia	Water	30	36	93–95	55	144–145
Ammonia	Alcohol (95%)	30	39	93–95	60	143–144
Ammonia (14 *M*)	Water	0			95	146
Ammonia (14 *M*)	Water	30	28	92–93	65	123–125

[a] The melting points of these products were raised by recrystallization to those reported in the literature: for nitrile, 94–95°; for β-aldoxime, 146°. [b] On standing this oxime had changed to the α-isomer (m. p. 110°).

Experimental

Acetyl-α- and acetyl-β-3,4-methylenedioxybenzaldoximes were prepared according to methods previously described.[2a,b] Samples (1–2 g.) of these compounds were dissolved in 4–6 cc. of amine, the relative yields of oxime and nitrile produced from the β-isomer with certain primary and secondary amines being dependent upon the method of treatment. The solutions of *n*-butylamine, piperidine, diethylamine, pyridine and triethylamine, after standing at least an hour, were shaken with several volumes of crushed ice, and the mixtures filtered through sintered glass crucibles of the Gooch type.[2b] The precipitates were washed with water until free of amines, and then treated with cold 2 *N* sodium hydroxide to dissolve out oxime. The solid remaining in the crucible was identified as nitrile or in certain cases as unchanged acetyl-α-aldoxime. The oxime was precipitated from the alkaline solution with carbon dioxide in the usual manner. In certain cases additional oxime was obtained from the amine filtrates by treatment with carbon dioxide.

The reaction solution obtained from aniline was dissolved in ether and extracted several times with small portions of cold 2 *N* sodium hydroxide. Oxime was precipitated from the alkaline solution by means of carbon dioxide. After drying with "Drierite," the ether solution was saturated with dry hydrogen chloride, the aniline salt filtered off, and the ether evaporated. A small amount of nitrile was obtained in this manner when the reaction had been carried out at 97–100°.

Blanks were run with β-3,4-methylenedioxybenzaldoxime in solutions of *n*-butylamine and pyridine; the oxime was recovered unchanged from these solutions.

The products from the reactions of acetyl-β-aldoxime (1–2 g. samples) with 50 cc. of 1 M solutions of amine in water and in dry dioxane were isolated as follows: after standing several days at 0 or 30°, the solids were filtered off from the aqueous mixtures, and the oxime separated from nitrile by means of alkali; in certain cases additional oxime was obtained from the aqueous amine filtrate. The dioxane solutions were evaporated to dryness in an air-draft, and the residue treated with alkali. In the reactions with aqueous and alcoholic ammonia, oxime and nitrile were isolated in a similar manner.

It has been found also that certain other acetyl-β-aldoximes with aniline give only the corresponding oxime; the yields of this product from acetyl-β-benzaldoxime and acetyl-β-3-nitrobenzaldoxime were 85 and 99%, respectively.

Summary

1. A study has been made of the reactions of acetyl-α- and acetyl-β-3,4-methylenedioxybenzaldoximes with certain primary, secondary and tertiary amines.

2. It has been found that when the acetyl-α-aldoxime is dissolved in the primary or secondary amines it is converted to the corresponding aldoxime; this reaction appears to be quantitative. The acetyl-α-aldoxime, however, is stable in the presence of the tertiary amines under ordinary conditions.

3. The acetyl-β-aldoxime reacts with the tertiary amines to form only nitrile, but, in general, with primary and secondary amines to form both nitrile and β-aldoxime, the yields of these products depending upon the temperature of reaction and apparently upon the basic strength of the amine used.

Durham, N. C. Received June 10, 1936

[Communication No. 591 from the Kodak Research Laboratories]

The Alkaline Decomposition of Cellulose Nitrate. I. Quantitative Studies[1]

By W. O. Kenyon and H. LeB. Gray

Previous workers have shown that the action of alkalies, especially potassium or sodium hydroxides, on aliphatic nitrates is not one of simple saponification regenerating the alcohol and forming sodium nitrate, but is a profound decomposition yielding also sodium nitrite and oxidation products of the aliphatic group. Thus, alkyl nitrates[2–5] give rise to ethers, alcohols, inorganic nitrates and nitrites, aldehydes and resinous bodies when treated with alkalies. Ethylene dinitrate[3,4,6] is stated to yield carbon dioxide, oxalic acid and glycol. The products of the alkaline decomposition of glycerol trinitrate[3,7–13] are stated to include: ammonia, carbon dioxide, formic acid, acetic acid, oxalic acid, mesoxalic acid, alkali cyanides, alkali nitrates, alkali nitrites and intermediate peroxides. The presence of glycerol is affirmed[13] and denied.[7] From nitrated mannose,[3] the formation of nitrates, nitrites, oxalic acid and unidentified organic acids is reported. Glucose,[14–16] levulose and starch trinitrates are said to yield products from which the osazones of oxypyruvic acid or its homologs may be isolated. Partially denitrated carbohydrates were also found.

The products reported by various authors as formed by the alkaline decomposition of cellulose nitrate are naturally greater in number and more complex. These include inorganic nitrates and nitrites,[17,18] ammonia,[18] cyanide,[19] carbon dioxide,[20] oxalic,[17,21,3] malic,[21] glycolic,[21] trioxy-

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[1] The material contained in this paper comprises a portion of a thesis presented by William O. Kenyon to the University of Rochester in partial fulfilment of the degree of Doctor of Philosophy, 1935.

(2) Berthelot, *Ann. chim. phys.*, **53**, 447 (1860).

(3) Mixter, *Am. Chem. J.*, **13**, 507 (1891).

(4) Millon, *Ann. chim. phys.*, [3] **8**, 233 (1845).

(5) Nef, *Ann.*, **309**, 126 (1899).

(6) Henry, *Ann. chim. phys.*, [4] **27**, 243 (1872).

(7) Hay, *Moni. Sci.*, [3] **27**, 424 (1885).

(8) Hay, *Trans. Roy. Soc. Edinburgh*, **32**, 67 (1885).

(9) Berthelot, *Compt. rend.*, **131**, 519 (1900).

(10) Berthelot, *Chem. Ind.*, **19**, 1038 (1900).

(11) Klason and Carlson, *Ber.*, **39**, 2752 (1906).

(12) Berl and Delpy, *ibid.*, **43**, 1421 (1910).

(13) Railton, *J. Chem. Soc.*, **7**, 222 (1855).

(14) Berl and Smith, *Ber.*, **41**, 1837 (1908).

(15) Berl and Smith, *J. Soc. Chem. Ind.*, **27**, 534 (1908).

(16) Berl and Smith, *Moni. Sci.*, [4] **23**, 51 (1909).

(17) Hadow, *J. Chem. Soc.*, **7**, 201 (1855).

(18) Béchamp, *Compt. rend.*, **41**, 817 (1855).

(19) Will, *Ber.*, **24**, 400 (1891).

(20) Vohl, *Dinglers polytech. J.*, **112**, 236 (1849).

(21) Berl and Fodor, *Z. ges. Schiess- Sprengstoffw.*, **5**, 296 (1910).

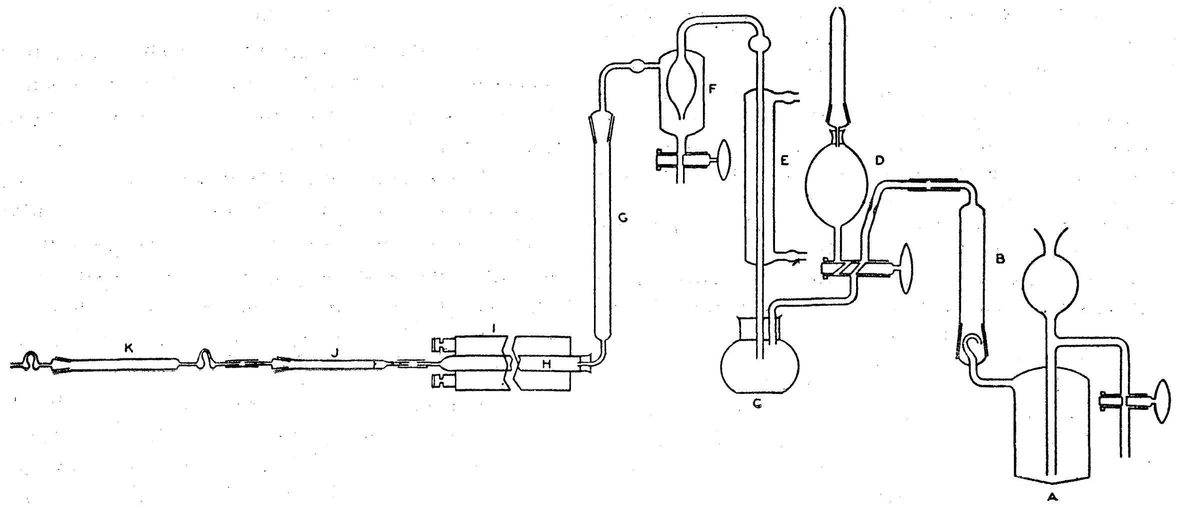

Fig. 1.

glutaric,[21] dioxybutyric,[21] malonic,[21] and tartronic acids,[21] sugars,[18,22] modified celluloses[18] and their nitrates,[23] and partially denitrated cellulose nitrates.[24,22,25] Unidentified complex acids are described.[17,26]

From the products of alkaline decomposition an osazone has been isolated which corresponds to the osazone of oxypyruvic acid.[14,15,16,19,21] Since this osazone may arise from several organic acids, attempts have been made to identify the acid present. One author[27] presents evidence for the presence of oxypyruvic acid (so-called keto form) while others believe the acid to be the semialdehyde of tartronic acid (aldehyde form).[28]

Quantitative studies of this reaction are more or less fragmentary. The formation of nitrites by the action of alkali on alkyl nitrates and the nitrates of ethylene glycol, glycerol, erythritol, mannitol, dulcitol and cellulose has been quantitatively measured.[29–31] Measurements of decomposition of various cellulose nitrates have been made by determination of the alkali consumed.[32,33]

Since no extended studies of the quantitative decomposition of cellulose nitrate could be found, we have studied in a quantitative manner the effect of certain variables: alkali concentration, ratio of alkali to ester, time, temperature and degree of nitration of the cellulose.

Experimental

A. **General Procedures.**—The cellulose nitrate was dried and 10-g. samples weighed to the nearest centigram (±0.1%). These were placed in flasks of suitable size with the amount of water which would yield the desired final concentration of alkali when the calculated amount of standard alkali was added. The water used in all of these experiments was freshly boiled, distilled water containing no amount of carbon dioxide capable of affecting the subsequent analyses.

The standard alkali used in all of these determinations possessed the following analysis: 0.77724 g. of sodium hydroxide per cc. at 25°; 0.007738 g. of sodium carbonate per cc. at 25°. The alkali concentrations given in this paper are expressed as grams of alkali per 100 cc. of water, *i. e.*, 20% = 20 g. per 100 cc. of water.

The aqueous suspensions of the cellulose nitrate were placed in a large water-bath and allowed to come to equilibrium with the temperature of the bath. The alkali was then quickly added with shaking to ensure complete mixing. The flasks were closed with rubber stoppers and placed in the bath until the decomposition was complete as evidenced by the disappearance of the suspended cellulose nitrate. During the reaction, the color of the liquid became reddish-brown. The temperature and total volume of the solutions were measured and the volume calculated to 25°, which was the temperature used for measurements of aliquots for analyses. Portions of the solutions were removed at various intervals, cooled to 25° and aliquots taken for the following measurements: (1) carbon dioxide, (2) optical rotation, (3) nitrites, (4) reducing power. The methods used for making these measurements were as follows.

(1) **Carbon Dioxide.**—Since we have been unable to find volatile organic acids other than carbon dioxide in the products of decomposition, the following method was adopted.

The apparatus used, Fig. 1, is an adaptation of that described by Kemmerer and Hallett.[34] It consists of a

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(22) Béchamp, *Bull. soc. chim.*, **3**, 289 (1863).

(23) Berl and Fodor, *Z. ges. Schiess- Sprengstoffw.*, **5**, 254 (1910).

(24) Béchamp, *Ann. chim. phys.*, **46**, 338 (1856).

(25) Eder, *Ber.*, **13**, 169 (1880).

(26) Schönbein, *Ann. chim. phys.*, **52**, 290 (1833).

(27) Aberson, *Z. physik. Chem.*, **31**, 17 (1899).

(28) Neuberg and Silbermann, *Z. physiol. Chem.*, **44**, 134 (1905).

(29) Vignon and Bay, *Compt. rend.*, **135**, 507 (1902).

(30) Carlson, *Arkiv. Kemi. Mineral. Geol.*, **3**, Art. 8, 1–15.

(31) Carlson, *Ber.*, **40**, 4191 (1907).

(32) Silberrad and Farmer, *J. Chem. Soc.*, **89**, 1759 (1906).

(33) Piest, *Z. angew. Chem.*, **23**, 1009 (1910).

(34) Kemmerer and Hallett, *Ind. Eng. Chem.*, **19**, 1352 (1927).

bulb A containing sulfuric acid which acts as a drying chamber for the incoming air as well as a bubble counter. The tube B contains Ascarite to remove carbon dioxide from the air. C is a 100-cc. Pyrex extraction flask in which the sample is placed and D is a dropping funnel to introduce the acid. This is closed by a stopper carrying another Ascarite tube. The evolved gases pass through the condenser E, the bubble counter F containing sulfuric acid and the drying tower G containing Dehydrite. The silica tube H is 35.5 cm. long, the portion within the furnace I being filled with a mixture of lead dioxide and shredded asbestos maintained at 180°. After the gases have passed through this tube, water is absorbed in the phosphorus pentoxide tube J and the dry carbon dioxide absorbed in the tube K, Ascarite being the absorbing medium.

The determination is made by connecting the source of vacuum to the drying tube J by means of the stopcock which serves to regulate the flow of gas through the apparatus. The carefully measured sample is placed in C and enough carbon dioxide-free distilled water added to bring the volume to 10 cc. The flask is replaced and the outfit swept out by passing air through it for one-half hour at a rate of about 100 bubbles per minute. The Ascarite tube K is then placed in the train and the rate of bubbling reduced to about 20–30 per minute. An excess of 5% sulfuric acid solution (boiled to expel carbon dioxide) is added from the dropping funnel (50–100 drops). The contents of the evolution flask are then heated to boiling with a micro burner and boiled for two minutes. The burner is removed and the apparatus swept out at the same rate for one-half hour. The tube K is removed and weighed.

In order to test the accuracy of the method, a series of determinations was made using varying amounts of a standard sodium carbonate solution (4.385 mg. of carbon dioxide per cc. by titration) and a solution containing sodium nitrate and sodium nitrite made up by accurately weighing the pure sodium salts. This latter solution contained 0.075 mole of sodium nitrite per liter and 0.025 mole of sodium nitrate per liter, this composition being approximately that shown by nitrite analyses to be present in the alkaline decomposition mixture. The results are tabulated in Table I.

Table I

Na_2CO_3 soln., cc.	Na_2CO_3, mg.	Nitrate–nitrite soln., cc.	$NaNO_2$, mg.	$NaNO_3$, mg.	Na_2CO_3 found, mg.
1	4.385	..	....	....	4.397
1	4.385	..	....	....	4.391
2	8.770	..	....	....	8.775
4	17.540	..	....	....	17.602
1	4.385	2	10.351	4.250	4.368
1	4.385	4	20.702	8.500	4.396
1	4.385	4	20.702	8.500	4.3875
1	4.385	8	41.404	17.000	4.374
1	4.385	12	62.106	25.500	4.428

It will be seen that good agreement was obtained in all cases. The runs containing 4 cc. of the nitrate–nitrite solutions correspond closely to the greatest nitrate–nitrite concentration encountered in the experiments and even a three-fold excess (12 cc.) had little effect on the determinations.

The carbonate determinations on the decomposition solutions are corrected for the amount of carbonate present in the alkali used.

(2) **Nitrite Determinations.**—The method employed was an adaptation of the procedure of Green and Rideal[35] in which the aniline solution used by them was replaced by a solution of sodium sulfanilate.

(3) **Reducing Power.**—The procedure used in these determinations was the modified method of Bertrand.[36] Using the relationships established experimentally by Bertrand for the reducing power of glucose, we have expressed the total reducing power of the alkaline decomposition solution in terms of glucose. This will be a fairly accurate measure of the moles of reducing substance present assuming one actual or potential aldehyde group for each molecule of reducing substance present.

(4) **Optical Rotation.**—Due to the brown color of the solutions, they were diluted before measuring the rotatory power. The desired amount of the alkaline solution was measured from a buret into a 10-cc. volumetric flask and diluted to 10 cc. The rotation was measured in a Hilger–Lippich half-shade polarimeter using light from a mercury arc lamp which was filtered to give a wave length of 546.1 mμ. A tube length of 0.5 dm. was used in each case. The measurements with this instrument are accurate to ±0.01°.

In each of the various determinations, the results are calculated on the basis of the total amount of solution produced in each experiment. Since the same amount of cellulose nitrate was used in each case, the results are, therefore, expressed on the basis of the same weight of cellulose nitrate.

B. Decomposition at 30°. Constant Ratio of Alkali to Cellulose Nitrate (12.2% *N*). Varying Alkali Concentrations.—The data for the solutions used in this series of experiments are given in Table II. Under the heading "Time of Decomposition" are given the times required for disappearance of the cellulose nitrate. The exact time of disappearance is difficult to judge but the values given represent, at least, the relative order of magnitude.

Table II

No.	Cellulose nitrate, g.	NaOH soln., cc.	NaOH concn., %	Time of dec., hrs.
1	10	100	20	2.58
2	10	200	10	11.13
3	10	400	5	23.33
4	10	800	2.5	170.9
5	10	2000	1.0	245.0

Samples were withdrawn from the solutions at various times and analyzed. Samples from solution 1 are designated as 1A to 1D inclusive, those from solution 2 as 2A to 2D inclusive, etc. The results are tabulated in Table III.

Under the heading "Time of Sampling" are given the intervals elapsed between the addition of the alkali and the withdrawal of samples for analyses.

C. Decomposition at 60°. Constant Ratio of Alkali to Cellulose Nitrate (12.2% *N*). Varying Alkali Concentrations.—This set of experiments was run at 60°, all other conditions as shown in Table IV being the same as in B.

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(35) Green and Rideal, *Chem. News*, **49**, 173 (1884).

(36) Bertrand, *Bull. soc. chim.*, **35**, 1285 (1906).

TABLE III

No.	Time of sampling, hrs.	CO_2 moles ($\times 10^{-3}$)	Moles CO_2 per mole cellulose nitrate	Nitrite moles ($\times 10^{-2}$)	Conversion to nitrite, %	Glucose equiv. moles ($\times 10^{-3}$)	Glucose equiv. moles per mole cellulose nitrate	Optical rotation degrees
1A	2.57	7.17	0.191	5.75	66.05	5.95	0.159	−1.2
1B	14.40	8.012	.214	5.58	64.20	4.41	.118	−1.6
1C	30.73	8.877	.237	5.75	66.05	3.43	.092	−1.5
1D	292.0	10.639	.284	5.75	66.05	1.82	.049	−1.6
2A	12.97	8.987	.239	5.89	67.70	6.39	.170	−0.5
2B	28.80	9.472	.252	6.05	69.55	6.11	.163	− .5
2C	51.30	9.818	.262	5.80	66.65	4.40	.114	− .75
2D	603.3	10.918	.291	5.97	68.80	3.65	.097	− .75
3A	23.33	8.420	.225	5.39	61.95	6.05	.162	− .30
3B	48.33	8.956	.239	5.68	65.25	5.61	.150	− .375
3C	196.83	10.087	.269	5.86	67.35	5.32	.142	− .375
3D	609.83	12.384	.330	5.84	67.10	2.67	.071	− .375
4A	170.88	11.594	.309	5.96	68.50	3.48	.093	− .18
4B	218.88	12.065	.322	5.96	68.50	3.48	.093	− .18
4C	360.88	13.119	.349	5.98	68.80	2.44	.065	− .19
4D	627.4	14.868	.397	6.00	68.95	2.22	.059	− .18
5A	245.0	10.491	.279	5.60	64.40	5.37	.143	− .06
5B	315.5	10.911	.291	5.66	65.00	4.40	.117	− .06
5C	585.0	13.388	.357	5.66	65.00	3.31	.088	− .06
5D	651.0	14.254	.380	5.65	64.95	3.02	.081	− .06

TABLE IV

No.	Cellulose nitrate, g.	NaOH soln., cc.	NaOH concn., %	Time of dec., hrs.
6	10	100	20	0.05
7	10	200	10	0.23
8	10	400	5	0.83
9	10	800	2.5	8.0

The results are tabulated in Table V.

D. Decomposition at 60°. Constant Concentration. Varying Ratio of Alkali to Cellulose Nitrate (12.2% *N*).—The data for the solutions used in this series of experiments are given in Table VI. The time of decomposition of the cellulose nitrate was about one hour in each case.

Samples were removed from each solution after 1104 hours (forty-six days) and analyzed. The results are tabulated in Table VII.

TABLE V

No.	Time of sampling, hrs.	CO_2 moles ($\times 10^{-3}$)	Moles CO_2 per mole cellulose nitrate	Nitrite moles ($\times 10^{-2}$)	Conversion to nitrite %	Glucose equiv. moles ($\times 10^{-3}$)	Glucose equiv. moles per mole cellulose nitrate	Optical rotation degrees
6A	19.70	11.246	0.300	6.17	70.92	1.18	0.0315	−1.10
6B	67.53	11.718	.312	6.17	70.92	1.05	.028	−1.10
6C	117.2	12.200	.326	6.09	70.00	0.76	.0203	−1.10
6D	1053.2	16.749	.447	6.02	69.19	.28	.0074	−1.10
7A	21.37	13.599	.362	6.22	71.50	1.43	.0381	−0.90
7B	70.62	14.630	.390	6.32	72.64	1.24	.0331	− .60
7C	144.13	15.699	.418	6.32	72.64	0.73	.0194	− .60
7D	1080.13	19.906	.531	6.32	72.64	.52	.0138	− .60
8A	23.33	15.456	.412	6.10	70.12	1.64	.0437	− .30
8B	72.92	15.977	.426	6.10	70.12	1.22	.0325	− .325
8C	145.83	17.448	.465	6.25	71.84	1.13	.0301	− .30
8D	1151.10	19.964	.532	6.22	71.50	1.03	.0275	− .275
9A	25.25	14.492	.386	6.16	70.80	1.96	.0523	− .175
9B	78.33	15.904	.424	6.14	70.57	1.73	.0461	− .15
9C	150.42	16.656	.444	6.14	70.57	1.68	.0448	− .15
9D	1153.16	18.537	.494	6.02	69.19	1.27	.0339	− .1375

TABLE VI

No.	Cellulose nitrate, g.	NaOH soln., cc.	NaOH concn., %	Ratio NaOH to cellulose nitrate (mole)
10	10	100	5.0	3.33
11	10	200	5.0	6.66
12	10	400	5.0	13.32
13	10	800	5.0	26.64
14	10	1600	5.0	53.28

Sample 10 was acid to litmus after decomposition and had the odor of oxides of nitrogen.

E. Decomposition at 60°. Constant Ratio of Alkali to Cellulose Nitrate (9.34% *N*). Varying Alkali Concentrations.—As shown in Table VIII this series of experiments was run under the same conditions as C except that a cellulose nitrate of lower nitrogen content was used. The times of decomposition were approximately the same as in C.

TABLE VII

No.	CO_2 moles ($\times 10^{-3}$)	Moles CO_2 per mole cellulose nitrate	Nitrite moles ($\times 10^{-2}$)	Conversion to nitrite, %	Glucose equiv. moles ($\times 10^{-3}$)	Glucose equiv. moles per mole cellulose nitrate	Optical rotation degrees
10	18.70	0.499	4.94	56.82	2.43	0.0648	−8.0
11	18.05	.481	6.26	71.95	1.10	.0293	−0.90
12	20.54	.548	7.16	82.26	1.01	.0269	− .375
13	15.65	.417	6.22	71.77	0.94	.0251	− .20
14	13.12	.350	6.28	72.24	0.85	.0226	− .00

TABLE VIII

No.	Cellulose nitrate, g.	NaOH soln., cc.	NaOH concn., %
15	10	100	20.0
16	10	200	10.0
17	10	400	5.0
18	10	800	2.5
19	10	2000	1.0

Samples were removed from each solution after 116 hours and analyzed. The results are tabulated in Table IX.

TABLE IX

No.	CO_2 moles ($\times 10^{-3}$)	Moles CO_2 per mole cellulose nitrate	Nitrite moles ($\times 10^{-2}$)	Conversion to nitrite %	Glucose equiv. moles ($\times 10^{-3}$)	Glucose equiv. moles per mole cellulose nitrate	Optical rotation degrees
15	9.15	0.213	3.33	49.93	0.561	0.0131	−2.20
16	9.24	.215	2.63	39.43	.742	.0173	−1.45
17	9.41	.219	3.18	47.68	.967	.0225	−0.60
18	9.68	.225	3.15	47.21	2.100	.0489	− .35
19	10.14	.236	3.02	45.28	4.250	.0990	− .14

Attempts were made to investigate quantitatively the alkaline decomposition of cellulose nitrates containing 5.0 and 1.2% of nitrogen. Neither of these decomposed to yield completely water soluble products even when heated for twenty-four hours on the steam-bath in the presence of 20% alkali.

Discussion

Cellulose nitrate, when decomposed by aqueous sodium hydroxide solutions, yields alkali soluble products among which are carbon dioxide and substances capable of reducing alkaline copper solutions. This oxidative decomposition of the cellulose molecule is accompanied by reduction of the nitrate groups to nitrite groups. The time required to decompose a given weight of cellulose nitrate decreases with increasing temperature and alkali concentration but appears independent of the alkali–cellulose nitrate ratio at constant concentration.

The amount of carbon dioxide formed at 30° from cellulose nitrate containing 12.2% *N* (Table III) varied between 0.191 and 0.397 mole per mole of cellulose nitrate, which is equivalent to about 3 to 6% by weight of the cellulose nitrate used. About 60 to 70% of the nitrate groups present were reduced to nitrite. When the solutions were allowed to stand, the amount of carbon dioxide increased and the reducing power decreased.

At 60°, the same cellulose nitrate (Table V) yielded larger amounts of carbon dioxide at the same alkali concentrations, the values increasing with time. The conversion of nitrate to nitrite was about 70 to 72%. The reducing powers of the solutions produced at 60° were decidedly lower than those formed at 30°. The initial reducing powers of the solution were greater when lower concentrations of alkali were used but in each case decreased with increasing reaction time.

The values for carbon dioxide and nitrite conversion, at constant concentration and varying alkali/cellulose nitrate ratio (Table VII), appear to pass through a maximum. The reducing powers of the solutions decreased with increasing alkali ratio.

Experiments at 60° with cellulose nitrate containing 9.34% nitrogen (Table IX) indicated that the amount of carbon dioxide produced increased with decreasing alkali concentration. The conversion of nitrate to nitrite (39–50%) was less than when cellulose nitrate containing 12.2% nitrogen was used. The reducing power of the solutions increased with decreasing concentrations of alkali.

Summary

The decomposition of cellulose nitrates in aqueous sodium hydroxide has been studied in a quantitative manner.

A relatively small amount of carbon dioxide is produced and a relatively large per-

centage of the nitrate groups is reduced to nitrite.

The production of carbon dioxide and of reducing substances appears to be related to time, concentration of alkali, ratio of alkali to cellulose nitrate and the temperature.

ROCHESTER, N. Y. RECEIVED MAY 6, 1936

[CONTRIBUTION NO. 265 FROM THE INDUSTRIAL FARM PRODUCTS RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Magenta Series. II. Some Higher Basic Members

BY JOHN T. SCANLAN

In a previous publication[1] the results of an investigation of the "nitrobenzene process" and the "formaldehyde process" for the preparation of Magenta (Fuchsine) were given. In the latter process 4,4′-diaminodiphenylmethane, or one of its homologs, reacts with aniline or its homologs, and it was shown that the reaction involves a scission of the diphenylmethane. This report covers an extension of the same investigation to three of the higher members of the series in which the methyl groups are ortho to the amino groups and not more than two occur in any benzene nucleus. The simplified system of nomenclature explained in the previous publication is used (see Table I).

TABLE I

NOMENCLATURE

Name used in this paper	Scientific name
Magenta IV	3,3′,3″,5-Tetramethyl-4,4′-diaminofuchsonimonium chloride
Magenta V	3,3′,3″5,5′-Pentamethyl-4,4′-diaminofuchsonimonium chloride
Magenta VI	3,3′,3″,5,5′,5″-Hexamethyl-4,4′-diaminofuchsonimonium chloride

The results are even more clean-cut than those obtained with the lower homologs and confirm the conclusions previously stated. As shown by the data in Table II and the corresponding absorption curves in Fig. 1, when 4,4′-diamino-3,3′-dimethyldiphenylmethane reacts with *v-m*-xylidine (Experiments 5Fa and 5Fb) the product is not Magenta IV but Magenta V and when 4,4′-diamino-3,3′,5,5′-tetramethyldiphenylmethane reacts with *o*-toluidine (Experiment 6F) the product is not Magenta V, but Magenta IV. This conclusion is readily arrived at by comparing the products of the above two reactions with that of the reaction between *as-m*-xylidine and *v-m*-xylidine (Experiment 6N, "nitrobenzene process") which must obviously be Magenta V. No attempt was made to prepare Magenta IV and Magenta VI by the "nitrobenzene process" because a necessary intermediate, mesidine, was not readily available and it was thought that further evidence was not required.

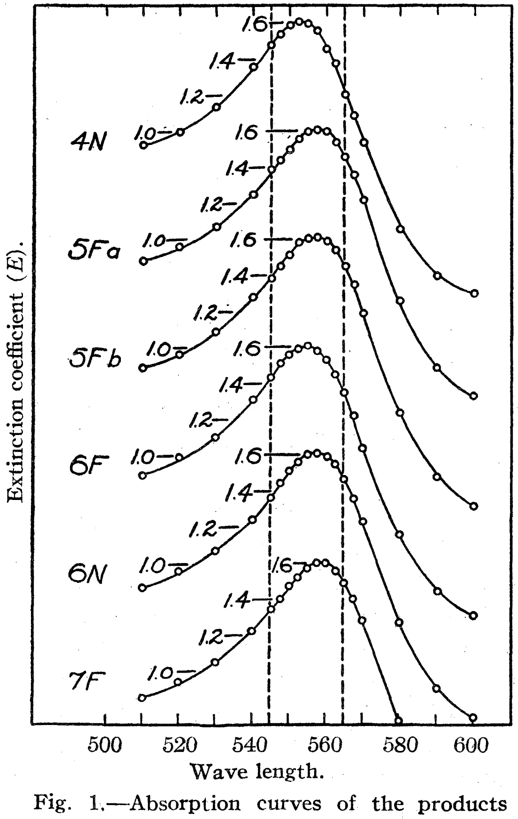

Fig. 1.—Absorption curves of the products obtained in the experiments indicated by the numbers. Solvent, 50% alcohol. The dyes corresponding to the curves are as follows: 4N, magenta III (repeated from previous paper for comparison); 6F, magenta IV; 5Fa, 5Fb and 6N, magenta V; 7F, magenta VI. Further data are given in Table II.

As in the case of the lower homologs, the solubility of these dyes (hydrochlorides) in alcohol decreases with increasing molecular weight. How-

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[1] Scanlan, THIS JOURNAL, **57**, 887 (1935).

TABLE II

COMPARISON OF PRODUCTS OBTAINED BY DIFFERENT METHODS OF PREPARATION

(See absorption curves in Fig. 1)

Experiment[a]	Intermediates used	Magenta obtained	Analysis of carbinol base %, N Calcd.	Analysis of carbinol base %, N Found	Ratio E at 545 mμ[b] / E at 565 mμ Original dye	Ratio E at 545 mμ[b] / E at 565 mμ Dye from base
5Fa	4,4′-Diamino-3,3′-dimethyldiphenylmethane, *v*-*m*-xylidine, nitro-*m*-xylene	V	11.20	11.04	0.93	0.92
5Fb	4,4′-Diamino-3,3′-dimethyldiphenylmethane, *v*-*m*-xylidine, *o*-nitrotoluene	V	11.20	11.19	.92	.92
6F	4,4′-Diamino-3,3′,5,5′-tetramethyldiphenylmethane, *o*-toluidine, *o*-nitrotoluene	IV	11.63	11.68	1.06	1.05
6N	*as*-*m*-Xylidine, *v*-*m*-xylidine, nitro-*m*-xylene	V	11.20	11.08	0.92	0.91
7F	4,4′-Diamino-3,3′,5,5′-tetramethyldiphenylmethane, *v*-*m*-xylidine, *o*-nitrotoluene	VI	10.80	10.89	.87	.88

[a] Letter indicates method used: N, nitrobenzene process; F, formaldehyde process. [b] Solvent, 50% alcohol.

ever, while Magenta IV and Magenta V are quite soluble in water, Magenta VI is much less so. All three are easily salted out. The carbinol bases show decreasing solubility in hot, aqueous alkaline solutions with increasing molecular weight. The absorption bands, of course, show progressive shifting toward the red end of the spectrum.

Experimental

Method of Identification.—These higher homologs were identified by the method described in the previous paper; namely, spectrophotometric examination and analysis of their carbinol bases. The absorption ratios[2] are given in Table III.

TABLE III

ABSORPTION RATIOS FOR IDENTIFICATION

Solvent, 50% Alcohol

The ratios for Magenta III are repeated from the previous paper for comparison. The others represent only one batch in each case.

Dye	Absorption ratios E, mμ...520 / E, mμ...560	530 / 560	540 / 560	545 / 565	540 / 570	550 / 570
Magenta III	0.68	0.77	0.93	1.19	1.49	1.75
Magenta IV	.63	.70	.84	1.07	1.23	1.48
Magenta V	.58	.66	.78	0.92	1.02	1.23
Magenta VI	...	...	.75	.87	0.92	1.12

Preparation of Intermediates

4,4′ - Diamino - 3,3′ - dimethyldiphenylmethane.—The method of preparing this compound was described in the previous publication.

Nitro-*m*-xylene.—Prepared by nitration of *m*-xylene[3] and purified by fractional distillation. The fraction boiling at 243–252° was used.

***v*-*m*-Xylidine.**—Technical xylidine[4] from which *as*-*m*-xylidine had been removed was freed from *p*-xylidine[5] and treated according to the method of Winkelhausen[6] to obtain *v*-*m*-xylidine sulfate. Part of this was converted to the chloride by treatment with barium chloride and the balance to the base by treatment with sodium hydroxide. Two kilograms of the technical xylidine yielded 130 g. of *v*-*m*-xylidine base and 189 g. of *v*-*m*-xylidine hydrochloride.

4,4′ - Diamino - 3,3′,5,5′ - tetramethyldiphenylmethane.—Fifty-seven grams of *v*-*m*-xylidine hydrochloride, 2 cc. of concentrated hydrochloric acid and 14 g. of 40% formaldehyde solution were dissolved in 150 cc. of water and heated at 70–75° for four hours. Near the end of the reaction time sufficient warm water was added to dissolve the precipitated hydrochloride. The mixture was then made alkaline with potassium hydroxide and steam distilled. The residual material was redissolved by the addition of hydrochloric acid and fractionally precipitated with ammonium hydroxide as described in the previous paper.[1] The first of the two fractions thus obtained was rejected and the second recrystallized from alcohol; yield 32 g.; m. p. 122.5–123.5°.

Friedländer and Brand[7] give the melting point as 126°.

Preparation of the Dyes

Experiment 5Fa (Magenta V, Formaldehyde Process).—The intermediates used were 40 g. of 4,4′-diamino-3,3′-dimethyldiphenylmethane, 25 g. of *v*-*m*-xylidine hydrochloride, 60 g. of *v*-*m*-xylidine (base), 25 g. of nitro-*m*-xylene and 16 g. of $FeCl_2 \cdot 4H_2O$. The procedure was the same as described for this process in the previous publication. The product was salted out and recrystallized from alcohol. It separates from this solvent in feathery clusters of very fine needles which form a felt-like mass on the filter. When thoroughly dried and ground it has a dull, gray-green color; yield 46 g.; 65% of the theoretical.

The carbinol base was prepared by mixing a hot solution of 4 g. of the dye in 1000 cc. of water with a hot solution of 5 g. of sodium hydroxide in 800 cc. of water. The base precipitated immediately and after boiling the mixture for about an hour, it was allowed to cool, the base was filtered off, washed with dilute ammonium hydroxide and dried over phosphorus pentoxide; yield 2.5 g.; small, ir-

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(2) Holmes, *Ind. Eng. Chem.*, **17**, 918 (1925); Holmes and Peterson, *Stain Tech.*, **5**, 65 (1930).

(3) Noelting and Forel, *Ber.*, **18**, 2674 (1885).

(4) Obtained through the courtesy of Dr. E. K. Bolton of E. I. du Pont de Nemours & Co.

(5) Hodgkinson and Limpach, *J. Chem. Soc.*, **77**, 65 (1900); German Patent 39,947; *Friedländer*, **1**, 19 (1888).

(6) Winkelhausen, German Patent 251,334; *Friedländer*, **11**, 153 (1915).

(7) Friedländer and Brand, *Monatsh.*, **19**, 640 (1898).

regular prisms, buff-colored and showing only a very slight tendency to become red on standing.

Anal. Calcd. for $C_{24}H_{29}N_3O$: N, 11.20. Found: N, 11.04.

Experiment 5Fb (Magenta V, Formaldehyde Process).—The intermediates used were 26 g. of 4,4′-diamino-3,3′-dimethyldiphenylmethane, 14.5 g. of *v*-*m*-xylidine hydrochloride, 68 g. of *v*-*m*-xylidine (base), 12.6 g. of *o*-nitrotoluene and 9.1 g. of $FeCl_2\cdot 4H_2O$; procedure as above. The product separated from alcohol in feathery clusters of very fine needles. When thoroughly dried and ground it was dull, gray-green in color; yield 13.5 g.; 30% of theoretical.

The carbinol base was prepared as above using 3.5 g. of the dye; yield 1.5 g.; small, irregular prisms, buff-colored and showing only a very slight tendency to become red on standing.

Anal. Calcd. for $C_{24}H_{29}N_3O$: N, 11.20. Found: N, 11.19.

Experiment 6F (Magenta IV, Formaldehyde Process).—The intermediates used were 25 g. of 4,4′-diamino-3,3′,-5,5′-tetramethyldiphenylmethane, 12 g. of *o*-toluidine hydrochloride, 57 g. of *o*-toluidine (base), 12 g. of *o*-nitrotoluene and 8 g. of $FeCl_2\cdot 4H_2O$; procedure as above. The product separated from alcohol as very bright green, rather coarse needles; yield 13.5 g., 36% of theoretical.

Using 3 g. of dye the carbinol base was prepared as above except that in this case it was sufficiently soluble in hot aqueous alkali to permit filtration before it separated; yield 1.3 g.; small, irregular prisms, faintly pink when first precipitated, but acquiring an intense purple coloration on standing.

Anal. Calcd. for $C_{23}H_{27}N_3O$: N, 11.63. Found: N, 11.68.

Experiment 6N (Magenta V, Nitrobenzene Process).—The intermediates used were 36 g. of *as*-*m*-xylidine, 83 g. of *v*-*m*-xylidine hydrochloride, 64 g. of *v*-*m*-xylidine (base), 91 g. of nitro-*m*-xylene and 12 g. of $FeCl_2\cdot 4H_2O$. The procedure was the same as described for the nitrobenzene process in the previous publication. The product was salted out and recrystallized from alcohol. It separated as feathery clusters of very fine needles. When dried and ground it was dull, gray-green in color; yield 32 g., 27% of theoretical.

The carbinol base was prepared from 4 g. of the dye as described under Experiment 5Fa; yield 3.2 g.; small irregular prisms with only a very slight tendency to become red on standing.

Anal. Calcd. for $C_{24}H_{29}N_3O$: N, 11.20. Found: N, 11.08.

Experiment 7F (Magenta VI, Formaldehyde Process).—The intermediates used were 25 g. of 4,4′-diamino-3,3′-5,5′-tetramethyldiphenylmethane, 13 g. of *v*-*m*-xylidine hydrochloride, 65 g. of *v*-*m*-xylidine (base), 12 g. of *o*-nitrotoluene and 8 g. of $FeCl_2\cdot 4H_2O$.

The procedure was the same as that previously described for the formaldehyde process except that, because of the low solubility of this homolog, it could be separated by filtration from the hot solution immediately after the steam distillation. Some large, fused lumps of tarry material were removed manually and the balance was recrystallized from alcohol. A voluminous precipitate of feathery clusters of very fine needles was obtained which, when dried and ground, had a dark gray-blue color; yield 25 g., 60% of theoretical.

The carbinol base was prepared from 4 g. of the dye as described under Experiment 5Fa; yield 3.6 g.; small, irregular prisms, golden-yellow with practically no color change on standing.

Anal. Calcd. for $C_{25}H_{31}N_3O$: N, 10.80. Found: N, 10.89.

Summary

1. Three new homologs of Magenta were prepared, and their identity was established by spectrophotometric examination of the dyes and analysis of their carbinol bases. Absorption curves and absorption ratios suitable for their future identification are given.

2. Examination of these data confirms the conclusion, previously published, that in the "formaldehyde process" for the preparation of Magenta, scission of the diaminodiphenylmethane nucleus occurs.

WASHINGTON, D. C.

RECEIVED JUNE 1, 1936

[CONTRIBUTION NO. 264 FROM THE INDUSTRIAL FARM PRODUCTS RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS
UNITED STATES DEPARTMENT OF AGRICULTURE]

Some Ketonimine Dyes and Related Compounds

BY J. DAVID REID* AND D. F. J. LYNCH

In a previous investigation for the development of new bactericides the preparation of some symmetrical diamino dyes related to auramine O (the hydrochloride of 4,4′-tetramethyldiaminobenzophenonimine) and their salts was described.[1] This report concerns the preparation of the monoamino ketonimines which correspond to the diamino dyes previously reported, as well as several other new compounds prepared during the course of the investigation.

Experimental

Alkylated Diaminodiphenylmethanes.—The following new propyl and butyl derivatives of 4,4′-diaminodiphenylmethane were prepared with a view to converting them to the corresponding ketones by oxidation with chloranil as was done by Kliegl[2] with the tetramethyl derivative. However, this method of oxidation was not found applicable.

4,4′ - Tetra - *n* - propyldiaminodiphenylmethane.—This compound was prepared according to the method used by Biehringer[3] for the methyl homolog.

35.9 g. of di-*n*-propylaniline was dissolved in 22 g. of 36% hydrochloric acid and diluted with 14 cc. of water. Six grams of 40% formaldehyde was added, and the mixture was held under reflux at 90° for six hours. The mixture was made alkaline with sodium carbonate and extracted with ether. The ether was dried and evaporated. The residual oil was distilled *in vacuo*, and 7 g. of di-*n*-propylaniline was recovered at 105° at 7 mm. pressure. The methane distilled as a heavy oil at 260° at 7 mm.; yield 70%; sp. gr., 0.971^{20}_{20}.

Anal. Calcd. for $C_{25}H_{38}N_2$: N, 7.65. Found: N, 7.50, 7.76.

Dipicrate of 4,4′ - Tetra - *n* - propyldiaminodiphenylmethane.—The dipicrate was prepared as a solid derivative by dissolving 0.6 g. of the methane base and 0.82 g. of picric acid separately in 10-cc. portions of hot alcohol and mixing the two solutions. A gummy mass separated which solidified on cooling. It was crystallized from 40 cc. of alcohol as bright yellow needles; m. p. sinters 165°, decomposes 175°.

Anal. Calcd. for $C_{37}H_{44}N_8O_{14}$: N, 13.59. Found: N, 13.69, 13.74.

4,4′ - Tetra - *n* - butyldiaminodiphenylmethane.—To 10.5 g. of di-*n*-butylaniline in 5.5 cc. of 36% hydrochloric acid plus 4 cc. of water, was added 1.5 g. of 40% formaldehyde. The mixture was treated as described above. The methane distilled as an oily liquid at 270–280° at 6 mm. pressure; yield, about 70%; sp. gr., 0.953^{20}_{20}.

Anal. Calcd. for $C_{29}H_{46}N_2$: N, 6.63. Found: N, 6.26, 6.29.

Dipicrate of 4,4′-Tetra-*n*-butyldiaminodiphenylmethane.—This was prepared as described above for the corresponding propyl compound; m. p. 156°, corr.

Anal. Calcd. for $C_{41}H_{52}O_{14}N_8$: N, 12.72. Found: N, 12.60, 12.41.

***sym* - 4,4′ - Di - *n* - butyldiaminodiphenylmethane.**—To 6 g. of 40% formaldehyde were added 31 g. of *n*-butylaniline in 22 g. of 36% hydrochloric acid and 14 cc. of water. It was treated as above. Four grams of butylaniline was recovered at 100° at 10 mm., and the methane distilled at 260–270° at 8 mm. After standing for one week it crystallized as colorless flat plates; m. p. 45°, corr.; yield, about 80%.

Anal. Calcd. for $C_{21}H_{30}N_2$: N, 9.03. Found: N, 8.76, 8.80.

4-Di-*n*-propylaminobenzoic Acid.—In the attempted preparation of 4,4′-tetrapropyldiaminobenzophenone by the method Michler[4] used to make first 4-dimethylaminobenzoic acid and then his ketone, the corresponding dipropyl acid was synthesized.

Four grams of phosgene was absorbed in 15 g. of di-*n*-propylaniline and allowed to stand overnight. The mass was dissolved in dilute hydrochloric acid, filtered and made alkaline with sodium hydroxide. The dipropylaniline was recovered in ether. The solution was made slightly acidic and allowed to stand overnight. The acid crystallized out. It may be extracted also with ether. It was recrystallized as long tetragonal prisms from 50% alcohol; m. p. 142°, corr.; yield, about 80% based on dipropylaniline used up.

Anal. Calcd. for $C_{13}H_{19}NO_2$: N, 6.33. Found: N, 6.14, 6.22.

4-Di-*n*-propylaminobenzophenone.—The 4-dimethyl and 4-diethylaminobenzophenones used below as well as the new 4-di-*n*-propylaminobenzophenone were prepared by the method of Meister, Lucius and Brüning, as modified by C. D. Hurd and C. N. Webb.[5]

In the preparation of the propyl ketone, 13 g. of phosphorus oxychloride was added to a mixture of 25 g. of di-*n*-propylaniline and 10 g. of benzanilide. The mixture was heated cautiously to 105–125°, at which point the temperature rose very suddenly to about 200°. It was cooled in ice water in time to keep the temperature below 200° and then heated under reflux in a boiling water-bath for four hours. It was then poured into 250 cc. of 10–15% hydro-

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(*) This work has been submitted by J. David Reid in partial fulfilment of the requirements for the degree of Doctor of Philosophy at The American University, Washington, D. C.

(1) D. F. J. Lynch and J. David Reid, THIS JOURNAL, **55**, 2515 (1933).

(2) A. Kliegl, *Ber.*, **39**, 1274 (1906).

(3) J. Biehringer, *J. prakt. Chem.*, [2] **54**, 240 (1896).

(4) W. Michler, *Ber.*, **9**, 401 (1876).

(5) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1928, p. 211.

chloric acid and warmed until solution took place. The intermediate hydrolyzed overnight to the ketone. The solution was filtered and diluted to 1.5 liters to get the crystalline ketone. It was recrystallized from petroleum ether (b. p. 30–65°) as hexagonal colorless prisms; yield, about 25%; m. p. 100°, corr.

Anal. Calcd. for $C_{19}H_{23}NO$: N, 4.98. Found: N, 5.00, 5.02.

4-Di-*n*-butylaminobenzophenone apparently cannot be prepared by the above method. In several trials only two had the characteristic exothermic reaction. In each case a thick resinous material insoluble in acid was obtained, which was not hydrolyzed by water or alcohol.

Hydrochloride of 4-Aminobenzophenonephenylimide.—The method devised by Madelung[6] to make 4,4′-diaminobenzophenonimine was applied to the preparation of 4-aminobenzophenonimine. The phenylimide intermediate was made by heating 13 g. (0.1 mole) of aniline hydrochloride and 19.7 g. (0.1 mole) of 4-aminobenzophenone in 50 cc. of aniline at 160–180° with occasional stirring for about an hour, or until the mass solidified. After cooling, the aniline was removed by extraction with ether, and the intermediate, 4-aminobenzophenonephenylimide hydrochloride, crystallized from alcohol; yield, about 95%; sinters about 275–280°; no melting point to 400°.

Anal. Calcd. for $C_{19}H_{17}N_2Cl$: N, 9.08. Found: N, 8.97, 8.93.

The phenylimide hydrochloride dyes silk and tannin-mordanted cotton a light yellow but is not fast to light or washing.

The base was liberated from the aqueous solution of the hydrochloride by precipitating with alkali. It was crystallized from benzene after treatment with charcoal; m. p. 154°, corr.

Anal. Calcd. for $C_{19}H_{16}N_2$: N, 10.30. Found: N, 10.22, 9.96.

3,5-Dinitrobenzoate of 4-Aminobenzophenonimine

Method I. From 4-Aminobenzophenonephenylimide Hydrochloride.—Ten grams of the phenylimide hydrochloride was suspended in 100 cc. of alcohol, and ammonia gas was bubbled into the solution until it was saturated and then the liquid was brought to boiling. As done by Madelung, this step was repeated three times to split off the aniline more effectively. The resulting liquor was cooled and the precipitate filtered off and dissolved in about 400 cc. of water, which was just faintly acid with hydrochloric acid. The solution was made alkaline and the imine base extracted with ether. The ether solution was dried over sodium sulfate, and the imine was precipitated as the 3,5-dinitrobenzoic acid salt; yield about 5%; m. p. 198°, corr. A mixed melting point taken with a sample of the same salt prepared by Method II as described below was 198°.

Method II. From 4-Aminobenzophenone.—Ten grams of 4-aminobenzophenone and 10 g. of phosphorus pentachloride, each dissolved in 30 cc. of hot toluene, were cautiously mixed in a steel bomb (100-cc. capacity), and cooled in ice, and liquid ammonia was added cautiously until the weight increased 15 g. The bomb was capped and heated for twelve hours at 100–105°. It was then cooled and opened and the solution evaporated to dryness with an air blast. The mixture of ketone and imine was dissolved in ether and the imine precipitated as a yellow salt by the slow addition of an ether solution of 3,5-dinitrobenzoic acid. The pure base was not obtained, due to the difficulty of separating the imine and the ketone by crystallization. The imine rapidly hydrolyzed to the ketone on treating the salt with alkali. Crystallized from alcohol, the salt had a melting point of 198°, corr. When it was mixed with an equal quantity of 3,5-dinitrobenzoic acid (m. p. 204°) the melting point was depressed to about 110°; yield, about 50%.

Anal. Calcd. for $C_{20}H_{16}N_4O_6$: N, 13.73. Found: N, 13.69, 13.58.

3,5-Dinitrobenzoate of 4-Dimethylaminobenzophenonimine.—Ten grams of 4-dimethylaminobenzophenone[4] was dissolved in 40 cc. of hot toluene, and 10 cc. of phosphorus oxychloride was added. It was cooled and treated with ammonia as in Method II for the preparation of 4-aminobenzophenonimine. Evaporation of the filtered toluene gave an oil from which only the ketone could be crystallized. Distillation of the oily residue *in vacuo* gave a liquid which apparently was about equal parts of ketone and ketonimine. (Calcd.: N, 12.5. Found: N, 9.5.) This material, dissolved in ether and precipitated by 3,5-dinitrobenzoic acid, crystallized from alcohol as yellow needles; yield, about 30%; m. p. 214°, corr.

Anal. Calcd. for $C_{22}H_{20}N_4O_6$: N, 12.84. Found: N, 12.67, 12.68. (Phosphorus pentachloride gave a negligible yield when used in place of the oxychloride. Phosphorus trichloride (b. p. 77°) gave a yield of 5%.)

3,5-Dinitrobenzoate of 4-Diethylaminobenzophenonimine.—This salt was prepared as above, from the 4-diethylaminobenzophenone. However, the precipitate first obtained had to be treated with very dilute alkali, shaken out with ether and reprecipitated in order to free it of ammonium 3,5-dinitrobenzoate. It crystallized from alcohol as yellow needles; yield, about 30%; m. p. 141°, corr.

Anal. Calcd. for $C_{24}H_{24}N_4O_6$: N, 12.07. Found: N, 12.22, 12.11.

An effort was made to prepare 4-di-*n*-propylaminobenzophenonimine from the corresponding ketone by the above method, but no solid product could be isolated. The only action noted was that a yellow color was produced when acid was added to the ether solution of the product.

Benzoyl - 4,4′ - tetraethyldiaminobenzophenonimine. (Benzoyl Ethyl Auramine.)—The benzoyl derivative of 4,4′-tetraethyldiaminobenzophenonimine was made by the method used by Finckh and Schwimmer[7] in preparing the benzoyl derivative of the corresponding methyl compound.

Four grams of 4,4′-tetraethyldiaminobenzophenonimine[1] was refluxed in 20 cc. of benzene with 2.9 g. of benzoic anhydride for five hours. The solution was then diluted to 80 cc. with petroleum ether (b. p. 30–65°). The thick red liquid resulting was separated, and crystallized on standing. It was recrystallized from methyl alcohol as long yellow needles; m. p. 165°, corr.; yield, about 60%.

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[6] W. Madelung, *J. prakt. Chem.*, **114**, 42 (1926).

[7] J. Finckh and M. Schwimmer, *ibid.*, [2] **50**, 434 (1894).

Although this compound is an indicator similar to Benzoyl Auramine G,[8] the color change from yellow to blue is not so sharp. The *p*H range is 4.0–5.2.

Anal. Calcd. for $C_{28}H_{33}N_3O$: N, 10.12. Found: N, 10.01, 9.95.

Solid Salts of Amines.—In working with the alkyl anilines used, it was found convenient to prepare solid derivatives by the use of 3,5-dinitrobenzoic acid. The salt of dimethylaniline has been prepared previously by the same method.[9]

0.002 mole of the dialkylaniline and 0.004 mole of the 3,5-dinitrobenzoic acid (0.002 mole with monobutylaniline) were dissolved in a few cc. of absolute alcohol and allowed to crystallize overnight. The salt was then recrystallized from absolute alcohol with char treatment. All the four salts crystallized as hexagonal prisms (see Table I).

TABLE I

3,5-Dinitrobenzoic acid salt of	M. p., °C., corr.	Nitrogen, % Calcd.	Nitrogen, % Found		Neut. equivalent Calcd.	Neut. equivalent Found
Diethylaniline	120	12.22	12.33	12.41	286.6	280
Di-*n*-propylaniline	118	11.65	11.84	11.90	300.5	294
Di-*n*-butylaniline	104	11.14	11.14	11.34	314.5	308
n-Butylaniline	98.5	11.63	11.40	11.49	361.3	352

Summary

In a study of the ketonimine dyes:

1. Di-*n*-butyldiaminodiphenylmethane, tetra-*n*-butyldiaminodiphenylmethane and tetra-*n*-propyldiaminodiphenylmethane have been synthesized. The picrates of the latter two are also given.
2. 4-Di-*n*-propylaminobenzoic acid has been made.
3. 4-Aminobenzophenonephenylimide and its hydrochloride have been prepared.
4. 4-Aminobenzophenonimine, 4-dimethylaminobenzophenonimine and 4-diethylaminobenzophenonimine have been made and characterized as their solid 3,5-dinitrobenzoic acid salts.
5. Benzoyl ethyl auramine was made, and its properties as an indicator are described.
6. The solid derivatives of diethyl-, di-*n*-propyl-, di-*n*-butyl- and *n*-butyl-aniline with 3,5-dinitrobenzoic acid have been prepared and characterized.

WASHINGTON, D. C.

RECEIVED JUNE 2, 1936

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[8] J. T. Scanlan and J. D. Reid, *Ind. Eng. Chem., Anal. Ed.*, **7**, 125 (1935).

[9] C. A. Buehler, E. J. Currier and R. Lawrence, *ibid.*, **5**, 277 (1933).

[CONTRIBUTION FROM THE PEDIATRIC RESEARCH LABORATORY OF THE JEWISH HOSPITAL OF BROOKLYN]

Synthesis of Derivatives of Symmetrical Diphenylethane Related to Materials Occurring Naturally. I. Synthesis of the Ring System Proposed for Calciferol

BY SAMUEL NATELSON AND SIDNEY P. GOTTFRIED

A general and flexible method for the synthesis of compounds related to the naturally occurring derivatives of diphenylethane, which include compounds as widely distributed in nature as alkaloids, sterols, bile acids, sex hormones, toad poisons and cardiac aglycones[1] should be of value for the synthesis of degradation products and ultimately for the synthesis of some of the naturally occurring materials themselves.

This report offers a new route to this biologically important series which is capable of wide variation. As an example of its application, a compound having the ring system proposed for calciferol was synthesized in good yield. The formulas proposed by Windaus,[2] Heilbron,[3] Lettré[4] and Müller[5] assume that the phenanthrene ring is open to give a hydrogenated diphenylethane structure to calciferol and tachysterol.

As can be seen from the accompanying flow sheet, the starting materials for this synthesis are the readily available phthalic anhydride and phenylacetic acid.

Phthalic anhydride and phenylacetic acid condense in good yield to form benzal-phthalide (I).[6] The relationship of benzal-phthalide to the naturally occurring materials was recognized and this material and its derivatives were then built up to

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[1] L. F. Fieser, "Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Co., New York City, 1936; L. F. Small, "Chemistry of the Opium Alkaloids," U. S. Treasury Dept., Supplement No. 103, 1932. These two monographs offer an inspiring and complete review of the literature on this subject.

[2] Windaus and Thiele, *Ann.*, **521**, 160 (1935).

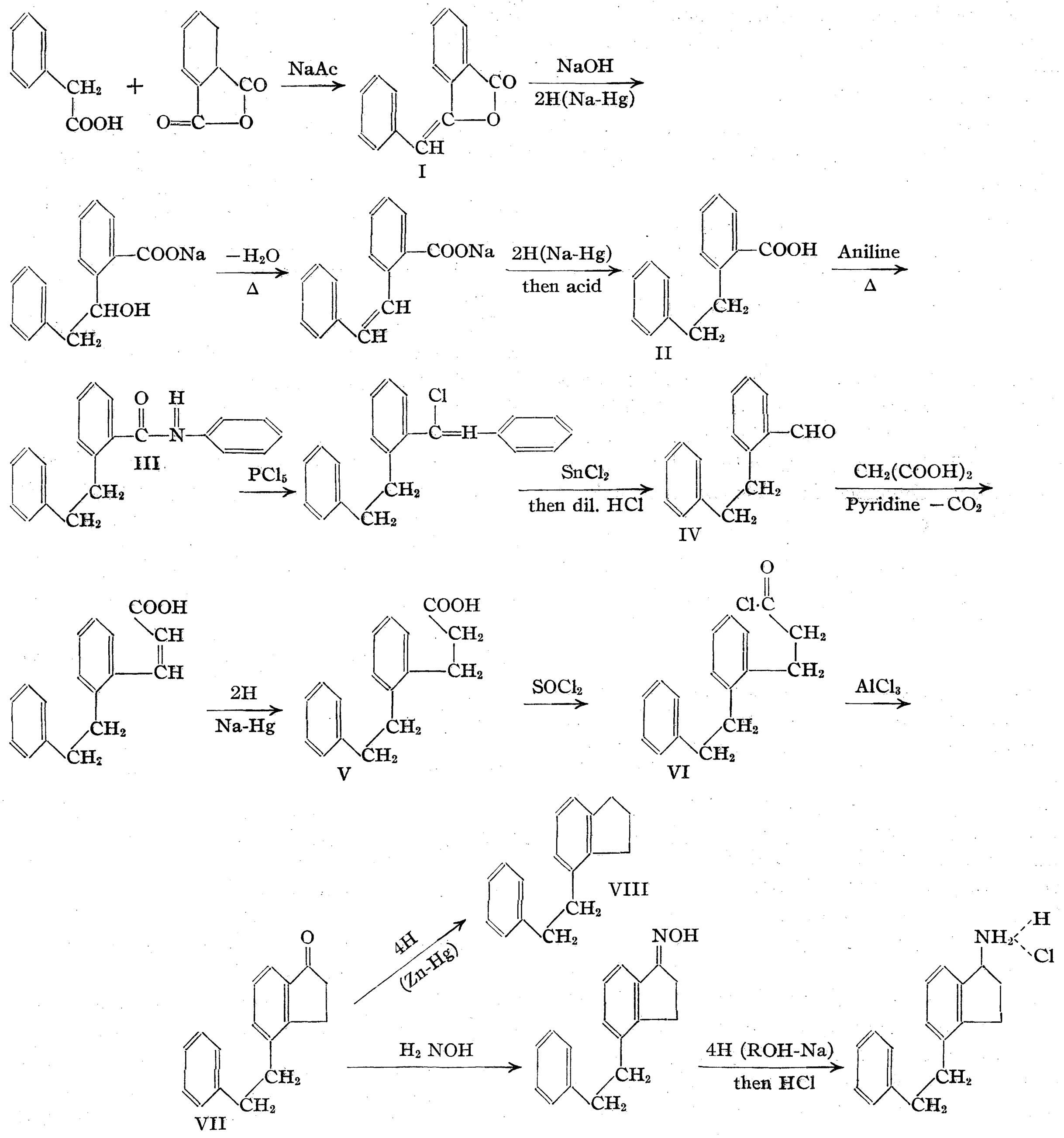
[3] Heilbron and Spring, *Chem. Ind.*, **54**, 795 (1935).

[4] Lettré, *Ann.*, **511**, 280 (1934).

[5] Müller, *Z. physiol. Chem.*, **233**, 223 (1935).

[6] "Organic Syntheses," Vol. XIII, 1933, p. 10; Gabriel, *Ber.*, **18**, 3470 (1885).

FLOW SHEET



form 4-β-phenethylindane (VIII), the structure proposed for the calciferol nucleus. This was accomplished by converting benzal-phthalide to *o*-β-phenethylbenzoic acid (II) by a reduction, dehydration and further reduction applying and improving the method of Gabriel.[7] The acid was then reduced to the corresponding aldehyde (IV) applying the general procedure of Sonn and Müller. Before this procedure was resorted to, several different methods of reduction had been tried, but all had been abandoned either because of poor yield or inability to be applied to large quantities. The following procedures were found to be inapplicable for preparing the aldehyde from the acid: catalytic reduction of the acid chloride, distillation of the calcium salt of the acid with calcium formate, reduction of the ester with sodium and butyl alcohol followed by chromate oxidation, reduction of the amide electrolytically and with so-

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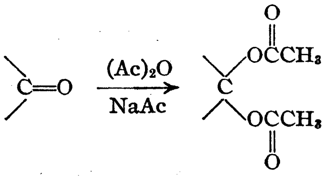
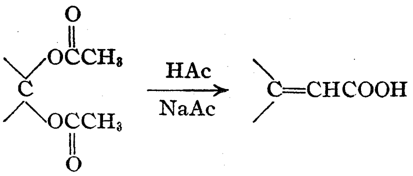
[7] Gabriel and Posner, *Ber.*, **27**, 2506 (1894).

dium amalgam, reduction of the anhydride (mixed) of this acid (II) and acetic acid.

When the Perkin reaction was applied to ortho-β-phenethylbenzaldehyde to form the substituted cinnamic acid, the main product of the reaction was found to be the substituted benzylidine diacetate, although some *o*-β-phenethylcinnamic acid was formed.



o-β-Phenethylbenzylidine diacetate when heated with sodium acetate in the presence of glacial acetic acid yielded the *o*-β-phenethylcinnamic acid. This would seem to be in line with the old Nef theory as to the mechanism of the Perkin reaction.[8]



Because of the poor yields obtained from the Perkin reaction when applied to *o*-β-phenethylbenzaldehyde (IV), this aldehyde was condensed quantitatively with malonic acid in the presence of small amounts of pyridine as a sort of modified Knoevenagel reaction. The reaction between malonic acid and the aldehyde in the presence of traces of pyridine is so satisfactory that it could be used to determine the percentage of aldehyde in a sample, by titrating the water-insoluble acid produced.

The *o*-β-phenethylcinnamic acid was then reduced to *o*-β-phenethylhydrocinnamic acid (V). This acid was then cyclized by treatment of its acid chloride (VI) with aluminum chloride in the presence of petroleum ether. The 4-β-phenethylindanone-1 formed was then reduced by the Clemmensen reduction to 4-β-phenethylindane, the ring system for the proposed structure for calciferol (vitamin D_2) and tachysterol. The formula of (VIII) is written in such a way as to indicate the close relationship to the cholane nucleus.

The over-all yield was good, 230 g. of benzal-phthalide yielding from 34–45 g. of the final product. As can be seen from the experimental part of this paper, the yields can be almost doubled if *o*-β-phenethylbenzoic acid is converted to its anilide (III) from its acid chloride by the action of thionyl chloride. The danger of using this method is that the whole yield can be ruined if traces of mercury, from earlier treatment, are present.

It is noteworthy that the ketone group in 4-β-phenethylindanone-1 is in the same position as the ketone group in androsterone and is in a favorable position for the addition of side chains in the synthesis of compounds related to sterols and bile acids.

It is apparent that by the use of substituted derivatives of phenylacetic acid and phthalic anhydride, various derivatives may be prepared. For example, 6-nitro-3-methoxyphenylacetic acid is being employed in an attempt to bring about a phenanthrene ring closure by the Pschorr method and at the same time prepare a cyclopentenophenanthrene derivative with an hydroxyl group in the same position as for cholesterol or androsterone. The close relationship between the alkaloids and sterols can be emphasized in that benzal-phthalide is closely related to benzylisoquinoline. This observation has suggested an attempt at a new method for the synthesis of benzyl isoquinoline alkaloids.

At the present time a mild reduction of calciferol and its degradation to a product which might be synthesized by this method has been undertaken to test the structure proposed for the antirachitic irradiation product produced from ergosterol.

Experimental

Benzal-phthalide.—Benzal-phthalide was prepared by the method of Weiss[6] using double the quantities specified. The yield of once crystallized material, m. p. 98–99°, is 77–84%. Care should be taken not to allow the temperature to rise above 240° for any length of time, for the yield may be completely destroyed.

Benzyl-phthalide.—Two hundred and thirty grams of benzal-phthalide is dissolved by heating with a solution of 60 g. of potassium hydroxide in 100 cc. of water. Benzal-phthalide is insoluble in hot dilute alkali. The dark red solution is then diluted to 1.5 liters with water and poured onto sodium amalgam, prepared by adding 2100 g. of mercury to 70 g. of molten sodium under mineral oil, with stirring. The solution is vigorously stirred until the color completely disappears, about four to six hours, depending upon the efficiency of the stirrer. The material is then transferred to a large separatory funnel and the mercury is drawn off. Ether is added and the mixture is shaken to remove traces of mineral oil. The lower layer is removed and acidified. The benzyl-phthalide comes down as an oil and then crystallizes in heavy colorless crystals which are

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[8] Nef, *Ann.*, **298**, 277 (1897).

filtered off, m. p. 61° (recrystallized from dilute alcohol); b. p. 190–200° (5 mm.); yield quantitative.

o-**Carboxystilbene.**—The still moist benzyl-phthalide, from the above preparation, is dissolved in 400 cc. of 95% alcohol with warming; 60 g. of potassium hydroxide is added and the whole is gradually heated in a sand-bath, in a liter flask, until all the alcohol is removed and the light brown residue begins to foam, the temperature is raised to 180° and kept there until the foaming ceases and the whole material solidifies (two to four hours). The solid while still warm is dissolved in 1.5 liters of water. If this acid is desired, the solution is washed with ether, acidified, filtered and dried to give *o*-carboxystilbene. The yield is almost quantitative (210 g.); m. p. 160° (recrystallized from dilute alcohol).

o-*β*-**Phenethylbenzoic Acid.**—The 1.5 liters of solution containing the dissolved sodium salt of *o*-carboxystilbene is added to an amalgam of 70 g. of sodium in 2100 g. of mercury. The mixture is stirred vigorously until a large part of the amalgam reacts. As the reaction proceeds, the solution becomes warm and remains warm until reduction is complete when it goes back to room temperature (four to six hours). The solution is transferred to a separatory funnel, the mercury separated and then washed with ether. All traces of colloidally suspended mercury must be removed if the acid is to be converted to the acid chloride. The solution is therefore filtered through two thicknesses of filter paper with suction, acidified and then either allowed to stand overnight or cooled with crushed ice to complete the crystallization of the acid. The acid is filtered off and dried at 60°; yield 210–211 g.; m. p. 130° (recrystallized from alcohol).

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.64; H, 6.19. Found: C, 79.30; H, 6.27.

Acid Chloride of *o*-*β*-**Phenethylbenzoic Acid.**—Two hundred and ten grams of dried, mercury-free *o*-*β*-phenethylbenzoic acid is placed in a flask fitted with a reflux condenser; 400 cc. of thionyl chloride is slowly added through the top of the condenser. This large excess of thionyl chloride is necessary before the reaction will proceed to completion. The excess over the amount consumed is recovered on distillation at the end of the reaction. The acid slowly reacts and dissolves. When addition is complete a calcium chloride tube is placed on top of the condenser and refluxing is continued for one hour on a water-bath. The excess thionyl chloride is recovered under mild vacuum on a water-bath and the residue is distilled, preferably for so large a volume at less than 10 mm. The pale yellow distillate crystallizes when scratched after cooling; yield 190 g.; m. p. 50–55°; b. p. 202° (20 mm.), 180° (5 mm.).

Anal. Calcd. for $C_{15}H_{13}O_2Cl$: Cl, 14.52. Found: Cl, 14.39.

If traces of mercury are present, large amounts of hydrogen chloride are given off and the material turns black and resinifies on attempted distillation. The ability of the smallest traces of mercury to split out large amounts of hydrogen chloride has been pointed out already.[9]

Ethyl Ester of *o*-*β*-**Phenethylbenzoic Acid.**—Two hundred and ten grams of *o*-*β*-phenethylbenzoic acid was added to 500 cc. of absolute alcohol which had been saturated with dry hydrogen chloride. Dry hydrogen chloride was passed through the cooled mixture for one hour when a large part of the acid dissolves. The mixture is then refluxed gently, in the hood, for two hours when a heavy pale yellow oily lower layer is formed. The alcohol is distilled off and the residue is vacuum distilled on a glycerol bath. The yield of pure ester, pale yellow oil, which slowly hydrolyzes in air, is 210–220 g.; b. p. 205° (18 mm.); sp. gr. 1.063 (25°); $n^{29}{}_D$ 1.5528.

Anal. Calcd. for $C_{17}H_{18}O_1$: C, 80.31; H, 7.09. Found: C, 79.99; H, 7.01.

When 64 g. of this ester is reduced with 40 g. of sodium in 400 cc. of anhydrous normal butyl alcohol with 150 cc. of toluene, 30 g. of a pale yellow liquid of b. p. 170–195° (20 mm.) is obtained. On fractional distillation this is separated into two fractions b. p. 177° (20 mm.) and 195° (20 mm.). On careful study neither of these seemed to be the alcohol. It is intended to make a detailed study of this reduction.

Mixed Anhydride of *o*-*β*-**Phenethylbenzoic Acid and Acetic Acid.**—Ten grams of *o*-*β*-phenethylbenzoyl chloride, 3 g. of sodium acetate and 8 g. of acetic anhydride are heated together for six hours at 180°. Water is added and the solution is neutralized with dilute sodium carbonate. The precipitate was filtered off and recrystallized from alcohol in which it is very soluble hot and insoluble cold; heavy colorless prisms which are rather inert but hydrolyze slowly on boiling in water. On hydrolysis by boiling in alkali and then acidification, *o*-*β*-phenethylbenzoic acid and acetic acid are obtained; m. p. 95°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.12; H, 5.97. Found: C, 76.21; H, 6.03.

o-*β*-**Phenethylbenzanilide. Method 1.**—Two hundred and ten grams of dry *o*-*β*-phenethylbenzoic acid is placed in a liter, three-necked flask, fitted with thermometer, dropping funnel and bent tube leading to a receiver; 96 g. of aniline is added and the material is slowly heated in a sand-bath to 250° when about one-half the aniline distils over with some water. The melt is kept at 250° while 125 g. of aniline is added through the dropping funnel at such a rate that the temperature never drops below 240°. Aniline continues to distil through the bent tube into the receiver carrying the water formed in the reaction with it. After all the aniline has been added (three to four hours) the temperature is kept at 240° until all the aniline distils off. The melt is poured into an aluminum dish and allowed to solidify. The solid is ground to a fine powder in a mortar, washed with dilute hydrochloric acid, transferred back to the original flask and extracted with two hot 400-cc. portions of sodium carbonate solution containing 50 g. of sodium carbonate in each portion. The residue is filtered off, washed with water and recrystallized from hot alcohol, in which it is very soluble hot and difficultly soluble cold. On acidification, the combined sodium carbonate washings yielded 75 g. of the original acid. Hence the percentage yield should be based on 135 g. of the acid; yield 125 g. of the anilide, needle-like crystals slightly colored by this method; m. p. 137°.

Anal. Calcd. for $C_{21}H_{19}ON$: C, 83.72; H, 6.31; N, 4.64. Found: C, 84.22; H, 6.18; N, 4.58.

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(9) Natelson, *Ind. Eng. Chem.*, **25**, 1391 (1933).

Method 2.—One hundred and ninety grams of the pure crystalline acid chloride is ground in a porcelain dish with 180 g. of aniline. The mixture becomes warm and forms a homogeneous melt. When the reaction has ceased the mixture is heated further on a water-bath for thirty minutes at 90°. On cooling the mass solidifies and is washed with dilute hydrochloric acid and then warm dilute sodium carbonate. On recrystallization from alcohol colorless needles are obtained, m. p. 137°, yield 200 g.

***o*-β-Phenethylbenzaldehyde.**—Three hundred grams of anhydrous stannous chloride, prepared by heating the hydrate over a small flame in a porcelain dish in the hood until all water has been removed and the material solidifies, is dissolved in one liter of anhydrous ether by passing a rapid stream of dry hydrogen chloride through the ether. Two layers form, the heavy oily lower layer contains the dissolved tin. Sonn and Müller in the preparation of this complex for reduction purposes dried their tin salt in a desiccator.[10] This does not dry the tin completely and accounts for inconsistent yields as reported by subsequent investigators. Evidence that their tin was never dry is evinced by the fact that their tin solution was homogeneous. This happens every time moisture gets into the reaction. If dry, the tin solution always separates into two layers before addition of the material to be reduced.

One hundred and twenty grams of recrystallized and dried *o*-β-phenethylbenzanilide is mixed with 110 g. of phosphorus pentachloride in a 500-cc. Claisen flask. The mixture is warmed in a water-bath until the mixture begins to liquefy. The flask is removed from the water-bath and shaken as the reaction proceeds slowly, until the mixture is all liquid except for the lumps of excess phosphorus pentachloride. The phosphorus oxychloride is removed under vacuum over a water-bath and the residue is dissolved from the excess phosphorus pentachloride by two 200-cc. portions of anhydrous ether. The ether washings are added to the stannous chloride solution and allowed to stand overnight. A vigorous reaction immediately ensues and the lower layer turns red, the tin complex of the aldehyde anil crystallizing out in yellow plates. The complex is filtered off from the heavy oily mixture and washed with ether, until the red color has been washed out; yield 138 g., yellow crystals, dec. 213°.

Anal. Calcd. for $C_{21}H_{20}NCl_3Sn$: N, 2.77. Found: N, 3.00.

To the crystals of the tin complex is added 50 cc. of 10% hydrochloric acid and steam is passed through the mixture in a steam distillation outfit. A pale yellow oil separates at the top of the solution and a small amount of the material steam distils over. The distillate and residue are combined and extracted with ether. The ether is dried over anhydrous sodium sulfate, filtered and the ether is evaporated off; yield 60 g. of a pale yellow oil; sp. gr. 1.089; n^{29}_D 1.5827.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.71; H, 6.67. Found: C, 86.00; H, 6.51.

Phenylhydrazone of *o*-β-phenethylbenzaldehyde was prepared by heating 1 g. of the aldehyde with a few drops of phenylhydrazine in 5 cc. of alcohol, adding water and recrystallizing from 80% alcohol; colorless feathery needles which turn brown on standing, m. p. 95°.

Anal. Calcd. for $C_{21}H_{20}N_2$: N, 9.33. Found: N, 9.02.

This aldehyde forms a sodium bisulfite derivative on long shaking with a saturated solution of sodium bisulfite.

***o*-β-Phenethylcinnamic Acid.**—Sixty grams of *o*-β-phenethylbenzaldehyde is added to 35 g. of malonic acid in a 600-cc. flask fitted with a calcium chloride tube; 6 g. of pyridine is added and the mixture is warmed on a water-bath at 90° for two hours. The material separates into two layers and the lower layer slowly dissolves as carbon dioxide slowly is given off. At the end of two hours the material crystallizes on shaking or cooling. The material is dissolved in 40 g. of sodium carbonate dissolved in 500 cc. of warm water. If *o*-β-phenethylhydrocinnamic acid is desired the solution is reduced directly. If *o*-β-phenethylcinnamic acid is desired the solution is extracted with ether, to remove pyridine and impurities, acidified, filtered and dried. Drying has to be finished in a desiccator for this acid holds the last traces of water tenaciously; yield 71–72 g.; m. p. 149–150° (from dilute alcohol).

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.95; H, 6.34. Found: C, 80.31; H, 6.47.

***o*-β-Phenethylhydrocinnamic Acid.**—The solution in sodium carbonate of *o*-β-phenethylcinnamic acid is poured directly onto sodium amalgam, prepared by dissolving 24 g. of sodium in 620 g. of mercury, and vigorously stirred until the solution has come back to room temperature and most of the amalgam has been decomposed (four to six hours). The mixture is transferred to a separatory funnel, the mercury separated, and the solution washed with ether. The aqueous layer is separated and filtered through a double suction filter. Since the next step is the conversion to the acid chloride, every trace of suspended mercury must be scrupulously removed even if it is necessary to filter several times. The solution is acidified, allowed to stand for several hours, filtered, washed with water and dried; yield 72 g.; colorless thick crystals; m. p. 110–111° (recrystallized from dilute alcohol).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.30; H, 7.08. Found: C, 80.11; H, 7.20.

Perkin Reaction on *o*-β-Phenethylbenzaldehyde

1. With Sodium Acetate.—Ten grams of the aldehyde, 2.5 g. of sodium acetate and 8 g. of acetic anhydride heated together for sixteen hours at 180–200° yields on extraction with sodium carbonate solution and acidification, 0.5 g. of *o*-β-phenethylcinnamic acid, m. p. 149–150° (from dilute alcohol), 1.0 g. of *o*-β-phenethylbenzylidine diacetate and 8 g. of unchanged aldehyde (average of several experiments).

2. With Potassium Acetate.—Ten grams of the aldehyde, 3 g. of potassium acetate and 8 g. of acetic anhydride heated together for six hours yield 1 g. of *o*-β-phenethylcinnamic acid, m. p. 149–150°, 8.6 g. of *o*-β-phenethylbenzylidine diacetate and practically no aldehyde. *o*-β-Phenethylbenzylidine diacetate melts at 85°.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.08; H, 6.41. Found: C, 73.51; H, 6.24.

3. Conversion of the Diacetate to *o*-β-Phenethylcinnamic Acid.—Eighteen grams of *o*-β-phenethylbenzylidine diacetate, 33 g. of acetic acid and 28 g. of sodium acetate heated at 200° for ten hours yields 10 g. of *o*-β-phenethyl-

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[10] Sonn and Müller, *Ber.*, **52**, 1927 (1919).

cinnamic acid, m. p. 149–150° (from dilute alcohol). The acids obtained from the Perkin reaction all reduced quantitatively to *o*-β-phenethylhydrocinnamic acid, m. p. 110–111°.

***o*-β-Phenethylhydrocinnamoyl Chloride.**—To 70 g. of *o*-β-phenethylhydrocinnamic acid is added 140 cc. of thionyl chloride. The mixture is refluxed for one hour and the excess thionyl chloride is removed on a water-bath. Vacuum is applied and everything that can be removed up to 100° at 10 mm. is removed. The material is transferred quantitatively with the aid of a small amount of ether to a 300-cc. distilling flask, which is sealed off at the top and connected by means of a wide side-arm to an inner seal in a 125-cc. receiving flask. The ether is evaporated off from the outfit under vacuum on a water-bath and the receiver is connected to a high vacuum produced by a mercury vapor pump backed by an oil pump. The traps are cooled with alcohol–solid carbon dioxide mixture while the receiver is cooled by an ordinary ice and salt-bath. The pressure is measured on a McLeod gage. The distilling flask is heated in a dibutyl phthalate bath. The temperature was determined by placing a thermometer in the bath. The acid chloride comes over as an almost colorless, pale yellow, mobile liquid at a bath temperature of 155–165° (slow heating) at a pressure of 0.002–0.004 mm.; yield 57 g. On heating with sodium hydroxide solution the acid chloride dissolves and on precipitation regenerates *o*-β-phenethylhydrocinnamic acid; m. p. 110°; b. p. 155–165° (0.002–4 mm.); sp. gr. 1.015; n^{29}D 1.5664.

Anal. Calcd. for $C_{17}H_{17}OCl$: Cl, 13.27. Found: Cl, 13.20.

4-β-Phenethylindanone-1.—Fifty-seven grams of *o*-β-phenethylhydrocinnamoyl chloride is dissolved in 200 cc. of redistilled, over sulfuric acid, anhydrous petroleum ether, b. p. 45–65°, 57 g. of fresh anhydrous aluminum chloride is covered with 50 cc. of petroleum ether and the petroleum ether solution of the acid chloride is added, refluxing the solution on the water-bath. Refluxing is continued for one-half hour after the final addition. Almost all the color goes from the petroleum ether layer to the aluminum chloride which now becomes a deep brown. The mixture is cooled, decomposed with crushed ice and dilute hydrochloric acid and extracted with two 250-cc. portions of ether. The combined extracts are dried with anhydrous sodium sulfate, and the mixture of petroleum ether and diethyl ether is evaporated off. The residue is extracted with hot sodium carbonate solution to recover unchanged acid, dissolved in ether, washed with water, dried with anhydrous sodium sulfate and evaporated. The residue is then distilled under high vacuum as for the acid chloride. A pale yellow viscous oil comes over up to 160° at 0.0003 mm. A better vacuum could be maintained in the absence of the acid fumes; yield 42 g. of a viscous oil which gelled at room temperature but would not crystallize. It softens to a mobile liquid just below 38° and its melting point is probably in that vicinity. On standing for several months, during which time this compound was prepared numerous times in order to attempt to obtain it crystalline, the material partly resinified. The material as first obtained is of a high degree of purity as shown by analysis and in that it gave an 88% yield of oxime and a 92% yield of hydrocarbon on reduction.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.80. Found: C, 86.08; H, 6.98.

4-β-Phenethylindanoxime-1.—Four grams of 4-β-phenethylindanone-1 is dissolved in 50 cc. of alcohol. To this mixture is added 1.6 g. of hydroxylamine sulfate dissolved in 6 cc. of water. Two drops of phenolphthalein solution are added and 10% potassium hydroxide solution is added drop by drop from a pipet until the solution is just alkaline. The mixture is refluxed and drops of alkali are added from time to time to keep the solution just alkaline. At the end of one hour the barely alkaline solution is allowed to cool, when flat glistening plates of the oxime crystallize out. If rapidly cooled the oxime comes out as needles, m. p. 135° (from alcohol in which it is very soluble hot and insoluble cold).

Anal. Calcd. for $C_{17}H_{17}ON$: N, 5.56; C, 81.31; H, 6.77. Found: N, 5.49; C, 81.40; H, 6.44.

4-β-Phenethylindanamine-1.—Three grams of 4-β-phenethylindanoxime-1 is dissolved in 100 cc. of absolute alcohol, 3 g. of sodium is added in small bits and the solution is refluxed under a condenser with a calcium chloride tube for one hour, the sodium dissolving. The solution is cooled and neutralized with concd. hydrochloric acid, 50 cc. of water is added and the alcohol is evaporated off. Some of the hydrochloride of the amine crystallizes from the aqueous solution at this point. The whole mixture is made alkaline with 10% sodium hydroxide and the amine is extracted with 50 cc. of benzene in two portions. The benzene solution is dried with anhydrous sodium sulfate and filtered. The dry benzene solution is saturated with dry hydrogen chloride and then evaporated to 10 cc. on a steam-bath; 75 cc. of anhydrous petroleum ether is added and the hydrochloride of the amine comes out in fine crystals. The crystals are filtered and washed with a 3 to 1 mixture of petroleum ether and benzene; yield 2.8 g.; m. p. 192°.

Anal. Calcd. for $C_{17}H_{21}NCl$: N, 5.12; Cl, 12.98. Found: N, 5.16; Cl, 12.96.

4-β-Phenethylindane.—Into a two-liter flask fitted with a reflux condenser, 300 g. of zinc dust is added and 4 g. of mercuric chloride dissolved in 25 cc. of hot water. The solution is slowly added to the zinc dust and thoroughly shaken and warmed.

Forty grams of 4-β-phenethylindanone-1 is dissolved in 500 cc. of alcohol which is added to the zinc dust from the top of the condenser; 400 cc. of concd. hydrochloric acid is added from the top of the condenser drop by drop refluxing the alcohol until all the hydrochloric acid has been added and a large amount of the zinc has dissolved (four hours). The condenser is turned down and the alcohol is distilled off. Care must be taken not to go too far, for the hydrocarbon which comes out as a colorless oil has a tendency to steam distil to some extent. The oil which separates at the surface of the residue is taken up in ether, dried with anhydrous sodium sulfate, filtered and the ether is evaporated off. The oil which remains is distilled under high vacuum to a colorless mobile liquid, b. p. 115–120° (0.0001 mm.); sp. gr. 1.020 (25°); n^{29}D 1.5640; yield 34 g.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.89; H, 8.11. Found: C, 91.31; H, 8.10.

The authors are indebted to Dr. B. Kramer and Albert E. Sobel for their advice and encouragement during the course of this investigation.

Summary

1. A new route to derivatives of diphenylethane related to materials occurring naturally is demonstrated.

2. 4-β-Phenethylindane is synthesized as representing the ring system for the proposed structure for calciferol and tachysterol.

BROOKLYN, N. Y. RECEIVED MAY 11, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Modification of the Clemmensen Method of Reduction[1]

BY ELMORE L. MARTIN

While a great many compounds containing the carbonyl group can be reduced by the method of Clemmensen,[2] the results sometimes leave much to be desired. Substances which neither dissolve appreciably in the acid mixture nor melt at the boiling temperature usually present difficulties and a number of readily available β-aroylpropionic acids which are of use in the synthesis of polynuclear hydrocarbons are of this type. Thus Fieser and Peters[3] observed that β-3-acenaphthoylpropionic acid is but little affected by prolonged boiling with hydrochloric acid and amalgamated zinc, Haworth and Mavin[4] found β-1-methyl-4-naphthoylpropionic acid to be unusually resistant to reduction, and Cook and Hewett[5] were unable to reduce β-1-pyrenoylpropionic acid by any of the usual modifications in the original procedure of Clemmensen. Although the addition of a miscible solvent such as alcohol, acetic acid, or dioxane facilitates the reduction of certain ketonic compounds (ketocholanic acids, hydrindones), this leads in the above cases only to resinification. The keto acid appears to undergo polymolecular reduction or condensation at the surface of the metal with the formation of a gummy, insoluble coating which obstructs the normal functioning of the zinc.

It was found by Fieser and Peters[3] and by Haworth and Mavin[4] that the reduction of the above two keto acids can be accomplished by the use of the lower-melting esters, but the yield in the first case was only 40% and the process was tedious. After repeating Fieser and Peters' experiments with the same results it was found that when toluene was added in quantity sufficient to retain the ester in a clear surface layer the yield of the pure reduction product rose to 60% and the process was greatly simplified. The surface of the metal remained clean and bright throughout the reaction and the product was easily isolated from the toluene layer. Attempts to reduce free β-3-acenaphthoylpropionic acid in the presence of toluene were successful only when a small amount of acetic acid was used to provide the required, slight concentration of the keto acid in the aqueous layer. The toluene probably is beneficial partly because it keeps the otherwise undissolved material out of contact with the metal and partly because in the two-phase system the reduction occurs at such a high dilution that polymolecular reactions are largely inhibited.[6]

Various fellow workers engaged in synthetic experiments in this Laboratory kindly coöperated in testing the toluene method, and the yields of purified products, usually checked in two or more experiments, are summarized in Table I. The author is indebted to Mr. C. K. Bradsher, Mr. J. T. Dunn, Mrs. L. F. Fieser, Dr. E. B. Hershberg, Mr. H. L. Holmes, Mr. W. C. Lothrop, Dr. M. S. Newman and Mr. C. C. Price for permission to report their results. The β-aroylpropionic acids investigated were invariably reduced more satisfactorily in the presence of toluene than without it, and two acids could be reduced in this way but not by the usual procedure. With β-1-pyrenoylpropionic acid, however, the results were negative both with and without toluene. The modification seems definitely advantageous with compounds containing methoxyl groups, for the difficulties frequently experienced are at least mini-

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[1] Paper prepared by L. F. Fieser.

[2] Clemmensen, (a) *Ber.*, **46**, 1838 (1913); (b) **47**, 51, 681 (1914).

[3] Fieser and Peters, THIS JOURNAL, **54**, 4374 (1932).

[4] Haworth and Mavin, *J. Chem. Soc.*, 2720 (1932).

[5] Cook and Hewett, *ibid.*, 398 (1933).

[6] Lewis, Ramage and Robinson [*ibid.*, 1414 (1935)] used anisole in two Clemmensen reductions but gave no results by the usual procedure for comparison.

TABLE I

COMPARISON OF YIELDS

	Clemmensen's procedure		Modified procedure		
Reduction of	Yield, %	Experimenter	Yield, %	M.p., ° C.	Experimenter
β-Benzoylpropionic acid	72–78[a]	E.L.M.	90	46–48	E.L.M.
β-*p*-Toluylpropionic acid	88[a]	J.T.D.	92	61–62	J.T.D.
β-*m*-Toluylpropionic acid	...	...	84	35–36	J.T.D.
β-*p*-*t*-Butylbenzoylpropionic acid	...	...	72	57–60	C.C.P.
β-1-Naphthoylpropionic acid	...	...	86	109	M.F.
β-2-Naphthoylpropionic acid	...	...	91	94–96	E.L.M.
β-3-Acenaphthoylpropionic acid	0	Ref. 3	50[b]	147–148	E.L.M.
Methyl ester	36–47	Ref. 3	60	147–148	E.L.M.
β-*t*-Butylnaphthoylpropionic acid	...	...	78[b,c]	...	C.C.P.
β-3-Methoxybenzoylpropionic acid	15	Ref. 7	25–60	45–47	E.L.M.
β-4-Methoxybenzoylpropionic acid	?	Ref. 8	85	60–61	E.B.H.
β-3-Methoxy-4-methylbenzoylpropionic acid	...	...	86	70–71	E.L.M.
β-3,4-Dimethoxybenzoylpropionic acid	?	Ref. 9	80[b,d]	61–62	H.L.H.
β-4-Methoxy-1-naphthoylpropionic acid	43	E.B.H.	53[b]	129–130	E.L.M.
β-2,5-Dimethyl-4-methoxybenzoylpropionic acid	92	Ref. 10	97	98	W.C.L.
5-Methoxy-6-methylhydrindone-1	...	...	85[e]	...	W.C.L.
1-Benzoylnaphthalene	63	C.K.B.	70	58–59	C.K.B.
β-Naphthyl methyl ketone	...	...	52[f]	...	M.S.N.
1-Benzoyl-4-methoxynaphthalene	0	C.K.B.	30[b]	82–83	E.L.M.
γ-Phenylbutyrolactone	...	...	81	46–48	E.L.M.

[a] Following the procedure of "Organic Syntheses," Vol. XV, 1935, p. 64. [b] Acetic acid was added to the reaction mixture. [c] Isolated as the ester; b. p. 185–187° at 6 mm. [d] Four 100-g. portions were reduced and the products combined for purification. The heating was continued in this case for forty-one hours; in earlier reductions continued for only twenty to twenty-two hours the yield was poorer by 10–15%. [e] To complete the reduction it was necessary to submit the crude product to further reaction with no added toluene. [f] B. p. 122–125° at 14 mm.

mized. With neutral ketones of very slight water-solubility it is sometimes difficult to effect complete reduction using toluene, and in the case of hydrindones it probably is better to use a water-miscible solvent.

γ-*m*-Methoxyphenylbutyric acid, a useful intermediate in synthesis, has been prepared from *m*-methoxybenzoyl chloride in about 2% yield in a two-step process involving a Clemmensen reduction[7] and from *m*-methoxybenzaldehyde in eight steps in about 35% yield.[11] A third method was tried in the present work but found unsatisfactory. β-*m*-Methoxybenzoylpropionic acid was obtained fairly satisfactorily from β-benzoylpropionic acid through the *m*-nitro compound, but, although on a small scale the Clemmensen reduction in the presence of toluene seemed promising (60% yield) in comparison with Thompson's results,[7] on a larger scale a resinous oil separated from the toluene layer, the product was difficult to purify, and the yield was poor.[11a] In contrast to this experience β-3-methoxy-4-methylbenzoylpropionic acid was prepared easily from β-*p*-toluylpropionic acid through the nitro compound and there was no difficulty in effecting the reduction on either a small or large scale, γ-3-methoxy-4-methylphenylbutyric acid being obtained in an over-all yield of 35%. The 3,4-dimethoxy compound (Table I) is also reduced smoothly, and it appears that the abnormal side reaction noted in one case is inhibited by a substituent in the position ortho to the methoxyl and para to the group undergoing reduction.

Turning to another type of reaction, it was found that anthracene and β-methylanthracene can be obtained in excellent yield and high purity by the reduction of the anthrones with zinc dust

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(7) Thompson, *J. Chem. Soc.*, 2314 (1932).

(8) Krollpfeiffer and Schäfer, *Ber.*, **56**, 630 (1923).

(9) Haworth and Mavin, *J. Chem. Soc.*, 1486 (1932).

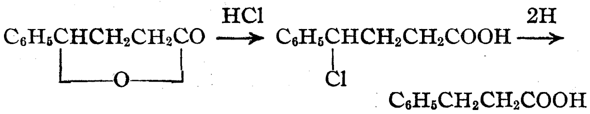
(10) Clemo, Haworth and Walton, *ibid.*, 2381 (1929).

(11) Robinson and Schlittler, *ibid.*, 1288 (1935).

(11a) In a paper which has come to our hands as the present communication is going to press, Chuang and Huang, *Ber.*, **69**, 1505 (1936), have described the same process for the preparation of γ-*m*-methoxyphenylbutyric acid. The procedures for carrying out the various steps differ in some details but the results are much the same up to the Clemmensen reduction. Regarding the final step we feel that Chuang and Huang have not adequately demonstrated that the reaction proceeds as well as their statements imply, for they report a yield (67%) only for the crude, alkali-soluble fraction remaining after evaporation of the ether (14-g. run). Martin's yield (60%) for 3–5 g. runs refers to material that had been re-methylated, distilled and obtained as a solid, m. p. 45–47°. It is the general experience in this Laboratory that methoxy compounds invariably are demethylated to some extent even when using toluene, and we found that the resinous material which appeared when operating with moderately large amounts is alkali-soluble and cannot be removed effectively except by distillation. In view of the irregular and generally unsatisfactory results obtained repeatedly by both Martin and Hershberg, we do not share the favorable opinion of the method expressed by the Chinese investigators.—L. F. FIESER.

and sodium hydroxide in the presence of toluene. The process is simpler and more convenient than the usual one.

An incidental observation having some bearing on the mechanism of the Clemmensen reaction is that γ-phenylbutyrolactone gives about as good a yield of γ-phenylbutyric acid as does β-benzoylpropionic acid. Clearly it is not the lactone itself which combines with hydrogen, for the carboxyl group could not then appear in unmodified form, and it may be inferred that the lactone ring first opens with the formation of either the γ-hydroxy acid or the γ-chloro acid and that it is one or the other of these substances which suffers reduction. The chloro compound probably is formed in preponderant amount:



$$C_6H_5\underset{\lfloor\_\_\_O\_\_\_\rfloor}{CHCH_2CH_2CO} \xrightarrow{HCl} C_6H_5\underset{Cl}{CH}CH_2CH_2COOH \xrightarrow{2H} C_6H_5CH_2CH_2COOH$$

Possibly the reduction of a carbonyl compound with zinc and hydrochloric acid normally proceeds through the alcohol and the chloride. The idea is supported to some extent by the observation that both benzyl alcohol and benzyl chloride, like benzaldehyde,[2a,12] yield a certain amount of toluene on reduction with zinc and hydrochloric acid. Benzhydrol,[12] triphenylcarbinol[13] and triphenylbromomethane[13] have been similarly reduced to the hydrocarbons, but these perhaps are special cases. On the other hand, there have been some reports of the failure to reduce primary[2b] and secondary alcohols, the most striking example being in the bile acid series. For the conversion of a hydroxycholanic acid into a cholanic acid the standard method is to oxidize the substance to a ketone and then apply the Clemmensen reaction, for the hydroxy acid usually is converted only into resinous products when treated directly with zinc and acid.[14] Although this would seem to indicate that the alcoholic compound is not an intermediate in the reduction of the ketone, the direct replacement of a hydroxyl group by hydrogen, however rare, has been observed in at least one case (3-hydroxy-12-ketocholanic acid).[14] Possibly the poor result obtained with a hydroxycholanic acid is due not to the failure of the substance to undergo reduction but to the occurrence of side reactions, such as dehydration, when the alcoholic compound is present from the start in high concentration. That the carbonyl compound gives a better result may be because the alcohol is never present in large amounts but is rapidly removed from the destructive influence of the acid by reduction, either as such or through the chloride. Possibly it is merely because the di- and tri-aryl carbinols are not subject to dehydration that the direct reduction presents no difficulties.

Experimental Part

Modified Clemmensen Method

General Procedure.—It was found that the time allowed for amalgamating the zinc can be shortened and equally active material obtained by shaking for five minutes a mixture of 100 g. of mossy zinc, 10 g. of mercuric chloride, 5 cc. of concentrated hydrochloric acid and 150 cc. of water. The solution was decanted and the other reagents were added in order as follows: 75 cc. of water, 175 cc. of concentrated hydrochloric acid, 100 cc. of toluene and 50 g. of the carbonyl compound to be reduced. In the case of substances very sparingly soluble in water a small amount (3–5 cc.) of glacial acetic acid was added. The mixture was refluxed briskly for twenty-four hours, three 50-cc. portions of concentrated hydrochloric acid being added at intervals of about six hours. Although this treatment usually is sufficient to complete the reduction, further heating of the reaction mixture with the addition of fresh acid does no harm and in some of the experiments there were indications that the yield is increased slightly by extending the refluxing period.

In the preparation of γ-phenylbutyric acid, its homologs, and other low-melting substances readily soluble in toluene the reaction mixture was cooled to room temperature, the toluene layer was separated and the aqueous layer was diluted and extracted with ether. After removing the solvent from the combined extracts the product was distilled in vacuum, giving material which ordinarily required no further purification. In working up the reaction mixtures from methoxylated keto acids the procedure was modified as follows to provide for the recovery of demethylated material. The combined solution in toluene and ether was mixed with an excess of dilute alkali, the solvent was removed by steam distillation, and after cooling the alkaline solution to about 80° an excess of dimethyl sulfate (20–25 cc.) was added, keeping the solution alkaline. In case the solution tended to darken, sodium hydrosulfite was added. Any ester which may be formed is saponified in the hot alkaline medium. The solution was clarified if necessary, after neutralizing the excess alkali, cooled and acidified. The product usually was dried in ether and purified by vacuum distillation. In preparing higher-melting, less soluble compounds such as the γ-naphthylbutyric acids the toluene layer was separated after allowing the solution to cool to 50–60°, benzene being used if necessary to keep the material in solution and for extraction of the water layer. In case the combined extracts contained coloring matter arising from the presence of impurities in the starting material, it was found most effective to clarify the solution with active carbon while still wet. A part of the solvent was removed by distillation along with any residual water, and on cooling the product

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[12] Steinkopf and Wolfram, *Ann.*, **430**, 113 (1923).

[13] Acree, *Ber.*, **31**, 616 (1898).

[14] Borsche and Hallwass, *ibid.*, **55**, 3325 (1922).

crystallized, usually in a very pure condition. To recover the material retained in the mother liquor it was sometimes convenient to steam distil the solvent from a mixture with soda solution, clarify the cooled aqueous solution, and precipitate the product.

In several cases the quantity of the carbonyl compound was increased to 100–150 g. without any essential change in the procedure or in the yield.

Special Cases.—In the reduction of γ-phenylbutyrolactone (Table I), 5 g. of material was used and the mixture was refluxed for thirteen hours. In attempting to reduce β-pyrenoylpropionic acid it was found that both the acid and the ester remained unchanged after long boiling and that the addition of acetic acid led only to the resinification of the product. *o*-Benzoylbenzoic acid was reduced successfully by the modified procedure but the process was less convenient than reduction with zinc dust and alkali and the yield was not as good. Benzyl alcohol was reduced by heating for nine hours a mixture of 25 g. of the material, 50 g. of amalgamated zinc, 90 cc. of concentrated hydrochloric acid and 40 cc. of water, adding 50 cc. more acid from time to time. Fractionation of the mixture yielded 4 g. (19%) of toluene, b. p. 110–113°, and there was considerable high-boiling material. Reduced in the same manner 25 g. of benzyl chloride gave 5 g. (27%) of toluene.

Reduction with Zinc Dust and Alkali

Anthracene from Anthrone.—Twenty-five grams of zinc dust was allowed to stand for a few minutes with an aqueous solution of 0.1 g. of copper sulfate crystals, the solution was poured off and to the activated metal were added 400 cc. of 2 *N* sodium hydroxide, 100 cc. of toluene, and lastly 10 g. of anthrone. The mixture was heated under reflux in an oil-bath and kept boiling gently for twelve hours. The aqueous layer at first assumed a bright red color, after about three hours it turned to a light yellow, and finally both layers became colorless. The mixture was allowed to cool slightly, 100 cc. of benzene was added, and the liquid mixture was transferred to a separatory funnel, using 100 cc. more benzene to wash the zinc residue. The hydrocarbon solution was treated with active carbon while still wet, concentrated to a volume of 50–60 cc., and allowed to cool. The anthracene separated in the form of thin, colorless, highly fluorescent plates, m. p. 216–216.5°, corr.; yield 8.6 g. (93%).

Anthracene from Anthraquinone.—Following the same procedure as above but starting with the quinone it was necessary to continue the refluxing for forty-eight hours and the anthracene, obtained in 80% yield, did not exhibit the beautiful fluorescence of the product from anthrone and melted about one degree lower.

β-**Methylanthracene** was prepared as above from 2-methylanthrone-9, the yield of once recrystallized material being 86%; m. p. 209–209.5° corr. The yield from β-methylanthraquinone was 80% and the reduction was complete only after four days.

γ-*m*-Methoxyphenylbutyric Acid

β-*m*-**Nitrobenzoylpropionic Acid.**—To a mechanically stirred mixture of 60 cc. of nitric acid (sp. gr. 1.5) and 6 cc. of concentrated sulfuric acid 30 g. of β-benzoylpropionic acid was added in portions while keeping the mixture at −10 to 0° by efficient cooling. This required twenty to twenty-five minutes. The temperature was then allowed to rise to 15° in the course of thirty minutes and the solution was slowly stirred into ice and water. The precipitated material was washed free of acid and crystallized from methyl alcohol, giving nearly colorless needles, m. p. 162–164°, corr., of the meta isomer; yield, 21–23 g. (57–62%). The substance crystallizes from water as long, faintly yellow needles.

Anal. Calcd. for $C_{10}H_9O_5N$: C, 53.79; H, 4.07. Found: C, 53.90; H, 4.05.

The methyl ester crystallized from ether–petroleum ether as colorless needles, m. p. 68–69°, corr.

Anal. Calcd. for $C_{11}H_{11}O_5N$: C, 55.67; H, 4.68. Found: C, 55.84; H, 4.63.

β-*m*-**Aminobenzoylpropionic Acid.**—A solution of 44.6 g. of the nitro compound in 125 cc. of ammonium hydroxide (sp. gr. 0.90) and 75 cc. of water was saturated with hydrogen sulfide, keeping the temperature from rising above 50° by good cooling. The ammonium salt of the starting material at first separated but later redissolved as the exothermic reaction proceeded. The resulting solution was allowed to stand at room temperature for one hour and boiled gently to expel excess gases, the color changing from dark orange-red to yellow-green. The addition of 1–2 g. of sodium hydrosulfite produced a pale yellow solution, and after removing the precipitated sulfur by filtration the solution was boiled with 50 cc. of concentrated hydrochloric acid to coagulate traces of sulfur, it was clarified with active carbon, treated with 50 cc. more of the concentrated acid, and evaporated under vacuum until crystals of the amine hydrochloride began to separate. After thorough cooling the slightly yellow hydrochloride which crystallized was collected and washed with a small amount of cold concentrated hydrochloric acid; yield, 35–40 g. (77–87%). The salt is readily soluble in water and is only partially precipitated by the addition of concentrated hydrochloric acid, giving colorless needles, m. p. above 250° with decomposition.

Anal. Calcd. for $C_{10}H_{12}O_3NCl$: C, 52.27; H, 5.27. Found: C, 52.52; H, 5.30.

The free amine was obtained by adding slightly less than one equivalent of alkali to a solution of the hydrochloride. Thin, colorless plates, m. p. 131–132°, corr., were obtained by crystallization from water (80% conversion).

Anal. Calcd. for $C_{10}H_{11}O_3N$: C, 62.14; H, 5.74. Found: C, 61.95; H, 5.68.

Reduction of the nitro compound with sodium hydrosulfite or stannous chloride was less satisfactory. Dr. E. B. Hershberg employed the method of catalytic hydrogenation with success and obtained about the same yield as above.

β-*m*-**Hydroxybenzoylpropionic Acid.**—A solution of 7.7 g. of the amine in 35 cc. of water containing 5.5 cc. of concentrated sulfuric acid was cooled to 0° and the paste of the sulfate was treated with a solution of 2.7 g. of sodium nitrite in 10 cc. of water. To the clear solution of the diazonium salt was added 5 cc. of concentrated sulfuric acid and 3.7 g. of boric acid and the mixture was slowly heated to gentle boiling. The evolution of nitrogen was complete soon after the mixture had reached the boiling point. Enough water was added to dissolve the hydroxy com-

TABLE II

Substance	Crystal form	Yield, %	M.p., °C., corr.	Formula	Analyses, % Calcd. C	H	Found C	H
β-3-Nitro-4-methylbenzoylpropionic acid	Needles	78	148–150	$C_{11}H_{11}O_5N$	55.67	4.68	55.75	4.60
Methyl β-3-nitro-4-methylbenzoylpropionate	Needles	90	50–51	$C_{12}H_{13}O_5N$	57.35	5.22	57.49	5.17
β-3-Amino-4-methylbenzoylpropionic acid hydrochloride	Needles	90	144–146	$C_{11}H_{14}O_3NCl \cdot H_2O$	50.46	6.16	50.56	6.12
β-3-Amino-4-methylbenzoylpropionic acid	Fine needles	85	148–149	$C_{11}H_{13}O_3N$	63.74	6.33	63.93	6.22
β-3-Hydroxy-4-methylbenzoylpropionic acid	Plates	80	172–173	$C_{11}H_{12}O_4$	63.43	5.81	63.40	5.83
β-3-Hydroxy-4-methylbenzoylpropionic acid semicarbazone	Needles		188–190	$C_{12}H_{15}O_4N_3$	54.32	5.70	54.13	5.41
β-3-Methoxy-4-methylbenzoylpropionic acid	Fine needles	85	120–121	$C_{12}H_{14}O_4$	64.83	6.35	64.92	6.49
β-3-Methoxy-4-methylbenzoylpropionic acid semicarbazone	Needles		172–173	$C_{13}H_{17}O_4N_3$	55.87	6.14	56.06	5.96
γ-3-Methoxy-4-methylphenylbutyric acid	Thin plates	86	70–71	$C_{12}H_{16}O_3$	69.20	7.75	69.20	7.64

pound and the solution was clarified with charcoal and the slightly yellow filtrate cooled in salt–ice. The product separated as nearly colorless crystals, m. p. 137–140°, yield 7 g. (90%). Crystallization from water (charcoal) gave colorless plates, m. p. 144–145°, corr.; yield 6.2 g. (80%).

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.82; H, 5.19. Found: C, 61.63; H, 5.33.

The semicarbazone crystallized from alcohol as colorless needles, m. p. 198–200°, corr.

Anal. Calcd. for $C_{11}H_{13}O_4N_3$: C, 52.57; H, 5.32. Found: C, 52.55; H, 5.46.

β-*m*-Methoxybenzoylpropionic Acid.—A solution of 6.2 g. of the hydroxy compound in 40 cc. of a 10% solution of sodium hydroxide was treated with 6 cc. of dimethyl sulfate at 40–50° and the ester produced was saponified by boiling in alkaline solution. Excess alkali was neutralized and the solution was treated with charcoal. The nearly colorless filtrate was cooled to 40° and acidified, and after thorough cooling the colorless, crystalline product was collected and washed; m. p. 102–104°, yield 6.1 g. (92%). Crystallization from methyl alcohol gave fine, colorless needles, m. p. 107–108°, corr.; yield 5.7 g. (86%). Thompson[7] reports the melting point of the acid as 110–111°.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.43; H, 5.81. Found: C, 63.20; H, 5.76.

The semicarbazone melted at 177–178°, corr., in agreement with the value given by Thompson.

When small amounts (3–5 g.) of the keto acid were reduced by the modified Clemmensen method the toluene layer remained clear and γ-*m*-methoxyphenylbutyric acid of apparently good quality was obtained in the final distillation in 60% yield. With larger amounts (15–25 g.) oily resinous matter separated from the toluene as stated above whether the mixture was boiled from the start or allowed to stand for several hours at room temperature, and also when the keto acid was added in small portions to the boiling mixture.

γ-3-Methoxy-4-methylphenylbutyric Acid

This acid was prepared from β-*p*-toluylpropionic acid in a series of processes entirely similar to those described above. The yields in the various reactions, given for purified products, and the physical constants and analyses of the compounds are given in Table II.

Summary

1. It is shown that in the reduction of carbonyl compounds by the Clemmensen method improved results are often obtained by adding a layer of toluene to the reaction mixture. The modification is particularly useful in the preparation of γ-arylbutyric acids and in the reduction of compounds containing the methoxyl group. The immiscible solvent also can be used to advantage in the reduction of anthrones to anthracenes with zinc dust and alkali.

2. It is suggested that the Clemmensen reduction of a carbonyl compound proceeds through the alcohol and the chloride, and one or two observations offering some support for this view are recorded.

3. A new route to γ-*m*-methoxyphenylbutyric acid has been investigated and found unsatisfactory in the final step, although by the same process the *m*-methoxy-*p*-methyl derivative can be prepared in good yield.

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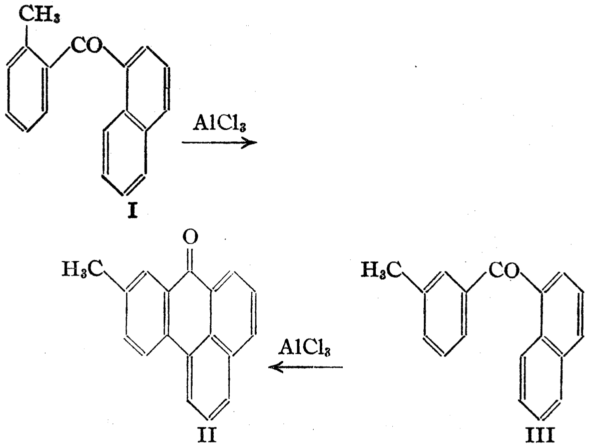
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Conversion of Tolyl Naphthyl Ketones into Methylbenzanthrones

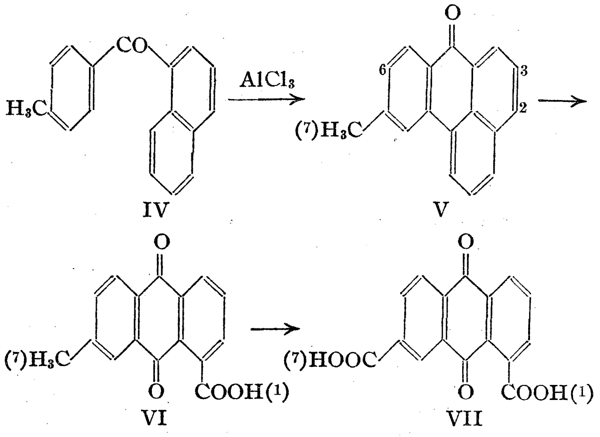
BY L. F. FIESER AND E. L. MARTIN

Among other instances of the migration of methyl groups in the course of the Scholl reaction reported by Mayer, Fleckenstein and Günther,[1] it was stated that both *o*-tolyl α-naphthyl ketone (I) and *m*-tolyl α-naphthyl ketone (III) yield the same (6)-methylbenzanthrone (II) on being heated with aluminum chloride. Scholl and Seer[2] had reported the reactions and established structure of the product from III by an independent synthesis of II, but had not recognized the identity of the substance obtained from the isomeric ketone, m. p. 64°, which they prepared from *o*-toluyl chloride and naphthalene and for which they assumed the structure I. In preparing a quantity of *o*-tolyl α-naphthyl ketone for a proposed study of the Elbs reaction we employed α-naphthylmagnesium bromide and *o*-tolunitrile and obtained a ketone, m. p. 52–53°, apparently different from that of Scholl and Seer, and since the observation cast some doubt on the reported rearrangement the matter was investigated further. Since a ketone having the melting point of the Scholl and Seer compound was obtained from *o*-tolylmagnesium bromide and β-naphthonitrile, it is probable that the purified product isolated by these investigators was *o*-tolyl β-naphthyl ketone. From the β-isomer we were unable to obtain a benzanthrone, while the pure α-isomer (I) was found to yield 6-methylbenzanthrone, II, which we also prepared from *m*-tolyl α-naphthyl ketone (III), synthesized by a method which establishes its structure. Although the original evidence was unsound, the conclusion of Mayer and co-workers is thus shown to be valid. It is probable that both earlier investigators employed the crude ketone mixture from the Friedel and Crafts reaction and that this contains a considerable proportion of the α-isomer (I) along with the substance actually isolated.



Samples of pure *m*-tolyl- and *p*-tolyl α-naphthyl ketone prepared by Grignard reactions corresponded in melting point and in their behavior with aluminum chloride to the descriptions of Scholl and Seer and of Mayer and co-workers. The corresponding β-isomers differ little in melting point but do not yield benzanthrones in the Scholl reaction.

The methylbenzanthrone obtained from pure *p*-tolyl α-naphthyl ketone (IV) corresponded to the earlier descriptions.[1,2] To test the assumption[1,2] that this is the 7-methyl derivative (V) and that no migration occurs in its formation, the substance was oxidized to a methylanthraquinone carboxylic acid and then to an anthraquinone dicarboxylic acid. The former substance yielded β-methylanthraquinone on decarboxylation, whence the original methyl group must be at the 2-, 3-, 6- or 7-position. Since 2- and 6-methylbenzanthrone are both known substances different from the compound in question, these positions are eliminated. The dicarboxylic acid could only be the 1,3- or the 1,7-derivative and on preparing the former substance[3] for comparison it was found to be different.



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[1] Mayer, Fleckenstein and Günther, *Ber.*, **63**, 1464 (1930).

[2] Scholl and Seer, *Ann.*, **394**, 111 (1912).

[3] Elbs and Günther, *Ber.*, **20**, 1364 (1887).

Therefore the oxidation products are the 1,7-derivatives VI and VII and the product of the Scholl reaction is 7-methylbenzanthrone (V). 6-Methylanthraquinone-1-carboxylic acid and anthraquinone-1,6-dicarboxylic acid were prepared for comparison from II.

Experimental Part

Preparation of the Ketones.—The components employed are indicated in Table I. The Grignard reagent was prepared under nitrogen from 3 g. of magnesium, 0.1 mole of the bromo compound and 120 cc. of dry ether, and to this was added a solution of 0.1 mole of the nitrile in 125 cc. of dry, thiophene-free benzene. A crystalline solid usually separated but when the ether was removed by slow evaporation in the nitrogen stream this dissolved. The reddish-brown benzene solution was refluxed for twenty-four hours and poured onto a mixture of water (100 cc.), ice (100 g.) and concentrated hydrochloric acid (30 cc.). The mixture was submitted to steam distillation for one hour both to remove the solvent and unreacted nitrile and to effect hydrolysis of the ketimine. The residual oil was taken up in ether, washed with sodium carbonate solution, and on vacuum distillation the ketone was obtained as a pale yellow oil which afforded a colorless, crystalline product when a fairly dilute solution in methyl alcohol was allowed to stand for some time. Further crystallization did not alter the melting points of the first crystallizates and the yields are reported for these products.

TABLE I

TOLYL NAPHTHYL KETONES

Ketone	Prepared from	Yield (pure) %	M. p., °C. Found	M. p., °C. Lit.
o-Tolyl-α-naphthyl[a]	α-$C_{10}H_7MgBr$ + *o*-$CH_3C_6H_4CN$	57	52–53	
o-Tolyl-β-naphthyl	*o*-$CH_3C_6H_4MgBr$ + β-$C_{10}H_7CN$	53	63–64	64[2]
m-Tolyl-α-naphthyl	*m*-$CH_3C_6H_4MgBr$ + α-$C_{10}H_7COCl$	40	72–73	74–75[2]
m-Tolyl-β-naphthyl[b]	*m*-$CH_3C_6H_4MgBr$ + β-$C_{10}H_7CN$	55	76–77	
p-Tolyl-α-naphthyl	α-$C_{10}H_7MgBr$ + *p*-$CH_3C_6H_4CN$	65	83–84	85[2]
p-Tolyl-β-naphthyl[c]	*p*-$CH_3C_6H_4MgBr$ + β-$C_{10}H_7CN$	50	90–91	

[a,b,c] *Anal.* Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: (a) C, 87.97; H, 5.85; (b) C, 87.66; H, 5.56; (c) C, 87.66; H, 5.75.

The mother liquor often yielded 10–15% more material melting 2–3° low. The procedure was varied in some experiments by shaking the benzene solution with acetic acid (10 cc.), water (100 cc.) and ice (100 g.), discarding the water layer, and precipitating the ketimine hydrochloride as an oil by the addition of 100 cc. of concentrated hydrochloric acid. After decanting the liquor the oil was boiled with 200 cc. of water for one hour to effect hydrolysis, and the ketone was purified as above. The product was obtained in no better yield or purity than before and it seemed that the simpler procedure is preferable. In the experiment using β-naphthoyl chloride the Grignard reagent was added inversely to a solution of the chloride (0.1 mole) in 200 cc. of ether. The ketones were all obtained completely colorless, usually as needles, from methyl alcohol.

6-Methylbenzanthrone (II).—No difference was noted in the yield or quality of the material obtained from either *o*-tolyl α-naphthyl ketone or *m*-tolyl α-naphthyl ketone. When either ketone (3 g.) was heated with aluminum chloride (15 g.) at 150° the yield of pure product isolated was 0.5 g. (17%), but the yields were much improved by employing sodium aluminum chloride. To a melt prepared from 20 g. of aluminum chloride and 4 g. of sodium chloride 2.46 g. of either ketone was added and the temperature was raised from 90 to 150° in one and one-half hours and maintained at 150° for two hours. The red melt was stirred into ice and hydrochloric acid and the tarry product was extracted with acetic acid and precipitated with water and then crystallized to a constant melting point from alcohol; yield 1.4 g. (58%). The compound formed fine, bright yellow needles, m. p. 167–168°, in agreement with the literature.[1,2]

7-Methylbenzanthrone (V) was obtained from *p*-tolyl α-naphthyl ketone in 16–20% yield (pure) using aluminum chloride and in 50% yield with sodium aluminum chloride; fine, bright yellow needles, m. p. 158–159°.

6-Methyl- and 7-Methylanthraquinone-1-carboxylic Acid.—A solution of 1 g. of 6-methylbenzanthrone in 20 cc. of glacial acetic acid was prepared at 70° and treated slowly with 4 g. of chromic anhydride in 2 cc. of water diluted with 20 cc. of acetic acid, keeping the temperature at 60–70° by occasional cooling. Soon after the addition was complete the product was precipitated by adding water. The crude acid was dissolved in dilute ammonia solution, and after clarification with Norite the light yellow filtrate was acidified at the boiling point. On crystallization from dilute alcohol 6-methylanthraquinone-1-carboxylic acid (a) separated slowly as light yellow needles, m. p. 264–266°; yield 0.7 g. (64%). 7-Methylanthraquinone-1-carboxylic acid (b), obtained similarly from V in 55% yield, formed stout yellow needles, m. p. 310–312° from acetic acid. Mayer, *et al.*,[1] report 312–314°. The alkaline solutions of the acids are pale yellow, the vats are deep red.

Anal. Calcd. for $C_{16}H_{10}O_4$: C, 72.15; H, 3.79. Found: (a) C, 72.20; H, 3.75; (b) C, 72.01; H, 3.82.

Each acid was decarboxylated in quinoline solution at 170° in the presence of Naturkupfer C, and the product was obtained by pouring the mixture onto water and adding hydrochloric acid. Crystallized from alcohol, the product in each case melted at 173–174° alone or when mixed with authentic β-methylanthraquinone; yield 90%.

Anthraquinone-1,6- and 1,7-Dicarboxylic Acids.—After heating 0.2 g. of 6-methylanthraquinone-1-carboxylic acid with 3 cc. of nitric acid, sp. gr. 1.1, in a sealed tube at 200–210° for five hours, there was obtained on cooling 0.21 g. of bright yellow needles of the 1,6-acid (a). This was purified by precipitation from a clarified ammonium hydroxide solution, by refluxing with a concentrated nitric acid (6 cc.)-water (1 cc.) mixture, which left the substance undissolved but less highly colored, and finally by crystallization from a large volume of alcohol; faintly yellow needles, m. p. 336–338°. Anthraquinone-1,7-dicarboxylic acid (b), similarly prepared and purified, formed light yellow, microscopic crystals, m. p. 346–348°. The alkaline solutions of the acids are nearly colorless, the vats are red.

Anal. Calcd. for $C_{16}H_8O_6$: C, 64.84; H, 2.72. Found: (a) C, 64.90; H, 2.90; (b) C, 64.64; H, 2.73.

Anthraquinone-1,3-dicarboxylic Acid.—Phthalic anhyhydride (7.4 g.) was condensed with *m*-xylene (25 cc.) by the addition of aluminum chloride (15 g.), heating the mixture on the steam-bath for one-half hour to complete the reaction. The keto acid precipitated from soda solution, yield 11.5 g. (91%), m. p. 130–133°, was heated with 55 cc. of concentrated sulfuric acid for one hour on the steam-bath, giving after one crystallization from alcohol 6.9 g. (63%) of 1,3-dimethylanthraquinone, m. p. 159–160°. For the oxidation 0.2 g. of material was heated with 3 cc. of nitric acid, sp. gr. 1.1, for six hours at 180–190°. The product formed pale yellow needles from dilute alcohol (0.15 g.). The substance decomposes at 320–325°.

Anal. Calcd. for $C_{16}H_8O_6$: C, 64.84; H, 2.72. Found: C, 64.60; H, 2.89.

Summary

On preparing the six possible tolyl naphthyl ketones by methods leaving no doubt as to their structures it was found that two of the isomers had been confused in the literature but that the previous conclusions regarding the formation of methylbenzanthrones by the action of aluminum chloride on the tolyl α-naphthyl ketones are substantiated by the results of experiments with the pure ketones and by more rigid evidence of the structure of one of the reaction products.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.
RECEIVED JUNE 26, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Activation of Specific Bonds in Complex Molecules at Catalytic Surfaces. I. The Carbon–Hydrogen Bond in Methane and Methane-d_4

BY KIYOSHI MORIKAWA,[1] W. S. BENEDICT AND HUGH S. TAYLOR

In a preliminary communication[2] to THIS JOURNAL we have recorded the ready interaction of methane and deuterium at reduced nickel catalyst surfaces at temperatures of 184° and upward. At that time we suggested that the reaction must be determined in rate by the activated adsorption of methane and called attention to the fact that, if this were so, we have in the exchange reaction a more sensitive index of activated adsorption than is available in adsorption measurements of gases on catalytic surfaces. The evidence that we present in the following pages confirms these views and lays the foundations for a comprehensive program of research upon the activation of specific bonds in complex molecules, a central problem in the field of contact catalysis, that of specific activity.

We have studied the interaction of methane and deuterium, of methane-d_4 and hydrogen, of methane and methane-d_4 and of methane and deuterium oxide at surfaces of catalytic nickel through a range of temperatures. From the measurements of reaction velocity and the derived energy of activation of the processes we are able to show that the rate-determining step is to be ascribed to the activation of the C–H bond of the methane molecule. These studies represent an extension to saturated hydrocarbon molecules of the phenomenon of isotope exchange already demonstrated to occur with unsaturated hydrocarbon molecules by the researches of Farkas, Farkas and Rideal[3] and by Polanyi and his collaborators.[4] We shall show that our results with the saturated hydrocarbons are of material importance in view of the theories of the exchange reaction developed by the latter group of authors.[4b]

Experimental Details

Materials.—The deuterium gas employed was obtained by electrolysis of our purest heavy water d^{25}_{25} 1.1079 containing 0.5 *M* NaOD as electrolyte. It was freed from oxygen by passage over a glowing platinum wire and dried by passage through a dry-ice trap.

Methane was prepared catalytically from carbon monoxide and excess hydrogen over a nickel catalyst at 255°, the excess hydrogen being removed by passage repeatedly over granular copper oxide at 300° after which carbon dioxide and water vapor were removed by soda lime and a solid carbon dioxide trap. The product used was further purified by fractional condensation and evaporation.

Methane-d_4 was prepared in a similar manner from carbon monoxide and pure deuterium, care being exercised to remove all hydrogen from the reaction system by exhaustion and repeated flushing with deuterium gas. The product was a very pure methane of which 98% of the bonds were found by analysis to be C–D bonds.

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[2] Morikawa, Benedict and Taylor, THIS JOURNAL, **57**, 592 (1935).

[3] Farkas, Farkas and Rideal, *Proc. Roy. Soc.* (London), **A146**, 630 (1934).

[4] (a) Horiuti, Ogden and Polanyi, *Trans. Faraday Soc.*, **30**, 663 (1934); (b) Horiuti and Polanyi, *ibid.*, **30**, 1164 (1934).

The deuterium oxide vapor employed came from our heavy water supply, d^{25}_{25} 1.1079.

The nickel catalyst was a very active nickel–kieselguhr preparation made by precipitation of the carbonate on kieselguhr, ignition and reduction in hydrogen (or deuterium) at progressively increasing temperatures to 450°. It contained 15% nickel and 2 g. was employed. At all times care was exercised to ensure absence of hydrogen when deuterium was being studied and *vice versa*. In experiments with the methanes alone residual adsorbed hydrogen or deuterium gas was removed by frequent evacuations and flushings with methane.

Analytical Procedure.—The progress of reaction was in every case followed by measurements of absorption in the infra-red region using a rock salt spectrometer system. The apparatus was calibrated by measurements of the absorption coefficients of the several deuteromethanes and of various mixtures of these gases as well as upon equilibrium mixtures of known H- and D-contents. Details of these measurements form the subject of a separate communication by Benedict, Morikawa and Barnes.[5] The absorption coefficients were measured on controlled pressures of gas (~200 mm.) in cylindrical Pyrex vessels with rock salt windows. The mixtures were analyzed in presence of the hydrogen and deuterium used in the experiments, since special test showed these to be without influence on the absorption measurements.

The absorption coefficients (ϵ) were normally measured at 3020 cm.$^{-1}$ (ϵ_H) and 2250 cm.$^{-1}$ (ϵ_D) to give check measurements on the percentages of C–H and C–D bonds, respectively. In general these measurements were concordant, though some deviations amounting to a 5% uncertainty in D-content have been observed. In the experiments with methane and methane-d_4 as reactants, additional measurements of absorption were made at 1160 and 1180 cm.$^{-1}$ and the measurements combined in a coefficient (ϵ_3) which measures the concentration of CH_3D, at 1090 cm.$^{-1}$ (ϵ_4) which measures CH_2D_2, and at 1035 cm.$^{-1}$ (ϵ_5) which includes both CHD_3 and CH_2D_2. The analytical results on these samples due to the more complete analysis are more accurate and the errors should not exceed 2% on the D-content. The values of ϵ given in the several tables are derived from the formula

$$\epsilon = \frac{-\log I/I_0}{lP} \times 10^7$$

where I and I_0 are the transmitted and incident intensities, l is the length of absorption path in cm. and P is the gas pressure expressed in mm. at 25°.

Experimental Procedure.—Known amounts of the reacting gases were introduced into a cylindrical Pyrex vessel of 100 cc. volume at the bottom end of which the nickel catalyst was placed. The gases were introduced through a trap of small volume cooled continuously to −78° which itself formed 30 cc. of the reaction volume. This trap served to remove the quantity of mercury vapor introduced with the gases and also, acting as a thermo-siphon, promoted a circulation of gases over the catalyst heated to controlled temperatures. Tubes of large diameter (15 mm.) were used for the connections between the vessel and trap to minimize resistance to this gas circulation. The total volume was ~150 cc. From time to time the gases were momentarily withdrawn from the reaction space and re-introduced in order to minimize stratification of the reactants. After completion of a run the gases were withdrawn by a Töpler pump and transferred to the analytical vessel.

Experimental Results

Methane–Deuterium Reaction.—The data of Table I indicate that no appreciable reaction occurs on our nickel preparation at 110°, but that from 184° upward an increasingly rapid exchange reaction can be measured. At the longer times of contact at each temperature, since the percentage of C–D bond approximates to 35% for equimolecular mixtures of CH_4 and D_2 it is apparent that the equilibrium state has been reached and that the equilibrium constant must be slightly greater than 1.

TABLE I

EXCHANGE REACTION BETWEEN METHANE AND DEUTERIUM ON NICKEL CATALYST

Catalyst no., 2 g. wt.	CH_4, cc.	D_2, cc.	Temp., °C.	Time, hrs.	ϵ_H	ϵ_D	% C–D bond
2	38.9	39.3	110	23	335	0	0
2	42.4	41.4	110	90	320	0	0
2	39.9	39.7	184	25.5	752	310	15
2	46.3	40.6	184	131.5	700	575	30
2	40.1	40.0	218	20	840	790	34
2	37.0	37.9	218	51	850	780	34
2	42.2	42.8	302	20	755	770	35
2	49.0	48.0	302	44	850	900	37
5	40.3	40.1	184	15	906	376	18
5	39.7	39.8	184	42	1056	816	32
5	39.7	39.7	218	10.2	1080	828	32
5	39.7	40.0	218	20	1190	950	35

The equilibrium state can be established from the methane-d_4–hydrogen side as well as from the methane–deuterium side as the data of Table II indicate.

TABLE II

EQUILIBRIUM FROM CH_4–D_2 AND CD_4–H_2

Catalyst no.	Cc.		Cc.		Temp., °C.	Time, hrs.	ϵ_H	ϵ_D	% C–D	K
	CH_4	CD_4	D_2	H_2						
2	38.4		78.3		218	75.5	790	1320	61	2.3
4		49.2		99.3	218	213	849	1130	56	1.8
2	42.0		83.9		255	50	830	1190	57	1.8
4		49.2		99.3	255	95			53	1.4
4		49.2		99.3	302	101	972	1125	50	1.1

No great accuracy can be assigned to these determinations since only the absorption coefficients ϵ_H and ϵ_D were determined. It is to be noted however that the mean values for the equilibrium constant $K = [C—D][H]/[C—H][D]$, at successive temperatures are: $K_{(200)} = 2.3$; $K_{(250)} = 1.6$;

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[5] Benedict, Morikawa and Barnes, *J. Chem. Phys.*, forthcoming publication.

TABLE III

COMPARATIVE VELOCITIES OF REACTION OF $CH_4 + CD_4$ AND $CH_4 + D_2$

CH_4, cc.	CD_4, cc.	D_2, cc.	Temp., °C.	Time, hrs.	ϵ_H	ϵ_D	ϵ_3[a]	ϵ_4	Conversion[b]
39.2			218	50	512	108			4.5 C–D
20.5	20.6		218	20	928	984			100%
20.3	20.3		218	7	880	1010	960	993	90%
20.7	20.7		218	1	708	823	760/560	800	51%
20.8	20.7		184	1.5	535	570	363/250	320	16.8%
20.7	20.7		255	0.33	764	860	850/640	900	60%
20.8	20.7		138	10	445	510	295/190	250	10.6%
40.5		41.0	184	6	795	360			17.5 C–D
39.3		39.3	218	1	715	316			14.5 C–D
39.5		39.1	255	0.5	894	708			30 C–D
40.0		40.0	138	96	604	96			6.5 C–D

[a] The absorption coefficient ϵ_3 refers to measurements at 1160 and 1180 cm.$^{-1}$. [b] The conversions in the final column have the following meanings. In the first and last four experiments of the table, the data given indicate the percentage of C–H bonds changed to C–D bonds. The remaining data give the percentage conversion from the original CH_4–CD_4 mixture to the equilibrium mixture of the five methanes.

$K_{(300)} = 1.2$. The values calculated from theoretical grounds[5] are 1.6, 1.5 and 1.4 at these temperatures. The agreement is within the rather large limits of experimental error in these analyses.

The Reaction between Methane and Methane-d_4.—A comparison of the velocities of reaction of $CH_4 + D_2$ and $CH_4 + CD_4$ can be obtained from the data of Table III. All of the experiments were conducted on the same catalyst, No. 6, 2 g. weight. It was reduced in deuterium for several hours at 450°, about 100 cc. of gas being consumed. The catalyst was evacuated for three and a half hours with a mercury vapor pump system but through 90 cm. of 3-mm. capillary tube and three stopcocks. The first experiment, with 39.2 cc. of methane alone, reacting at 218°, indicates that 3.6 cc. of D_2 (or D_2O) was still retained on the catalyst after evacuation and prior to the first experiment. Accordingly, before the next experiment, the catalyst was washed three times each with 14 cc. of methane, each washing being followed by evacuation at 218°. No deterioration of the catalyst occurred.

When the conversions recorded in the final column of Table III are recalculated to give initial rates of reaction at the several temperatures the data of Table IV are obtained. From these values, which must, however, be regarded as of only an approximate nature, it can be seen that the rate of reaction of $CH_4 + CD_4$ is several times faster at the lowest temperature, 138°, than that of methane–deuterium on the same surface at the same temperature. From a log rate *vs.* $1/T$ plot, straight lines result in each case giving activation energies, $E_{CH_4 + CD_4} \sim 19$ kcal. and $E_{CH_4 + D_2} \sim 28$ kcal.

TABLE IV

RATES OF REACTION OF METHANE WITH METHANE-d_4 AND WITH DEUTERIUM

Temp., °C.	$CH_4 + CD_4$ % conversion per hr.	$CH_4 + D_2$ % conversion per hr.
138	1.1	0.07
184	11.2	3.2
218	~60	15.5
255	~240	. . .

The higher activation energy of the reaction involving deuterium may be attributed to the influence of temperature in removing the more strongly adsorbed deuterium from the surface, giving greater accessibility to the methane. We shall later confirm this interpretation by a report of experiments on the interaction of ethane and hydrogen on such nickel catalysts. The activation energy of the $CH_4 + CD_4$ reaction, $E = 19$ kcal., is to be associated with the activation energy of desorption of the methane molecule, since, in these experiments, the processes occurring consist only in the activated adsorption and desorption of one or other of the methanes.

The Reaction between Methane and Deuterium Oxide.—In these experiments the reaction was conducted in a sealed vessel, 140 cc. in volume, to avoid difficulties due to stopcocks. The resultant gases were withdrawn for analysis through a connecting tube fitted with an internal capillary seal broken by a magnetically operated breaker on completion of an experiment. A slower reaction of methane occurs on the nickel catalyst with deuterium oxide than with deuterium as shown by the results in Table V.

Table V

Exchange Reaction between Methane and Deuterium Oxide

CH_4, cc.	D_2O vap., cc.	Temp., °C.	Time, hrs.	ϵ_H	ϵ_D	ϵ_3	ϵ_4	ϵ_5	% C–D
35	40	255	20	928	686	920/600	840	800	27.5
40.3	40	184	11	480	205	200/180	140	190	9
40.1	40	184	11	450	158	174/140	135	245	9

Analysis of the residual gas in the first two experiments indicated a slight reaction of methane and water to yield hydrogen and carbon dioxide. At 255° the gas contained 5% carbon dioxide and 8% $H_2(D_2)$; at 184° 1.5% of each gas was found. During this analytical work it was established that the exchange reaction did not occur on the copper–copper oxide mass which was used to burn hydrogen in the presence of methane at a temperature of 302°. On a 15-g. sample of oxide approximately 10% reduced to metal no exchange was found between 39.8 cc. of CH_4 and 40.3 cc. of D_2. The reaction time varied from one-half to one hour, during which the deuterium is rapidly burnt, but the water vapor formed remains in contact with the surface until condensed in the adjacent carbon dioxide traps. We also established the inertness of copper–copper oxide at this temperature with ethane–deuterium mixtures.

The slow reaction of methane and deuterium oxide is probably to be ascribed to the strong adsorption of water vapor on the nickel leaving little free surface for the activated adsorption of the methane. In the actual experiments it was observed that the whole charge of water vapor, $\sim$40 cc., was adsorbed at room temperature. The strong adsorption of water vapor would also account for the distribution of methanes obtained in the two last experiments which were as follows: CH_4, 83 and 80%; CH_3D, 8 and 12%; CH_2D_2, 4 and 5%; CHD_3, 3 and 2%; CD_4, 2 and 1%. The normal equilibrium distribution for a 9% C–D methane would be CH_4, 69; CH_3D, 27; CH_2D_2, 4; CHD_3, 0.5; CD_4, 0%. Such a distribution, however, is for the mixture in the gaseous phase and is evidently upset by the abnormal ratio of the two reactants on the surface. It would seem that an adsorbed methane molecule might suffer several substitutions with D atoms before escaping to the gas phase. The 27.5% C–D product, which we regard as close to the equilibrium point, was in fact a normal equilibrium distribution of the several methanes.

General Discussion

These exchange reactions between methane and deuterium and its compounds indicate that the same possibilities of replacement of hydrogen by deuterium exist in the case of saturated hydrocarbons as have hitherto been studied with unsaturated aliphatic hydrocarbons and benzene. The differences are of a quantitative nature but not of principle. The exchanges are slower than those of the unsaturated hydrocarbons and, for this reason, Farkas, Farkas and Rideal observed that the atomic exchange between deuterium and ethane does not occur under the conditions where the exchange reaction between ethylene and deuterium takes place rapidly. Indeed, such a conclusion was indicated in the results of Turkevich and Taylor[6] on the activated adsorption of hydrocarbons. The results now obtained indicate that the presence of a double bond in the reactant hydrocarbon is not an indispensable essential in such exchange processes, and that theories of mechanism, such as those of Horiuti and Polanyi,[4b] based upon the double bond characteristics can only be restricted considerations of the complete problem.

Unless one wishes to postulate the existence on the surface of associative complexes of the type CH_4D as intermediates in the exchange process, which we regard as very improbable, the conclusion is reached that the activated adsorption of the hydrocarbon is essentially a *dissociative* adsorption. The interaction of the two methanes CH_4 and CD_4 enforces this conclusion. The first stage of the dissociative process with methane would be the formation of CH_3 and H, entirely analogous to the now generally accepted postulate of the dissociation of hydrogen into two atoms on hydrogenation surfaces. The extent to which such dissociative processes of adsorption occur will obviously depend on the temperature, pressure and surface characteristics of the catalyst. In the limit, the dissociative process will proceed to the state in which all carbon and hydrogen bonds are severed, a condition which must obtain when the catalytic reaction $CH_4 = C + H_2$ occurs. All these dissociative processes

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[6] Turkevich and Taylor, This Journal, **56**, 2254 (1934).

on the surface establish there an equilibrium condition with the reverse processes, the association of adsorbed methyl radicals, or even more dissociated fragments with adsorbed hydrogen or deuterium atoms, yielding finally an equilibrium mixture of CH_xD_y, where $x + y = 4$. We see no reason why such dissociative processes of adsorption should not also occur with the more readily adsorbed ethylenic hydrocarbons, and contribute thereby to the exchange process. Such processes would supplement the associative type of mechanism

$$C_2H_4 + D \longrightarrow C_2H_4D \longrightarrow C_2H_3D + H$$

discussed in detail by Horiuti and Polanyi. These authors excluded the dissociative mechanism from consideration because of their observation, which agrees with our results with methane, that the exchange reaction rate is so greatly reduced when heavy water is used in place of deuterium. In our case, where a dissociative adsorption of the methane seems unavoidable, we ascribe this slower rate in presence of heavy water to the lower accessibility of the methane to the surface owing to the known stronger adsorption of the water relative to hydrogen.

Summary

1. The saturated hydrocarbon, methane, undergoes exchange with deuterium, methane-d_4 and deuterium oxide on active nickel catalysts at temperatures of 138° and higher.

2. At 184° the rate of reaction of methane with methane-d_4, deuterium and deuterium oxide decreases in the order given.

3. The activation energies of reaction with methane-d_4 and deuterium are $\sim$19 and $\sim$28 kcal., respectively.

4. The mechanism of reaction is associated with an activated, dissociative adsorption of methane on areas of surface unoccupied by hydrogen–deuterium or deuterium oxide.

PRINCETON, NEW JERSEY RECEIVED JUNE 8, 1936

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Wetting Characteristics of Solids of Low Surface Tension such as Talc, Waxes and Resins

BY F. E. BARTELL AND H. H. ZUIDEMA

The degree of wetting can most readily be determined by measuring the angle of contact formed with the liquid and solid in question. Degree of wetting is designated as the change in free surface energy, ΔF_s, which occurs when a liquid is brought into contact with a solid (*i. e.*, $\Delta F_s = S_1 - S_{1n}$).[1] Since the free surface energy of a system is numerically equal to the surface tension, the energy change expressed in ergs per sq. cm. is numerically equal to the adhesion tension, A_{1n}, expressed in dynes per cm.

$$S_1 - S_{1n} = A_{1n} \qquad \text{(I)}$$

The adhesion tension can be evaluated in terms of the surface tension of the liquid, S_n, and the contact angle, θ_{1n}, which the liquid forms with the solid, for, from the Young equation[2]

$$S_1 - S_{1n} = S_n \cos \theta_{1n} \qquad \text{(II)}$$

or, for water

$$S_1 - S_{13} = S_3 \cos \theta_{13} \qquad \text{(III)}$$

and hence

$$A_{1n} = S_n \cos \theta_{1n} \qquad \text{(IV)}$$

or

$$A_{13} = S_3 \cos \theta_{13} \qquad \text{(V)}$$

The adhesion tension and degree of wetting of a liquid against a solid cannot be measured directly if the contact angle is zero, but in such instances it can be determined by application of the Bartell–Osterhof[3] equation

$$A_{13} - A_{1n} = S_{n3} \cos \theta_{1n3} \qquad \text{(VI)}$$

if the interfacial contact angle, θ_{1n3}, is finite and measurable (as it usually is), and if the solid–water–air contact angle, θ_{13}, is finite, so that the adhesion tension, A_{13}, can be calculated from equation (V). For solids on which water gives a zero angle, some organic liquid can usually be found which gives a finite contact angle, and equation (VI) can be used to calculate A_{13}.

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(1) The symbols used in this paper are essentially the same as have been used in recent publications from this Laboratory. S_1 = surface tension or free surface energy of a solid in air, S_n = surface tension or free surface energy of an organic liquid and S_3, the surface tension or free surface energy of water. The subscripts 1, n and 3 refer to solid, organic liquid and water phases, respectively. In this paper an interfacial contact angle between solid, organic liquid and water will be represented by θ_{1n3}.

(2) Young, *Trans. Roy. Soc.* (London), **A95**, 65 (1805).

(3) Bartell and Osterhof, "Colloid Symposium Monograph," **5**, 113 (1927).

The Bartell–Osterhof equation (VI) can be derived mathematically by subtracting equation (II) from equation (III) and substituting in the Young[2] equation

$$S_{1n} - S_{13} = S_{n3} \cos \Theta_{1n3} \qquad \text{(VII)}$$

We thus obtain the equation

$$S_3 \cos \Theta_{13} - S_n \cos \Theta_{1n} = S_{n3} \cos \Theta_{1n3} \qquad \text{(VIII)}$$

and hence from equations (IV) and (V)

$$A_{13} - A_{1n} = S_{n3} \cos \Theta_{1n3} \qquad \text{(VI)}$$

It has been impossible, heretofore, to test the Bartell–Osterhof equation experimentally since for no solid examined could the value of each term be determined experimentally. In the present investigation, however, solids were studied which showed markedly different properties from those of solids previously studied and reported upon in papers from this Laboratory, and one of these solids, talc, has made possible the experimental testing of this equation.

The extent to which a liquid will spread over the surface of a solid is dependent upon the relative magnitudes of the three tensions involved, namely, S_1, the surface tension of the solid, S_{1n} or S_{13}, the interfacial tension solid–liquid and S_n or S_3, the surface tension of the liquid. If S_1 is greater than the sum of the other two tensions, the liquid will spread over the surface of the solid forming a continuous film. If S_1 is less than the sum of the other two tensions, spreading will be limited, a drop of the liquid will be formed which will give a definite angle of contact with the surface of the solid.

An indication of the relative surface tension values of solids is given by their relative hardness. In hard solids the atoms or ions are close together.[4-8] The force of attraction between the elementary units comprising the solids is therefore large, and the work of cohesion, and hence the surface tension, is high. In soft solids the elementary units are farther apart, and the force of attraction is much less. The work of cohesion and surface tension of soft solids is therefore small in comparison with the values for harder solids. Waxes, some resins and certain solids such as talc, pyrophyllite, graphite, etc., are very soft. Their force of cohesion, work of cohesion and hence surface tension are very low. Tests made upon some of these low surface tension solids showed that water or any organic liquid of fairly high surface tension value formed a drop, and hence a measurable contact angle upon the solid.

Experimental

The wetting characteristics of the solids studied were determined by contact angle measurements using the sessile drop method. Mack[9] has recently shown that the effect of gravity in deforming the spherical outline of sessile drops is negligible for drops of 0.5 mm. or less in diameter, except for contact angles very near 180°, and that for angles under 90° the effect is negligible even for somewhat larger drops (Figs. 1a, b and c). For a drop whose outline is the segment of a sphere, the contact angle may be calculated from the equation

$$\tan \Theta/2 = 2h/d \qquad \text{(IX)}$$

where h is the height, and d the diameter of the drop. This equation holds for acute and obtuse angles alike, and is of simple geometric derivation. Since all the drops used in this investigation were 0.5 mm. or less in diameter, equation (IX) could be used for calculating their angles of contact. Avoiding the effect of gravity by the use of small drops had the advantage that the dimensions of the drop in standard units were not required. It was necessary only to determine the ratio of h to $d/2$.

All contact angle measurements were made on freshly cleaved or freshly solidified surfaces, depending upon whether the solid was crystalline or amorphous. The liquids used were all very carefully purified and their surface tension values were in good agreement with the generally accepted values in the literature. Satisfactory results were obtained by the method if sufficient care was taken in the preparation of the surface and in placing the drop on the surface. All interfacial contact angles were measured through the water phase.

In carrying out a determination, a freshly cleaved crystal or freshly solidified surface of the solid was placed in a cell about 3 × 3 × 3 cm. with plane plate-glass sides. The solid was mounted in air or in a liquid, depending upon whether measurement was to be made of a solid–liquid–air contact angle or an interfacial contact angle. A cover, ground to fit, and having a very small hole in the center for the introduction of a

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(4) Friederich, *Fortschr. Chem. Physik physik. Chem.*, **18**, 5 (1926).

(5) Kuznetzov and Lavrentieva, *Z. Krist.*, **80**, 54 (1931).

(6) Reis and Zimmerman, *Z. physik. Chem.*, **102**, 298 (1922).

(7) Taylor, *Trans. Faraday Soc.*, **24**, 157 (1928).

(8) McBain, "The Sorption of Gases by Solids," George Routledge and Sons, Ltd., London, 1932, p. 295.

(9) Mack, *J. Phys. Chem.*, **40**, 159 (1936); Mack and Lee, *ibid.*, **40**, 169 (1936).

capillary pipet, was fitted over the top of the cell. The capillary pipet containing the liquid was next lowered by means of a ratchet and pinion device until it almost touched the surface of the solid. By applying air pressure at the top of the pipet, a drop of liquid was forced out on the solid, and was allowed to advance until it had a diameter of about 0.5 mm., when the pipet was removed by carefully raising it. A light source was placed behind the cell and the drop was observed with a microscope mounted in a horizontal position. The height and diameter of the drop were measured by means of a graduated ocular. On occasion, photographs were made of drops by means of a camera attached to the microscope.

Since individual drops show slight variations, a minimum of six individual determinations was made for each system investigated. If the angles of the individual drops varied by more than three or four degrees, eight or ten determinations were made.

Talc

The data obtained for talc are given in Table I. The data for contact angle in air, column 4, show that talc is neither strongly hydrophilic nor strongly organophilic since finite contact angles were measured on talc both with water and with a number of organic liquids. The data in column 6 show that talc must be considered to be organophilic in nature, however, since all the interfacial contact angles measured upon it (*i. e.*, measured through the water phase) were greater than 90°

TABLE I

CONTACT ANGLES IN AIR AND THE CALCULATED AND OBSERVED INTERFACIAL ANGLES OF A SERIES OF LIQUIDS ON TALC

$t = 25 \pm 1°$

	S_n (or S_3)	S_{n3}[a]	θ_{1n} (or θ_{13})	θ_{1n3}, calcd.	θ_{1n3},[a] obsd.
Water	72.1		86°		
Methylene iodide	50.2	48	53°	122°	121°
Alpha-bromonaphthalene	44.0	41.6	34°	139°	141°
Bromobenzene	35.9	39.6	12°	140°	142°
Acetylene tetrabromide	49.1	38.3	47°	138°	139°
Chlorobenzene	32.6	37.9	0°		140°
Toluene	28.1	36.1	0°		129°
Ethylene dibromide	38.1	36.0	26°	145°	145°
Benzene	28.2	34.6	0°		135°
Butyl acetate	24.1	13.2	0°		144°
Amyl alcohol	23.4	5.0	0°		100°
Benzyl alcohol	39.5	4.2[c]	32°	180°	122°
Water (satd. with benzyl alc.)	41.8[b]		42°		
Benzyl alcohol (satd. with water)	37.4[b]	4.2	32°	98°	122°

[a] Organic liquid "advancing." [b] Determined by the capillary rise method. All the other surface tension values given are from the literature. [c] The interfacial tension of benzyl alcohol against water was determined by means of the double cylinder method.[10] All the other interfacial tension values given are taken from the literature.

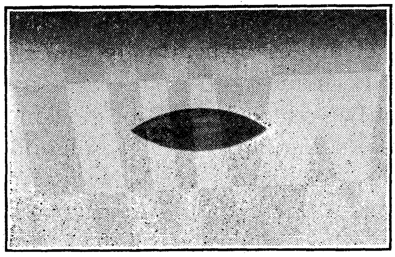

Fig. 1a.

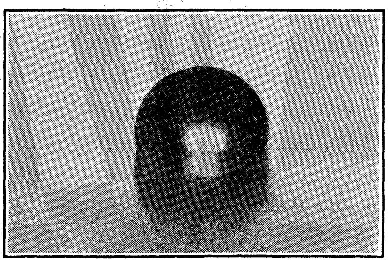

Fig. 1b.

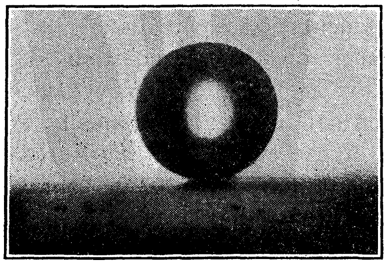

Fig. 1c.

The data in column 6 give the observed contact angles and the data in column 5 give the contact angles calculated from the Bartell–Osterhof equation (equation VIII). The observed interfacial angle values given in column 6 are all for organic liquid advancing angles. This does not mean that measurements were made on a dynamic advancing angle. The measurement was made on a static angle, but in each case the talc was first covered with water, the organic liquid was then introduced in the form of a drop which advanced over a surface previously wet by water. This method of procedure was considered best because

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[10] Bartell and Miller, THIS JOURNAL, **50**, 1961 (1928).

talc has a lower adhesion tension against water than against organic liquids, hence water will be more easily displaced from it by the organic liquid than will the organic liquid be displaced by water.

The agreement between the observed and calculated interfacial angles is remarkably close for all of the systems for which the calculation was possible with the single exception of the benzyl alcohol system. (Some of the organic liquids form zero contact angles with talc and the calculation could not be made.) The lack of agreement in the case of benzyl alcohol can be explained on the basis of the comparatively high solubility of the alcohol in water and its very low interfacial tension against water. In the development of the Bartell–Osterhof equation, the S_{1n} and S_{13} of equation VII are for organic liquid and water mutually saturated, for the two liquids are in contact with each other. The S_{1n} of equation II is for pure organic liquid, however, and the S_{12} of equation III is for pure water. The error thus introduced is apparently negligible for organic liquids of high interfacial tension against water and low solubility in water, but may become great when the interfacial tension is low and the mutual solubility appreciable. Benzyl alcohol has an interfacial tension value against water of only 4.2 dynes, as compared with values ranging from 34 to 48 dynes for the other five liquids for which the calculation was made.

As a check on this explanation for the discrepancy in the case of benzyl alcohol–water system, contact angle measurements were made with each of the two liquids saturated with the other. The data are included in Table I. It will be observed that the agreement between the observed and calculated interfacial angles is very much better than before, although not so close as was found for the other systems. Experimental error in the determination of any one of the four quantities, Θ_{1n}, Θ_{13}, S_n or S_3 introduces a large percentage error in the calculated Θ_{1n3}, for the calculation involves the small difference between $S_3 \cos \Theta_{13}$ and $S_n \cos \Theta_{1n}$.

It seems justifiable to conclude that the Bartell–Osterhof equation is applicable to systems of insoluble solids when used in conjunction with liquids of low mutual solubility and high interfacial tension. It is probably applicable also to systems involving liquids of low interfacial tension, provided the mutual solubility effects of the liquids are taken into account.

As has been pointed out above, talc shows a marked difference in behavior from the harder solids previously examined in that it forms contact angles with water and with organic liquids of high surface tension. Talc also shows another marked difference from the harder solids previously examined. The data in column 6, Table I, show that the interfacial angles formed on talc by different organic liquids against water are different. The empirical equations of Bartell and Bartell[10] do not therefore apply to talc. Talc has been shown to be organophilic in nature, but its relative degree of organophilic nature cannot be measured on the convenient K_{n3} scale of Bartell and Bartell.[11]

Waxes and Resins

Many amorphous substances such as waxes and resins are soft and have low surface tension values. Their wetting characteristics would therefore be expected to be similar to those of the soft crystalline solid, talc.

A large number of substances, including paraffin, Japan wax, beeswax, spermaceti, a number of synthetic waxes including halogenated naphthalenes and biphenyls, and many natural and synthetic resins were investigated. Practically all of them were found to give large angles with water, and most of them gave fairly large angles with the organic liquids of high surface tension. Many of them were somewhat soluble in the organic liquids, however. Five substances in which the solubility effects were fairly low were chosen for detailed study, namely, Glyptal resin,[12] de Khotinsky cement (hard), carnauba wax, shellac and Opal wax 20.[13]

Fresh surfaces of these substances were obtained by melting them and allowing them to solidify on clean glass plates. The data obtained for contact angles in air and for interfacial contact angles are given in Table II. The solid–liquid–air angles are easily reproducible, since for any solid with a low surface tension value (*i. e.*, low free surface energy) there is very little tendency for the solid to be carried to a lower energy level by the adsorption of water vapor, atmospheric gases, etc. This fact is probably responsible for the good agreement found in the literature for the contact angle of water on paraffin as reported by different investigators. The interfacial angles were measured with organic liquid "advancing."

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[11] Bartell and Bartell, This Journal, **56**, 2205 (1934).

[12] A commercial product known as Glyptal 1350.

[13] A commercial product.

TABLE II

CONTACT ANGLES IN AIR AND INTERFACIAL CONTACT ANGLES FORMED BY A SERIES OF LIQUIDS ON WAXES AND RESINS

	Glyptal resin		De Khotinsky cement		Carnauba wax		Shellac		Opal wax	
	θ_{1n}	θ_{n3}	θ_{1n}	θ_{n3}	θ_{1n}	θ_{n3}	θ_{1n}	θ_{n3}	θ_{1n}	θ_{n3}
Water	61°		106°		107°		107°		119°	
Methylene iodide	25°	90°	69°	122°	70°	128°	70°	133°	77°	123°
Acetylene tetrabromide	5°	133°	62°	130°	65°	140°	64°	128°	72°	136°
α-Bromonaphthalene	0°	88°	55°	123°	57°	146°	58°	126°	65°	149°
Benzyl alcohol	0°	160°	56°	137°	58°	142°	59°	132°	67°	134°
Ethylene dibromide	0°	90°	49°	137°	49°	145°	48°	146°	50°	151°
Bromobenzene	0°	96°	33°	138°	45°	148°	44°	135°	35°	156°
Chlorobenzene	0°	99°	29°	147°	35°	153°	35°	146°	27°	159°
Toluene	0°	87°	27°	148°	26°	154°	28°	145°	26°	161°
Butyl acetate	0°	130°	22°	143°	0–10°	166°	23°	156°	24°	153°
Amyl alcohol	0°	155°	19°	139°	0°	149°	20°	141°	25°	120°
Benzene		90°		136°		152°		144°		157°

The data obtained on waxes and resins cannot be considered as accurate data because of errors introduced by solubility effects. Measurements with the du Noüy Tensiometer showed that the surface tension of alpha-bromonaphthalene saturated with carnauba wax was practically the same as that of the pure liquid. The surface tension of water saturated with the wax was slightly lower than that of pure water, however, and the interfacial tension of alpha-bromonaphthalene against water was also lowered to some extent by the presence of carnauba wax.

Another factor to be considered is that the solids, being appreciably soluble in the organic liquids, are pitted when a drop of organic liquid is placed upon them. The surface under the drop is no longer plane. The measured angle is therefore not the true angle, for it is measured between the arc of the drop and the plane of the surface of the solid. Angles thus measured are reproducible and give an indication of the wetting properties of the solid, but they cannot be used for checking the Bartell–Osterhof equation. Since the interfacial angles measured on a given surface by water against different organic liquids were different, the indication is that the empirical equations of Bartell and Bartell[11] do not apply in these soft solids.

As has been pointed out, the behavior of soft solids can be explained on the basis of their low surface tension values. Waxes have very low surface tension values, the value for paraffin being given in the literature as 40 dynes. Measurements of the surface tension of molten waxes were made with the du Noüy Tensiometer. Temperature–surface tension curves were drawn and extrapolated to room temperature. They are shown in Fig. 2. The extrapolated values, which lie between 33 and 38 dynes (at 25°), should give a fairly accurate indication of the surface tension of the solid, for the curves are straight lines down to the point of solidification.

Since the waxes have surface tension values which are, presumably, lower than that of talc, they should give angles with liquids of fairly low surface tension which form zero angles on talc.

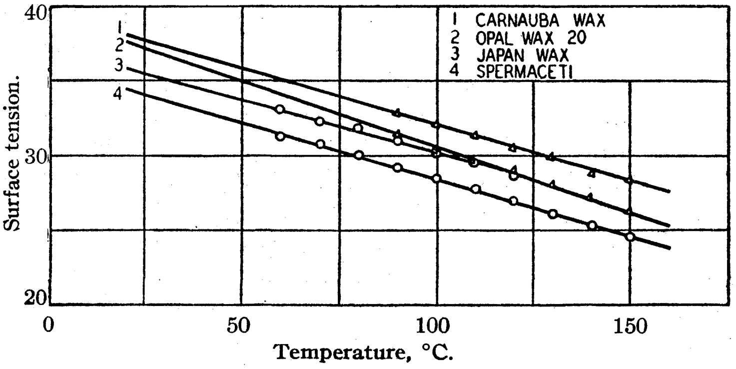

Fig. 2.

This has been shown to be the case. Talc gave a small angle with bromobenzene (S_n = 35.9) and larger angles with liquids with higher surface tension values, but gave zero angles with liquids of lower surface tension. The waxes and resins gave measurable angles with butyl acetate (S_n = 24.1), and some of them gave measurable angles even with amyl alcohol (S_n = 23.4).

Summary and Conclusions

1. The wetting characteristics of talc and of a number of waxes and resins have been studied by measurements of the contact angles formed by small drops of liquid on these solids.

2. Both water and organic liquids (of high surface tension) form contact angles on these solids, thus indicating that the surface tension of these solids is low.

3. Soft solids of low surface tension are wetted less readily by liquids than are hard solids which possess a higher surface tension.

4. On talc, accurate measurements could be made of interfacial contact angles as well as of contact angles in air both with water and with organic liquids. This made possible the experimental testing of the Bartell–Osterhof equation relating adhesion tension and interfacial contact angles. This equation was found to hold.

ANN ARBOR, MICHIGAN RECEIVED MAY 11, 1936

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Absorption Spectrum of Ethyl Methyl Ketone

BY A. B. F. DUNCAN, VICTOR R. ELLS AND W. ALBERT NOYES, JR.

The spectroscopy and photochemistry of acetone have been the subjects of numerous investigations. The spectrum consists of a broad absorption region extending from about 2200 to about 3200 Å. with a definite fine structure on the long wave end, a series of discrete bands extending from 1995 to about 1820 Å., and at shorter wave lengths other bands, some of which fitted a Rydberg formula predicting an ionization potential of 10.2 volts.[1] At still shorter wave lengths there is continuous absorption extending down to the limit of the observations made, about 800 Å. In the near ultraviolet fluorescence is observed, although attempts to find this phenomenon in the neighborhood of 1900 Å. failed.[2]

The next higher ketone is ethyl methyl ketone. The electronic structure of the carbonyl group must be very similar to that in acetone. However, the symmetry operations which may be performed on the two molecules differ considerably. If the methyl group forming part of the ethyl group is considered to execute a perfectly symmetrical rotation around the adjacent carbon–carbon bond, there will be only one symmetry operation aside from the identity, namely, reflection in the plane containing the carbonyl group and the two adjacent carbon atoms. However, due to various types of interaction between the different parts of the molecule, this particular rotation might not be expected to be completely symmetrical so that ethyl methyl ketone must be considered to possess a very low order of symmetry.

Experimental Procedure and Discussion of Results

The methyl ethyl ketone used in these experiments was prepared by the acetoacetic ester synthesis, using acetoacetic ethyl ester and methyl iodide. It was purified by formation of the sodium bisulfite compound, dried with potassium carbonate and fractionally distilled.[3]

For investigation of the near ultraviolet absorption a Hilger E_3 spectrograph was used together with Eastman III-O and 33 plates.

The absorption spectrum of the liquid in this region has been investigated, but that of the vapor has not been reported. Two absorbing columns of 1 and 10 meters with pressures of 3 to 86 mm. (the vapor pressure at 25°) were used. At the highest pressure the absorption extended from approximately 3200 to 2400 Å. No trace of vibrational fine structure was observed under any conditions.

Ethyl methyl ketone shows strong fluorescence when illuminated with approximately monochromatic 3130 Å. radiation. The fluorescence viewed with a hand spectrograph appeared to consist of a continuous band in the green. We were unable to obtain photographs of the fluorescence with the E_3 spectrograph, but the matter is being pursued further.

In view of this fluorescence, particular care was used in making the absorption measurements to vary the pressures over a wide range, and at each

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(1) (a) Damon and Daniels, THIS JOURNAL, **55**, 2363 (1933); (b) Scheibe, Povenz and Linstrom, *Z. physik. Chem.*, **B20**, 297 (1933); (c) Crone and Norrish, *Nature*, **132**, 241 (1933); (d) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, **1934**, 1456; (e) Noyes, Duncan and Manning, *J. Chem. Phys.*, **2**, 717 (1934); (f) Duncan, *ibid.*, **3**, 131 (1935).

(2) Howe and Noyes, THIS JOURNAL, **58**, 1404 (1936).

(3) The authors wish to express their appreciation to Professor C. B. Wooster for suggesting the method of synthesis and supervising its execution.

pressure to make a number of exposures for different lengths of time, in order to provide suitable contrast. It is possible that the lowest pressure was still too high to permit the observation of structure and a still longer column may be necessary.

The near ultraviolet spectrum is followed by a region of almost complete transmission extending down to 1975 Å. At this point a spectrum consisting of discrete bands begins, which continues, broken by short regions of high transmission, down to about 1550 Å. At still shorter wave lengths there is strong continuous absorption extending down to about 780 Å., the limit of the observations. No structure could be found in this continuum even at low pressures where the continuous absorption was weak. Any discrete bands must be weaker than the continuous absorption below 1567 Å.

A one-meter, normal incidence vacuum spectrograph with a 120,000 line glass grating was used to photograph this region. The modified Lyman continuum served as the source.[1e,1f] Eastman III-O plates sensitized with Nujol were used. The plates were measured and reduced in the usual way and emission lines in the source, chiefly due to carbon, were used as standards. The dispersion was approximately 8.5 Å./mm.

The frequencies of the bands are given in Table I with visually estimated intensities. The intensity of the weakest band is arbitrarily placed as 1, which means that some rather high values must be given without implying, however, any greater accuracy in estimating intensities than was obtained with acetone. The red edges of the bands are given.

TABLE I

FAR ULTRAVIOLET BANDS OF ETHYL METHYL KETONE

Frequency, cm.^{-1}	Intensity	Frequency, cm.^{-1}	Intensity
50634	8	53119	2
50675	8	58110	12
50728	8	58662	20
50857	6	59102	1
50891	6	59360	1
50948	6	62283	16
51209	4	63523	200
51915	3	63817	250
52426	3		

The edges of the first six bands are quite sharp and the accuracy should be five to ten wave numbers. For most of the other bands the edges were quite diffuse, but it is felt that in no case does the error exceed fifty wave numbers.

The first ten bands, 50,634 to 53,119 cm.$^{-1}$, evidently involve one upper electronic state. The spectrum here is similar to that in acetone in the region 51,000 to 55,000 cm.$^{-1}$. There are three main bands forming an upper state progression involving a frequency of 1281 cm.$^{-1}$. Two other upper state frequencies appear, one about 220 and the other 575. The origin of the system is the triple band (50,634, 50,675, 50,728), which corresponds to the (51,171, 51,226, 51,285) band in acetone which is also triple headed. Table II shows the arrangement of the bands.

TABLE II

ARRANGEMENT OF ETHYL METHYL KETONE BANDS (50,634 to 53,119)

(All transitions are considered to occur from the lowest level of the ground state)

v_1', v_2', etc. $= 0$	50634	50675	50728
	223	216	220
$v_1' = 1$	50857	50891	50948
	1281		
$v_2' = 1$	51915		
	1204		
$v_2' = 2$	53119		
	575		
$v_3' = 1$	51209		
	514		
$v_2' = 1$, $v_3' = 1$	52426		

The second electronic state involving a transition below 1975 is evidenced by four bands, the two of shortest wave length being of extremely low intensity. Acetone has an analogous state giving transitions between 60,086 and 62,529 cm.$^{-1}$. The two strongest bands are separated by 552 cm.$^{-1}$. It appears probable that this is an upper state difference and that the origin of this state lies at 58,110 cm.$^{-1}$. One of the weak bands, 59,360, is separated from this by 1250 cm.$^{-1}$.

The differences between the remaining three bands are as follows: 63,523 to 62,283 = 1240; 63,817 to 63,523 = 294. The two bands of highest frequency evidently belong to the same electronic transition; the first of the three may also belong to the same transition. If the three bands belong together, the intensity relationships are such that 62,283 cannot be the origin of the system, in which case 1240 would have to be a ground state difference. This is unlikely due to the small Boltzmann factor (0.0015) for such a large frequency. It seems better, then, to put 62,283 in a separate electronic transition. Whether the 294 difference for the remaining two bands is an upper or ground state difference cannot be determined.

The significance of the various frequency differences may be discussed briefly. v_2 is most probably a carbon–oxygen frequency which is 1734 cm.$^{-1}$ in the normal state. The corresponding frequency in acetone for this state is about 1200 cm.$^{-1}$ (1712 in the normal state). v_1 is probably analogous to 321 found in acetone in this region. It is probably associated with a simultaneous bending of the methyl and ethyl groups with respect to the carbon–oxygen axis. v_3 may possibly represent a motion in which the ethyl and methyl groups are stretched as units in reference to the carbonyl group.

The Electronic States of Ethyl Methyl Ketone

It is apparent from the above discussion that four, or more probably five, well separated excited electronic states of ethyl methyl ketone have been found here. The first excited state probably has unresolved fine structure, since fluorescence is caused by absorption in this region. The other states possess discrete vibrational levels as indicated. In addition there are other states, perhaps repulsive, which are necessary to account for the continuum overlying the discrete structure, particularly at short wave lengths.

Obviously no two of the origins of these states fit a Rydberg formula which would converge to a reasonable limit.[4] The band in ethyl methyl ketone most similar to a member of the acetone Rydberg series[1f] is either 63,525 or 63,817 (depending on which is considered to be the origin of this particular electron transition). One of these bands is believed to be the first member of a Rydberg series whose other members are masked by continuous absorption. Accordingly the ionization potential of the molecule could not be determined by spectroscopic means.

The ionization potential was then determined by the method of electron bombardment.[5] The value obtained was 10.5 ± 0.5 volts, as compared to 10.1 volts (by electron impact) for acetone.

According to Mulliken[4] a (2 p_yb_2) electron in formaldehyde should have a lower ionization potential than any other and the agreement between the theoretically predicted value and that obtained by convergence of a Rydberg series lends support to this statement.[6] In acetone a similar electron must be involved in the Rydberg series and this must be true for the hypothetical Rydberg series in ethyl methyl ketone. This electron is described as one occupying a non-bonding oxygen orbital and transitions involving it should change the fundamental frequency of the carbonyl group only slightly.

Since most of the discrete bands and the near ultraviolet continuum do not fit a Rydberg series, it is probable that other electrons of the bonding or anti-bonding types are involved in these transitions. Little of a definite nature can be said concerning these electron states, although others have attempted to correlate frequencies of the various states of carbon monoxide with the frequencies of the carbonyl group.

Summary

1. The absorption spectrum of ethyl methyl ketone has been investigated at room temperature from the visible down to about 780 Å.

2. Four (possibly five) different excited electron states in addition to any which may be involved in the short wave continuum must be used to explain the different absorption regions.

3. The bands in the region from 1975 to 1883 Å. may be classified as belonging to a single electron transition, using three vibration frequencies in the upper state.

4. A brief discussion, including a general comparison with the acetone bands, has been given.

PROVIDENCE, RHODE ISLAND RECEIVED JUNE 10, 1936

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[4] Mulliken, *J. Chem. Phys.*, **3**, 564 (1935).

[5] Noyes, *ibid.*, **3**, 430 (1935).

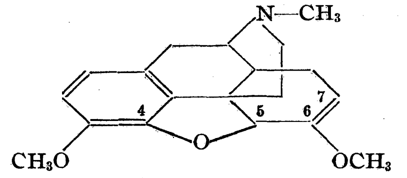
[6] Price, *Phys. Rev.*, **46**, 529 (1934).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

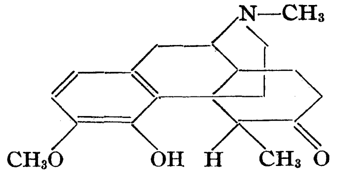
The Addition of Organomagnesium Halides to Pseudocodeine Types. II. Preparation of Nuclear Alkylated Morphine Derivatives[1]

BY LYNDON SMALL, HOWARD M. FITCH[2] AND WILLIAM E. SMITH

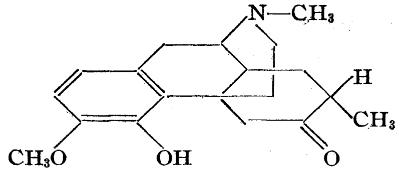
Derivatives of the morphine alkaloids having an alicyclic unsaturated linkage in the β,γ-position to the 4,5-ether linked oxygen atom (*i. e.*, allyl ether types) show a general tendency to undergo reduction or addition reactions in which both the ether oxygen and the double bond are involved.[3] In previous papers we have demonstrated that organomagnesium halides react with pseudocodeinone and desoxycodeine-C to yield phenolic bases containing the organic radical of the Grignard compound used,[4] probably at the 5- or 7-position in the nucleus. The present communication deals with the application of this reaction to dihydrothebaine and with the transformation of the product into a series of nuclear alkylated dihydromorphine derivatives.



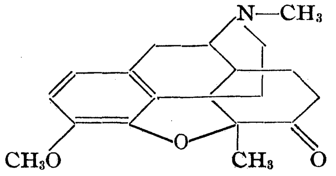
I. Dihydrothebaine



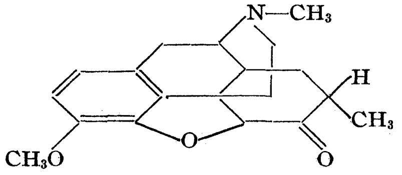
II. 5-Methyldihydrothebainone



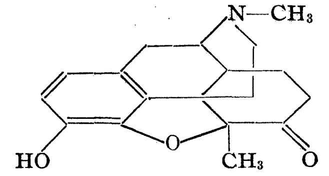
III. 7-Methyldihydrothebainone



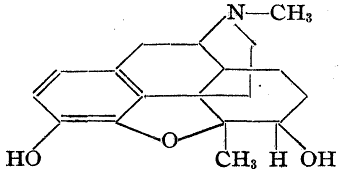
IV. 5-Methyldihydrocodeinone



V. 7-Methyldihydrocodeinone



VI. Methyldihydromorphinone (?)



VII. Methyldihydromorphine (?)

The structure of dihydrothebaine (I), at least as far as the position of the alicyclic unsaturation is concerned, is amply demonstrated by the facile hydrolysis to dihydrocodeinone,[5] and by the behavior toward ozone.[6] The double bond is located as in pseudocodeine and desoxycodeine-C; nevertheless, under the ordinary conditions imposed for reaction with Grignard's reagent, dihydrothebaine is not appreciably affected, a fact which may be attributed in part to its low solubility in ether, and perhaps in part to the presence of the enol ether group. When dihydrothebaine is extracted from a Soxhlet apparatus into boiling ethereal methylmagnesium iodide an addition compound slowly separates, and at the end of five days no more dihydrothebaine can be detected. The product consists principally of a phenolic ketone, methyldihydrothebainone (tentative formula II or III) and in small amount (10% yield), of an isomeric substance, isomethyldihydrothebainone. The enol ether group present in the starting material has been hydrolyzed, either during the reaction or more probably during the isolation of the reaction products, which is necessarily accomplished with the use of acidic reagents. In this respect the dihydrothebaine reaction presents a striking contrast to that of thebaine, where the products (phenyldihydrothebaine or the methyldihydrothebaines) are extremely resistant to hydrolysis. An enol ether of instability com-

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[1] The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

[2] Squibb Fellow in Alkaloid Chemistry.

[3] (a) Schöpf and Winterhalder, *Ann.*, **452**, 237 (1927); (b) Small and Cohen, THIS JOURNAL, **53**, 2214 (1931); (c) Lutz and Small, *ibid.*, **54**, 4715 (1932); (d) Morris and Small, *ibid.*, **56**, 2159 (1934).

[4] (a) Lutz and Small, *ibid.*, **57**, 2651 (1935); (b) Small and Yuen, *ibid.*, **58**, 192 (1936).

[5] Freund, Speyer and Guttmann, *Ber.*, **53**, 2250 (1920).

[6] Wieland and Small, *Ann.*, **467**, 17 (1928).

parable to that of the hypothetical intermediate methyldihydrothebainone methyl enolate has, however, been isolated in this Laboratory during the reduction of thebaine by the Wieland and Kotake procedure.[7]

The presence of the ketone group at C–6 in methyldihydrothebainone implies an active methylene group at C–5 (III) or at C–7 (II), depending upon whether methylmagnesium iodide has added to dihydrothebaine in the 1,4- or 1,2-manner. Schöpf has demonstrated for dihydrothebainone and for dihydrometathebainone the feasibility of reforming the 4,5-oxide bridge characteristic of the naturally-occurring bases of the morphine series.[8] The compound of formula III (and possibly II) should undergo ether ring closure under similar conditions. Methyldihydrothebainone reacts with two moles of bromine to form a dibromo derivative (not isolated), which on treatment with cold dilute sodium hydroxide is converted to the non-phenolic 1(?)-bromomethyldihydrocodeinone. Elimination of bromine (catalytic hydrogen) yields IV or V, methyldihydrocodeinone. By this series of reactions we arrive at the first known nuclear alkylated derivative of the morphine group.

It has been found by repeated experiments in this Laboratory[9] that dihydrocodeinone can be reduced at the carbonyl group by the catalytic method to give dihydrocodeine, with no detectable amount of the epimer, dihydroisocodeine. Methyldihydrocodeinone, under the same conditions, takes up one mole of hydrogen with formation of methyldihydrocodeine, in which the codeine configuration for the alcoholic hydroxyl group is assumed on the basis of the above cited evidence.

Like most saturated derivatives of the morphine series, the compounds of the group described in this communication are relatively stable toward rearrangement or decomposition in the presence of concentrated halogen acids, and methyldihydrocodeinone can be demethylated smoothly with 48% hydrobromic acid. The product is methyldihydromorphinone (VI), a homolog of the well known drug dihydromorphinone ("Dilaudid"). Methyldihydromorphinone can be reduced at the ketone group, with formation of methyldihydromorphine (VII).[10] The relationship of the latter to the above-mentioned methyldihydrocodeine was established by methylation with diazomethane.

Isomethyldihydrothebainone can be separated from the main reaction product through differences in solubility of the respective hydrochlorides and ultimately through its properties as a cryptophenol. The presence of the phenolic hydroxyl is shown by the formation of an acetyl derivative and by the solubility in alkali, from which, however, in contrast to methyldihydrothebainone, the base can be extracted with ether. On treatment with two moles of bromine, and subsequently with dilute alkali, isomethyldihydrothebainone yields a non-phenolic product, bromoisomethyldihydrocodeinone (not crystalline), which can be debrominated to isomethyldihydrocodeinone (Formula IV or V ?). The demethylation and reduction reactions which will lead to the isomethyldihydromorphinone and isomethyldihydromorphine types have been postponed until more material is available.

Determination of the position of the new methyl group in methyldihydrocodeinone presents serious difficulty, and definite proof will probably be obtained only by degradation. This is at present not practicable because of lack of material. It is certain that in the bromination of methyldihydrothebainone and its isomer one bromine atom enters at C–5, else the ether ring closure would not be possible. This fact may indicate that the methyl group occupies C–7, for it has been shown that in the bromination of 1-methylcyclohexanone, bromine substitutes at the methylene group adjacent to the carbonyl in preference to the methenyl group.[11] Furthermore, the presence of a methyl group on C–5 might well be expected to offer some hindrance to closure of the ether ring. If this reasoning were valid, then isomethyldihydrothebainone would be easily accounted for as a diastereomer, the methyl group having added at C–7 in both possible configurations. The last hypothesis is susceptible of direct proof. If methyldihydrocodeinone and isomethyldihydrocodeinone differ only in the configuration at C–7, their enol acetates must be identical[12] (V, V-a ⟶ VIII).

Both methyldihydrocodeinone and isomethyldihydrocodeinone can be acetylated under the conditions which are imposed to transform dihydrocodeinone to its enol acetate ("Acedicon").

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[7] Small, Morris and Browning, unpublished results.

[8] Schöpf and Pfeifer, *Ann.*, **483**, 157 (1930); Schöpf and Perrey, *ibid.*, **483**, 169 (1930).

[9] David E. Morris, unpublished results.

[10] Formulas VI and VII are offered with reservation concerning the position of the methyl group.

[11] Kötz and Steinhorst, *Ann.*, **379**, 10, 15 (1911).

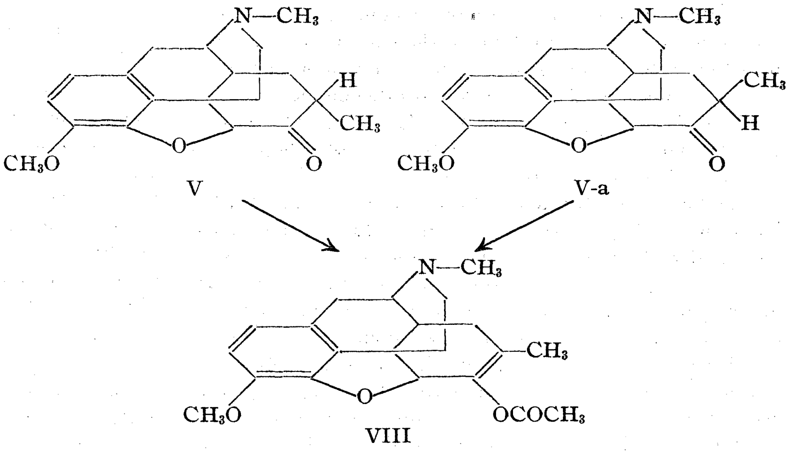
[12] This reasoning does not take into account the possibility of an enolization in which the hydrogen atom located on C-5 might participate.

The "methylacedicons" which are obtained from the isomeric ketones can scarcely be other than enol acetates, as is indicated by the ease with which they can be hydrolyzed back to the starting ketones, but they are not identical, a fact which we regard as weighing in favor of the 5-position for the new methyl group.

We have not neglected the possibility that methyldihydrothebainone and isomethyldihydrothebainone might have been formed by competing 1,2- and 1,4-additions of methylmagnesium iodide to the ether oxygen, double bond system of dihydrothebaine. The products in this case would owe their isomerism to the position of the methyl group at C-5 and C-7 (Formulas II and III), and, of the isomeric methyldihydrocodeinones, the 5-methyldihydrocodeinone (IV) should contain an active methylene group, in contrast to 7-methyldihydrocodeinone (V). An answer to this question was sought in the condensation reaction with ethyl oxalate according to Claisen,[13] a reaction which proceeds with methylene, but not with methenyl, groups adjacent to a carbonyl. Both of the methyldihydrocodeinones reacted with ethyl oxalate in the presence of absolute alcoholic sodium ethylate (although they were not affected by sodium ethylate alone), which again points to a location of the methyl group in two configurations at C-5. Against any final conclusion to be drawn from the evidence here presented we wish to cite the rather convincing stereochemical speculations of Schöpf,[14] which make it seem doubtful whether a 4,5-ring closure in more than one configuration would be possible.

The fact that one of the methyldihydrothebainones behaves as a cryptophenol while the other is normal in its phenolic nature suggests to us a greater structural difference than diastereoisomerism at C-5. Furthermore, when methyldihydrocodeinone is converted to its enol acetate, the specific rotation is changed only from −147 to −143°, while in the case of isomethyldihydrocodeinone the change is from −179 to −250°, indicating that in the latter an asymmetric center (C-7) may have been disturbed.

Incidentally, if it can be proved that the methyl group in one of our methyldihydrothebainones is located at C-5, the Knorr-Wieland formula for morphine (which we do not regard as yet disproved) will be put out of all question, for a linkage of the ethanamine chain at C-5 would exclude bromination and subsequent ring closure at this point.



The pharmacological action of the dihydromorphine and dihydrocodeine homologs described in this communication will be reported from the University of Michigan by N. B. Eddy and coworkers. The chemical studies in the series will be extended to embrace further conversion products of these bases (especially the desoxylated derivatives) and to include the introduction of groups other than methyl.

It is a pleasure to acknowledge our indebtedness to Merck and Co., Rahway, N. J., for the gift of the large amount of thebaine used in this research, and to E. R. Squibb and Sons for the fellowship grant under which most of the work was carried out.

Experimental Part

Dihydrothebaine.—The conditions influencing the hydrogenation of thebaine in acid solution have been so thoroughly studied by Schöpf and Winterhalder[3a] that we shall confine our description of the reduction to the convenient large scale preparation of dihydrothebaine without regard to the by-products formed. To a solution of 75 g. of thebaine (Merck and Co., Rahway, N. J.) in 150 cc. of 3 *N* acetic acid was added 4 cc. of concd. hydrochloric acid, 4 cc. of 1% palladous chloride solution and 0.1 g. of gum arabic. The solution was hydrogenated on the Adams machine at an initial pressure of 46 lb. (3.1 atm.); the pressure dropped 32 lb. (2.1 atm.) in twelve to twenty-four hours, corresponding to absorption of about 1.7 moles of hydrogen. Reduction was found to proceed much faster and more smoothly if the process was made continuous, the next 75 g. batch being put immediately

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[13] Claisen and Stylos, *Ber.*, **20**, 2188 (1887); *ibid.*, **24**, 111 (1891); Willstätter, *ibid.*, **30**, 2684 (1897).

[14] Schöpf and Pfeifer, *Ann.*, **483**, 162-164 (1930).

into the pressure bottle without removal of the residue of used catalyst.

Most of the colloidal palladium was removed by filtration through Norit, and the solution was treated slowly with an excess of dilute sodium hydroxide in the presence of a few cc. of ether. Dihydrothebaine separated crystalline, yield 30 to 40 g. (40–54%). It was recrystallized from alcohol, filtering to remove traces of palladium; 25 g. (33%) of pure white dihydrothebaine, m. p. 161–163°, was obtained, and from the mother liquors, 3 g. more of the same purity. Three kilos of thebaine yielded 1099 g. (36.4%) of dihydrothebaine. The alkaline mother liquors of a 75-g. run gave 15–20 g. of dihydrothebainone on treatment with ammonium chloride. The accumulated oily residues will be examined for the presence of Schöpf's epi-dihydrothebainone or other isomers.

The Grignard Reaction.—Forty grams of dihydrothebaine in a Soxhlet extractor, on a three-necked flask equipped with a mercury-sealed stirrer, was extracted into 600 cc. (500% of the calculated amount) of molar methylmagnesium iodide in thirty-six hours. Heating and stirring was continued for seventy-two hours longer, during which time the white precipitate increased notably. Attempts to shorten the reaction time by using isopropyl ether were unsatisfactory. The amorphous magnesium complex was decomposed with and dissolved in 800 cc. of 3 *N* hydrochloric acid, and the solution was extracted with 1.5 liters of ether, which removed a little oily material. The aqueous layer, made alkaline with ammonia, was extracted with eight liters of ether, with occasional addition of a little sodium hydrosulfite to prevent oxidation (evidenced by red coloration). Although further extraction with ether or chloroform removed no appreciable amount of material at this point, the aqueous layer gave a strong test with Mayer's reagent, and addition of picric acid precipitated 26 g. (37%) of an amorphous picrate. From this picrate only 1.6 g. of methyldihydrothebainone could be recovered, and the nature of the remaining (resinous) substance could not be ascertained. The ether extracts yielded 18 to 23 g. (45–58%) of oily crystals, which were recrystallized twice from absolute alcohol; yield of pure methyldihydrothebainone, 6 to 7 g. (15–17.5%). The alcohol mother liquors were concentrated and treated with alcoholic hydrogen chloride, giving 6 to 7 g. of hydrochloride, from which 4 to 6 g. of less pure methyldihydrothebainone could be recovered.

The alcohol filtrate from precipitation of the hydrochloride was freed of alcohol, dissolved in water, and treated with excess of sodium hydroxide. The clear alkaline solution was extracted with ether, from which 3.5 to 4.5 g. (9–11%) of crude isomethyldihydrothebainone was obtained. This was purified from acetone; yield 2 to 2.5 g.

Methyldihydrothebainone.—The base is very soluble in organic solvents, soluble in sodium hydroxide and precipitated from the alkaline solution by carbon dioxide. It can be purified from acetone or alcohol. It crystallizes in short rods from absolute alcohol, in plates from 95% alcohol, and the two forms are interconvertible. It sublimes in an oil-pump vacuum at 130°. In alcohol, $[\alpha]^{25}\text{D}$ −20.5° (c = 1.026) was found; the m. p. is 192–193°.

Anal. Calcd. for $C_{19}H_{25}O_3N$: C, 72.33; H, 7.99; OCH_3, 9.83. Found: C, 72.11; H, 7.96; OCH_3, 10.13.

The hydrochloride was prepared in absolute alcohol and purified from this medium. It also crystallizes well from water, m. p. 283–285° (evac. tube) with decomp.; $[\alpha]^{25}\text{D}$ −6.8° (water, c = 1.025).

Anal. Calcd. for $C_{19}H_{26}O_3NCl$: Cl, 10.08. Found: Cl, 10.18.

The methiodide was prepared by warming the base in methyl iodide, and was purified from acetone; m. p. 212–216° (evac. tube); $[\alpha]^{26}\text{D}$ +3.9° (water, c = 1.030).

Anal. Calcd. for $C_{20}H_{28}O_3NI$: I, 27.88. Found: I, 27.63.

The oxime hydrochloride separates crystalline when an aqueous suspension of methyldihydrothebainone is warmed with the calculated amount of hydroxylamine hydrochloride. After two crystallizations from water the hydrochloride had the m. p. 244° (evac. tube, gas evolution) and $[\alpha]^{24}\text{D}$ +38.9° (water, c = 0.514). Addition of sodium carbonate to an aqueous solution of the oxime hydrochloride caused precipitation of the oxime, which crystallized from dilute alcohol in rosets of white needles; m. p. 244° (evac. tube, gas evolution), and $[\alpha]^{24}\text{D}$ +69.4° (alcohol, c = 0.504).

Anal. Calcd. for $C_{19}H_{26}O_3N_2$: N, 8.48. Found: N, 8.51.

Acetylmethyldihydrothebainone.—One gram of methyldihydrothebainone in 15 cc. of acetic anhydride with 1.0 g. of dry sodium acetate was heated under reflux for one hour. After removal of excess acetic anhydride under diminished pressure at 60°, the oily residue was treated with ice and dilute ammonia, and extracted with ether. The product was recrystallized twice from ethyl acetate and sublimed at 0.01 mm., yield 0.4 g., of m. p. 179–179.5°. Prolonged heating with acetic anhydride yielded no diacetyl derivative. The monoacetyl compound has $[\alpha]^{26}\text{D}$ +13.1° (alcohol, c = 0.992).

Anal. Calcd. for $C_{21}H_{27}O_4N$: C, 70.55; H, 7.62. Found: C, 70.87; H, 7.81.

Bromomethyldihydrocodeinone.—A solution of 20 g. of methyldihydrothebainone in 200 cc. of glacial acetic acid, mechanically stirred, was treated dropwise with 193 cc. (2 moles) of a solution of bromine in glacial acetic acid (32 g. of bromine in 300 cc. of solution). The addition took about three hours, the bromine color being destroyed rapidly and hydrogen bromide evolved. The clear yellow solution was concentrated to a viscous mass at 70° under a water-pump vacuum, the oil was dissolved in water, treated with excess of 10 *N* sodium hydroxide, and the precipitated base extracted into ether. The ether was washed with four 100-cc. portions of normal sodium hydroxide and yielded 18.2 g. (73%) of slightly oily crystals of bromomethyldihydrocodeinone. The base is very soluble in organic media, but could be purified from ethyl acetate; white crystals of m. p. 143.5–145°; $[\alpha]^{24}\text{D}$ −109.4° (alcohol, c = 1.024). It sublimed in a high vacuum with slight decomposition.

Anal. Calcd. for $C_{19}H_{22}O_3NBr$: Br, 20.33. Found: Br, 20.08.

Bromomethyldihydrothebainone.—The alkaline mother liquor and washings from the preparation of bromomethyldihydrocodeinone were treated with an excess of ammonium chloride and extracted with ether until the Mayer's test was negative. The product was 4.1 g. of yellow powder which was obtained white by crystallization from acetone or ethyl acetate; it sublimes with slight decomposition in a high vacuum. The m. p. is 207–208° (evac. tube) with dec., $[\alpha]^{24}\text{D}$ −33.2° (alcohol, $c = 0.995$). Its nature as bromomethyldihydrothebainone was shown not only by analysis, but by catalytic debromination to methyldihydrothebainone. It appears to result from incomplete bromination of methyldihydrothebainone, but the use of correspondingly larger quantities of bromine did not increase the yield of the desired bromomethyldihydrocodeinone.

Anal. Calcd. for $C_{19}H_{24}O_3NBr$: Br, 20.23. Found: Br, 20.14.

Methyldihydrocodeinone.—A solution of 18.2 g. of crude bromodihydrocodeinone in 200 cc. of 2 *N* acetic acid with 5 g. of potassium acetate, a little gum arabic and 10 cc. of 1% palladous chloride solution took up 1142 cc. (corr.) of hydrogen (calcd. for one mole, 1062 cc.). The solution was made alkaline with sodium hydroxide after removal of the catalyst, and extracted with 2 liters of ether. The ether, after thorough washing with dilute alkali, yielded 12.0 g. (83%) of white crystalline methyldihydrocodeinone of m. p. 138–140°. The alkaline extracts gave 1.5 g. of a wax-like unidentified solid. Methyldihydrocodeinone is very soluble in organic media, but can be purified from ethyl acetate, acetone, or ether; long needles of m. p. 144–144.5°, $[\alpha]^{23}\text{D}$ −146.9° (alcohol, $c = 0.994$). It sublimes at 130° in a high vacuum.

Anal. Calcd. for $C_{19}H_{23}O_3N$: C, 72.80; H, 7.40. Found: C, 72.71; H, 7.41.

The methiodide was prepared by warming the base with methyl iodide, and crystallizing from alcohol. It melts at 246–248° (evac. tube) and has $[\alpha]^{24}\text{D}$ −74.2° (water, $c = 1.024$).

Anal. Calcd. for $C_{20}H_{26}O_3NI$: I, 27.88. Found: I, 27.67.

The oxalate, sulfate and hydrochloride are also crystalline.

Ethyl Oxalate Condensation.—Before attempting to demonstrate the presence of an active methylene group in methyldihydrocodeinone through Claisen's ethyl oxalate condensation, it was necessary to show that this condensation reaction proceeds with morphine bases which are known to contain an active methylene group, and does not take place with a typical base lacking such a group.[15] Two grams of dihydrocodeinone and 1.5 g. of ethyl oxalate were dissolved in 10 cc. of absolute alcohol containing 0.31 g. of sodium. After two days the solution was fluorescent red; removal of the alcohol left an amorphous mass, 90% of which was soluble in water and could not be extracted into ether. It probably consisted of dihydrocodeinone-7-glyoxalic acid, or its internal salt. Treatment of 2.0 g. of dihydrocodeine with ethyl oxalate in exactly the same manner resulted in recovery of 1.9 g. of unchanged dihydrocodeine.

Two grams of methyldihydrocodeinone, treated with ethyl oxalate as described above, gave a red fluorescent solution in two days. Alcohol was removed under diminished pressure, and the residue extracted with 500 cc. of ether, and 200 cc. of benzene; total extracted oily material, 0.3 g. The undissolved product was taken up in a little water (readily soluble), and extracted with ether (0.2 g. of unreacted methyldihydrocodeinone), then with much benzene and chloroform, which removed a little red oil. The aqueous layer, made just acid, was treated with excess of picric acid; yield 0.7 g. of picrate. The picrate was suspended in dilute hydrochloric acid, and extracted with isoamyl alcohol until all picric acid was removed. Evaporation of the aqueous layer gave the crystalline hydrochloride of methyldihydrocodeinone glyoxalic acid, which could be purified by recrystallizing from 3 *N* hydrochloric acid.

Anal. Calcd. for $C_{21}H_{24}O_6NCl$: C, 59.76; H, 5.73; Cl, 8.41. Found: C, 59.58; H, 5.81; Cl, 8.75.

Methyldihydrocodeinone in sodium ethylate solution without the ethyl oxalate was recovered unchanged.

Methyldihydrocodeinone Enol Acetate (Methyl Acedicon).—A solution of 1 g. of methyldihydrocodeinone in 15 cc. of acetic anhydride with 1 g. of anhydrous sodium acetate was heated under reflux for six hours. Acetic anhydride was removed under diminished pressure, and the oily residue was treated with ice and ammonia and extracted with ether. The crystals obtained from the ether (0.5 g.) were purified from ethyl acetate and sublimed in a high vacuum at 150°. The pure product melted at 191.5–194.5° and had in alcohol $[\alpha]^{23}\text{D}$ −142.9° ($c = 0.980$).

Anal. Calcd. for $C_{21}H_{25}O_4N$: C, 70.95; H, 7.10. Found: C, 70.87; H, 7.17.

On boiling the enol acetate for three minutes with 3 *N* hydrochloric acid, methyldihydrocodeinone was obtained.

Methyldihydrocodeine.—A solution of 1.9 g. of methyldihydrocodeinone in 30 cc. of alcohol with 0.1 g. of platinum oxide absorbed 183 cc. of hydrogen slowly (0.1 g. catalyst added during the reduction); calculated for one mole, 180 cc. The oil resulting from concentration of the solution crystallized when rubbed with ethyl acetate, yield 1.1 g. Methyldihydrocodeine crystallizes as the monohydrate in 8-sided crystals from acetone, ethyl acetate, ether or 50% alcohol; m. p. 98–102°, $[\alpha]^{24}\text{D}$ −84.8° (alcohol, $c = 0.990$).

Anal. Calcd. for $C_{19}H_{25}O_3N + H_2O$: C, 68.42; H, 8.17; H_2O, 5.41. Found: C, 68.39; H, 8.05; H_2O, 5.64.

By sublimation in a high vacuum, a crystalline anhydrous form of m. p. 85–88° is obtained.

The hydrochloride, which may be used advantageously to purify methyldihydrocodeine, was prepared in and purified from absolute alcohol. It melts at 286–287° (evac. tube) and has $[\alpha]^{23}\text{D}$ −64.5° (water, $c = 0.992$).

Anal. Calcd. for $C_{19}H_{26}O_3NCl$: Cl, 10.08. Found: Cl, 10.28.

The methiodide, prepared in the usual way, was purified from alcohol. It melts at 269–271° (evac. tube) and has $[\alpha]^{24}\text{D}$ −47.9° (water, $c = 1.024$).

Anal. Calcd. for $C_{20}H_{28}O_3NI$: I, 27.76. Found: I, 27.76.

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(15) An erroneous structural concept of pseudocodeinone was for many years based on the ability of this compound to condense with benzaldehyde [Knorr and Hörlein, *Ber.*, **40**, 3341 (1907)]; it has only recently been shown that a benzaldehyde condensation takes place with dihydrocodeine, and therefore is inacceptable as evidence for the $COCH_2$ group in the morphine series (ref. 4a).

Methyldihydromorphinone.—A solution of 2 g. of methyldihydrocodeinone in 10 cc. of 48% hydrobromic acid was boiled for twenty-five minutes (complete alkali solubility). The solution was diluted, made strongly alkaline, and extracted with ether (0.1 g. of unchanged material). Addition of ammonium chloride caused precipitation of the phenolic product, 1.7 g. of brown powder; yield after sublimation in a high vacuum at 180°, 1.4 g. of white crystals. Methyldihydromorphinone is only sparingly soluble in organic media. It crystallizes from alcohol in long needles of m. p. 243–245° (evac. tube, sintering at 235°); $[\alpha]^{24}\text{D}$ −140.7° (alcohol, c = 1.009).

Anal. Calcd. for $C_{18}H_{21}O_3N$: C, 72.18; H, 7.05. Found: C, 72.46; H, 7.10.

The hydrochloride was prepared in absolute alcohol and was recrystallized from alcohol. It melts with decomp. at 315–318° (evac. tube) and has $[\alpha]^{24}\text{D}$ −104.8° (water, c = 1.002).

Anal. Calcd. for $C_{18}H_{22}O_3NCl$: Cl, 10.57. Found: Cl, 10.67.

Methyldihydromorphine.—Preparation of methyldihydromorphine by demethylation of methyldihydrocodeine was unsuccessful because of extensive decomposition. A suspension of 1.4 g. of methyldihydromorphinone in 30 cc. of alcohol with 0.1 g. of platinum oxide absorbed one mole of hydrogen slowly (0.1 g. of catalyst added during the reduction). The product was isolated as in the case of methyldihydrocodeine, and was purified by crystallization from ethyl acetate and sublimation in a high vacuum at 180°; yield 1.2 g. The compound melts at 206–207° and has $[\alpha]^{24}\text{D}$ −92.9° (alcohol, c = 1.017).

Anal. Calcd. for $C_{18}H_{23}O_3N$: C, 71.71; H, 7.70. Found: C, 71.74; H, 7.72.

By methylation of methyldihydromorphine with diazomethane, the above-described methyldihydrocodeine was obtained.

Methyldihydromorphine hydrochloride was prepared in absolute alcohol and purified from alcohol. It melts at 316–317° with dec. (evac. tube) and has $[\alpha]^{23}\text{D}$ −65.7° (water, c = 1.004).

Anal. Calcd. for $C_{18}H_{24}O_3NCl$: Cl, 10.50. Found: Cl, 10.40.

The hydriodide was prepared in the usual way and purified from absolute alcohol. It melts at 289–291° (evac. tube) and has $[\alpha]^{23}\text{D}$ −50.5° (water, c = 0.991).

Anal. Calcd. for $C_{18}H_{24}O_3NI$: I, 29.58. Found: I, 29.42.

Isomethyldihydrothebainone.—This compound, isolated as described above, crystallizes from acetone in white needles of m. p. 168–168.5°. It is soluble in dilute sodium hydroxide, and is precipitated from the alkaline solution by carbon dioxide. It can be sublimed in an oil-pump vacuum at 140°. In alcohol, $[\alpha]^{24}\text{D}$ −57.0° (c = 1.023).

Anal. Calcd. for $C_{19}H_{25}O_3N$: C, 72.33; H, 7.99; OCH_3, 9.83. Found: C, 72.66; H, 8.03; OCH_3, 9.85.

The oxime was prepared by boiling an aqueous suspension of the base for several minutes with 2 moles of hydroxylamine hydrochloride. The oxime hydrochloride did not crystallize in this case, and the oxime was precipitated with sodium carbonate and recrystallized from alcohol, long silky needles of m. p. 191–192° (evac. tube, gas evolution at 210°); in alcohol, $[\alpha]^{24}\text{D}$ −82.4° (c = 0.498).

Anal. Calcd. for $C_{19}H_{26}O_3N_2$: N, 8.48. Found: N, 8.37.

Acetylisomethyldihydrothebainone.—The acetyl derivative was prepared exactly as described under methyldihydrothebainone, and was purified by crystallization from acetone and sublimation at 135° (0.01 mm.). It forms white crystals of m. p. 157–158°, $[\alpha]^{24}\text{D}$ −9.9° (alcohol, c = 0.452).

Anal. Calcd. for $C_{21}H_{27}O_4N$: C, 70.55; H, 7.62. Found: C, 70.43; H, 7.63.

Isomethyldihydrocodeinone.—A solution of 10.2 g. of isomethyldihydrothebainone in 100 cc. of glacial acetic acid was treated with 2 moles of bromine as described for methyldihydrothebainone. Acetic acid was removed at 60°, the oily product dissolved in water, treated with excess sodium hydroxide, and extracted with 3 liters of ether. The oil obtained from the ether was dissolved in hydrochloric acid, and precipitated as an amorphous powder with sodium hydroxide; yield of crude bromoisomethyldihydrocodeinone, 9.5 g. (75%). It could not be induced to crystallize. The crude product was hydrogenated as described under methyldihydrocodeinone (absorption, 1 mole) and yielded from ether 6.9 g. of crude isomethyldihydrocodeinone. It was dissolved in hydrochloric acid, and precipitated crystalline with excess of sodium hydroxide (yield 5.0 g.). Pure white crystals were obtained after two crystallizations from ethyl acetate. The compound sublimes in a high vacuum at 130°; the melting point is 144–145°. A depression of 25° is observed in the mixed melting point with methyldihydrocodeinone. In alcohol, isomethyldihydrocodeinone has $[\alpha]^{24}\text{D}$ −179.4° (c = 0.995).

Anal. Calcd. for $C_{19}H_{23}O_3N$: C, 72.80; H, 7.40. Found: C, 72.57; H, 7.32.

Condensation of isomethyldihydrocodeinone with ethyl oxalate under the conditions described above gave a water-insoluble oil from which no crystalline derivatives could be obtained. None of the ketone could be recovered unchanged from the reaction. While no analytical product could be isolated, it appears as though condensation with the ethyl oxalate must have taken place, for isomethyldihydrocodeinone was found to be largely unaffected by sodium ethylate in the absence of ethyl oxalate.

Isomethyldihydrocodeinone Enol Acetate.—Acetylation of 1 g. of isomethyldihydrocodeinone under the conditions described for methyldihydrocodeinone gave 1.1 g. of oily crystals which were purified from ethyl acetate and 50% alcohol, 0.6 g., m. p. 123–124°. It sublimes in a high vacuum at 110°; $[\alpha]^{24}\text{D}$ −250.3° (alcohol, c = 1.00).

Anal. Calcd. for $C_{21}H_{25}O_4N$: C, 70.95; H, 7.10. Found: C, 70.90; H, 7.30.

Hydrolysis of the enol acetate with 3 *N* hydrochloric acid gave isomethyldihydrocodeinone in poor yield.

Summary

1. Dihydrothebaine reacts with methylmagnesium iodide to yield two isomeric phenolic ketones, methyldihydrothebainone and isomethyldi-

hydrothebainone. In these the ether ring present in dihydrothebaine has been opened, the enol ether group at position-6 has been hydrolyzed, and a methyl group has been added to the nucleus.

2. Nuclear methylated analogs of dihydrocodeinone, namely, methyldihydrocodeinone and isomethyldihydrocodeinone, can be prepared by closure of the 4,5-ether bridge.

3. By demethylation and reduction, methyldihydrocodeinone can be converted to nuclear methylated analogs of dihydromorphinone, dihydromorphine and dihydrocodeine.

4. The nuclear position of the new methyl group is not certain, but the fact that the isomeric methyldihydrocodeinones yield isomeric enol acetates suggests that in one isomer the methyl group may be at C–5, and in the other at C–7.

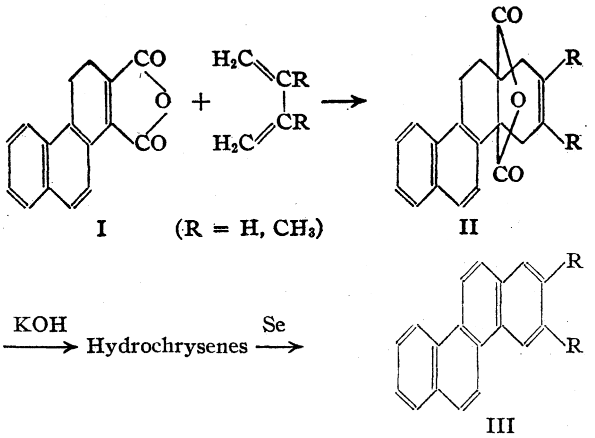
UNIVERSITY, VIRGINIA RECEIVED JUNE 1, 1936

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Synthesis of Phenanthrene and Hydrophenanthrene Derivatives. III. Hydrocarbons of the Chrysene, Acechrysene, and 3,4-Benzphenanthrene Series; 1,2-Benzpyrene Derivatives

BY L. F. FIESER, M. FIESER AND E. B. HERSHBERG

On investigating further applications of the hydrocarbon synthesis of Fieser and Hershberg[1] it has been found that chrysene and 2,3-dimethylchrysene can be obtained conveniently from 3,4-dihydrophenanthrene-1,2-dicarboxylic anhydride[2] (I) by the reactions indicated. The yields were very satisfactory throughout and the two aromatic hydrocarbons were easily obtained in a highly pure condition. The synthetic chrysene agreed well in melting point (254.5–255°, corr.) with other synthetic preparations[3] and it was indistinguishable from the purified material from coal tar employed in Baxter and Hale's[4] atomic weight work. Incidentally the synthetic phenanthrene previously described[1] was found to be incompletely dehydrogenated, and after suitable treatment the material melted at 100.7–101°, corr., a temperature appreciably higher than most values reported for highly purified samples from coal tar.[5]



The distillates obtained after fusing the diene addition products of the type II with alkali solidified easily but, as in the cases previously studied, they appeared to consist of mixtures of hydrocarbons in different stages of hydrogenation. The material from the butadiene product (R = H) seems to undergo disproportionation in solution, for after repeated crystallization some chrysene was obtained. The crude distillate gave with picric acid a stable compound having the composition of a dihydrochrysene picrate, and the regenerated hydrocarbon exhibited the same mutation in solution as the crude material.

In further extensions of the synthetic method little difficulty was experienced in obtaining the unsaturated anhydrides[2] required for the Diels–Alder reaction or in effecting the diene addition with these substances. 3,4-Dihydronaphthalene-1,2-dicarboxylic anhydride adds cyclopentadiene and cyclohexadiene about as readily as it does the open-chain dienes. The alkali fusion and the final step of dehydrogenation, however, are not always satisfactory. Although compounds of the type IV were obtained in good yield (80%) from 1,2-dihydrophenanthrene-3,4-dicarboxylic anhydride[2] and butadiene or 2,3-dimethylbutadiene, difficulties were encountered in attempting to con-

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(1) Fieser and Hershberg, THIS JOURNAL, **57**, 2192 (1935).

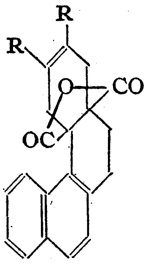
(2) Fieser and Hershberg, *ibid.*, **57**, 1851 (1935).

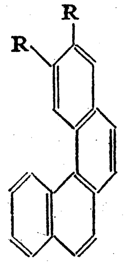
(3) Ruzicka and Hösli [*Helv. Chim. Acta*, **17**, 470 (1934)] record the value 255°, corr.

(4) Baxter and Hale, THIS JOURNAL, **58**, 510 (1936).

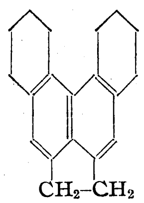
(5) Unfortunately a typographical error was made in reporting Dr. R. D. Haworth's melting point for 2,3-dimethylphenanthrene styphnate; this should read 147–148°.

vert the substances into 3,4-benzphenanthrenes, V. 6,7-Dimethyl-3,4-benzphenanthrene was obtained in this way in a satisfactory condition of purity, but both the potassium hydroxide fusion and the dehydrogenation proceeded poorly and the yield was quite low. Attempts to prepare the parent hydrocarbon by the same method were unsuccessful. An oil resulted in small amount from the fusion of IV (R = H) with alkali, but the material recovered after this had been heated with selenium or sulfur showed no difference in the boiling range or composition from the starting material. Hydrogenation of IV prior to the fusion did not improve the results and only resulted in an increase in the temperature at which reaction occurred.

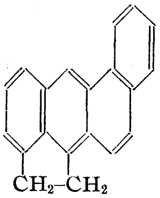

IV (R = H, CH$_3$)

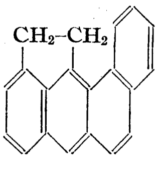

V (R = CH$_3$)

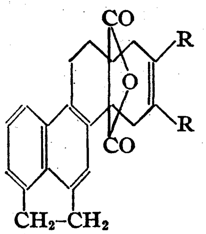
A similar difficulty was experienced in attempting to aromatize another hydrogenated 3,4-benzphenanthrene derivative (VI) investigated in conjunction with Mr. E. L. Martin. A quantity of the octahydro compound VI was prepared from a ketone previously synthesized[6] in this Laboratory from tetrahydroacephenanthrene, but attempted dehydrogenations with selenium, sulfur or platinum black resulted only in the complete destruction of the material.

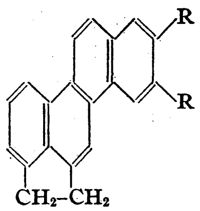

VI

3,4-Benzphenanthrene derivatives are of interest because of the discovery that the parent hydrocarbon[7] has cancer-producing properties.[8] The aromatic compound corresponding to VI would have an additional structural feature of interest in the dimethylene bridge extending across peri-positions. While 1,2-benzanthracene has little if any carcinogenic properties,[8] the addition of such a bridge in the 5,10-position leads to the potently tumor-inducing hydrocarbon cholanthrene (VII).[9,10] The isomeric 8,9-dimethylene derivative VIII (8,9-ace-1,2-benzanthracene) is less potent[10] than cholanthrene, but nevertheless active. It is of interest to learn if similar dimethylene derivatives of other hydrocarbons exhibit an enhanced activity, and as one step in this direction the synthesis of 6,7-acechrysenes of the type X was investigated. The required anhydrides (IX) were obtained without difficulty by condensing the ethyl ester of γ-(3-acenaphthyl)-butyric acid[6] with oxalic ester, cyclizing the product with 80% sulfuric acid to the unsaturated anhydride (a mixture of acetic and sulfuric acids gave the di-ester), and adding the appropriate diene. The remaining two steps presented the same difficulties as in the 3,4-benzphenanthrene series and again it was only in the case of the dimethyl derivative that the synthesis could be brought to a successful conclusion. 2,3-Dimethyl-6,7-acechrysene (X) was obtained in quantity sufficient for biological tests, if in poor yield, but the unsubstituted hydrocarbon could not be prepared. From the potassium hydroxide fusion of the anhydride IX (R = H) there was isolated an apparently pure hydrocarbon having the composition of a dihydro derivative, $C_{20}H_{16}$, but this was converted by sulfur or selenium treatment only into another substance of the same empirical formula.


VII


VIII


IX (R = H, CH$_3$)


X (R = CH$_3$)

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[6] Fieser and Peters, This Journal, **54**, 4373 (1932).

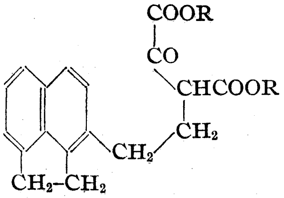
[7] Cook, *J. Chem. Soc.*, 2524 (1931).

[8] Barry, Cook, Haslewood, Hewett, Hieger and Kennaway, *Proc. Roy. Soc.* (London), **B117**, 318 (1935).

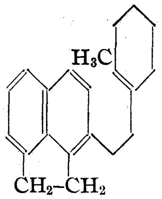
[9] Fieser and Seligman, This Journal, **57**, 2174 (1935).

[10] Shear, *Sci. Proc. Soc. Biol. Chem.*, XXX, lxxxix, *J. Biol. Chem.*, May, 1936.

The cyclization of the condensation product XI from the methyl ester of γ-(1-acenaphthyl)-butyric acid[6] and oxalic ester was much less satisfactory than in other cases investigated. In view of the low yield (27.5%) and the inaccessibility of the starting material the synthetic uses of the resulting unsaturated anhydride were not investigated. The unfavorable behavior of the 1-substituted acenaphthene derivative in contrast to the 3-isomer recalls the observation of Cook, Haslewood and Robinson[11] that difficulty was experienced in effecting a normal cyclization of the similarly constituted hydrocarbon XII. The fact that both reactions involve ring closure at a β-position of the naphthalene nucleus may be partly responsible for the poor results.

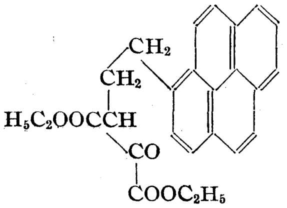


XI

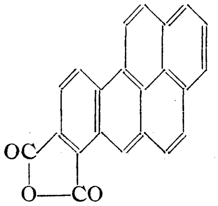


XII

It was found that 1,2-benzpyrene derivatives can be obtained readily by application of the Bougault reaction, for no difficulty was experienced in preparing and cyclizing the diethyl ester of α-oxalyl-γ-(1-pyrenyl)-butyric acid, XIII. The resulting unsaturated anhydride was dehydrogenated with sulfur to the aromatic anhydride XIV, which has been examined by Dr. M. J. Shear for possible carcinogenic activity. The anhydride itself produced no tumors after seven months and the disodium and dipotassium salts of the corresponding acid proved to be toxic to mice and produced hemorrhages.



XIII



XIV

Experimental Part[12]

Preparation of the Anhydrides

3,4-Dihydro-8,9-acephenanthrene-1,2-dicarboxylic Anhydride.—Ethyl γ-(3-acenaphthyl)-butyrate, b. p. 188–191° at 0.5 mm., was condensed with ethyl oxalate in the presence of potassium ethylate following the procedure outlined for the similar reaction of ethyl γ-phenylbutyrate.[2] The greater part of the reaction product separated in the form of the potassium salt, but a further small quantity was recovered by extraction of the acidified mother liquor. For cyclization the combined crude material was heated with 80% sulfuric acid for one-half hour at 70–80°, and the unsaturated anhydride was obtained in a good condition in 60% yield. The substance dissolves slowly in benzene and separates, after the solution has been concentrated, in the form of lustrous, deep orange needles. The melting point is dependent upon the material from which the capillary tube is constructed and upon the temperature at which the sample is introduced to the heating bath. When heated from 25° in a soft glass tube the melting occurs over the range 220–240°; in Pyrex the sample softens at 220° and melts at 230–232°. Introduced to a bath preheated to 222°, the sample melts completely at this temperature. In quartz the melting point is 229–232° with previous softening.

Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.24; H, 4.38. Found: C, 78.24; H, 4.63.

α-Oxalyl-γ-(3-acenaphthyl)-butyric acid diethyl ester was isolated as a solid in one experiment when the oily condensation product was allowed to stand until crystallization occurred. The substance formed fine, colorless needles, m. p. 83–85°, from ether–petroleum ether.

Anal. Calcd. for $C_{22}H_{24}O_5$: C, 71.70; H, 6.57. Found: C, 71.59; H, 6.42.

Diethyl 3,4-dihydro-8,9-acephenanthrene-1,2-dicarboxylate was obtained, along with some of the above anhydride, in an attempt to improve the yield in the Bougault ring closure by employing a mixture of equal parts of glacial acetic acid and 82% sulfuric acid (70–80°) in place of 80% sulfuric acid. The diester is much more soluble than the anhydride and it was obtained as yellow plates, m. p. 140.2–140.6°, by crystallization from benzene–ligroin.

Anal. Calcd. for $C_{22}H_{22}O_4$: C, 75.40; H, 6.33. Found: C, 75.49; H, 6.45.

For conversion to the anhydride the diester was hydrolyzed with alcoholic alkali and the free acid (2 g.) refluxed for a short time with a mixture of concentrated hydrochloric acid (20 cc.) and glacial acetic acid (125 cc.). The total yield of anhydride by this method was 50%.

3,4-Dihydro-5,10-aceanthrene-1,2-dicarboxylic anhydride was obtained in 27.5% yield by the standard procedure from methyl γ-(1-acenaphthyl)-butyrate, b. p. 223–226° at 8 mm. The Bougault reaction proceeded as above and the loss appeared to occur in the cyclization. The anhydride formed fine, orange-red needles from benzene, m. p. 276–277°.

Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.24; H, 4.38. Found: C, 77.75; H, 4.18.

1′,2′-Dihydro-1,2-benzpyrene-3′,4′-dicarboxylic Anhydride.—The required starting material was obtained by suspending γ-(1-pyrenyl)-butyric acid,[13] prepared in the manner previously reported[14] and with the same yields, in ethyl alcohol and passing in hydrogen chloride nearly to

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[11] Cook, Haslewood and Robinson, *J. Chem. Soc.*, 667 (1935).

[12] All melting points are corrected. Analyses by Mrs. G. M. Wellwood.

[13] Cook and Hewett, *J. Chem. Soc.*, 398 (1933).

[14] Fieser and Fieser, THIS JOURNAL, **57**, 782 (1935).

saturation. The acid soon gave way to the oily ester, and after distilling off most of the solvent this was dried in ether first with calcium chloride solution and then with sodium sulfate and distilled, b. p. 245–247°, uncorr., at 1 mm.; yield 91%. The distillate solidified and was obtained from ligroin as straw-colored prisms, m. p. 48.5–49°. The methyl ester was obtained as cottony clusters of colorless needles from hexane, m. p. 51.5–52°. Both preparations gave, on hydrolysis with alcoholic potassium hydroxide, followed by crystallization of the product from glacial acetic acid, completely colorless plates of γ-(1-pyrenyl)-butyric acid, m. p. 190–190.5°, whereas the acid as originally prepared and crystallized from xylene was invariably obtained as slightly brown or pink crystals.

The ester condensation of ethyl γ-(1-pyrenyl)-butyrate (10 g.) was carried out in the usual way,[2] the potassium salt of the product separating completely from the carmine-colored solution as a dark brown oil which slowly solidified. After decanting the mother liquor the salt was washed with dry ether and decomposed with an ice-cold mixture of 5 cc. of concentrated sulfuric acid and 100 cc. of water, when a solid oxalyl ester was obtained. This was taken up in benzene and the solution was washed with water and dried, and on adding ligroin a part of the oxalyl ester crystallized and a sample was purified as described below. The remainder of the material was recovered by evaporation under vacuum and treated with 80% sulfuric acid at 80–90° for one hour to effect cyclization. The orange anhydride soon separated and it was filtered off from the still warm solution and washed with 80% acid and then with alcohol; yield 7.5 g. The substance is very sparingly soluble in glacial acetic acid, acetic anhydride or toluene and moderately soluble in pyridine. After two crystallizations from tetrachloroethane (60 cc. per g.) it formed small rosets of feathery orange needles, m. p. 338–340°, dec. Further crystallizations from pyridine gave short, dark orange needles of the same melting point.

Anal. Calcd. for $C_{22}H_{12}O_3$: C, 81.46; H, 3.74. Found: C, 81.79; H, 4.13.

α-Oxalyl-γ-(1-pyrenyl)-butyric Acid Diethyl Ester (XIII).—The crude material on recrystallization from benzene–ligroin formed cream-colored needles, m. p. 106–107°.

Anal. Calcd. for $C_{26}H_{24}O_5$: C, 74.96; H, 5.81. Found: C, 74.62; H, 5.99.

1,2-Benzpyrene-3′,4′-dicarboxylic Anhydride (XIV).—For the dehydrogenation 2.75 g. of the dihydro compound was dissolved in 20 cc. of quinoline, 0.287 g. of sulfur was added and the solution was refluxed for two hours, when the evolution of hydrogen sulfide had practically ceased. On allowing the solution to cool the product separated as permanganate-colored prisms, and after sublimation in vacuum 2.4 g. of bright orange-red material, m. p. 378–380°, was obtained. The substance is practically insoluble in glacial acetic acid or dioxane. It is very soluble in quinoline and moderately so in pyridine, the latter solvent giving orange-brown prisms. After recrystallization from quinoline and from pyridine, followed by vacuum sublimation, the compound melted at 380–382°.

Anal. Calcd. for $C_{22}H_{10}O_3$: C, 81.96; H, 3.14. Found: C, 82.11; H, 3.66.

For conversion to the metal salts the anhydride was dissolved in pyridine, strong potassium or sodium hydroxide solution was added and most of the pyridine was removed by distillation. Methyl alcohol was added and the yellow salt was collected and washed. Both salts are readily soluble in water and the aqueous solutions show a strong blue fluorescence. In high dilution the potassium salt is hydrolyzed giving a colloidal solution of the acid.

The Diels–Alder Reaction

The previously reported preparation[1] of the addition products of the types II and IV by heating the components in dioxane solution was improved by raising the temperature. A shorter time was required in this case and usually heating for twenty-four hours at 160–180° was sufficient. The dioxane solution was then transferred to an all-glass distilling apparatus and after removing the solvent the residual oil was distilled in high-vacuum (3 microns). The reaction product was in this way obtained as a clean solid distillate free from polymerized diene, which otherwise hinders the process of crystallization. In the course of the subsequent crystallizations the addition product sometimes was found to be contaminated with a small amount of the completely aromatic anhydride evidently arising from a partial dehydrogenation of the starting material. This by-product can be removed easily by virtue of its sparing solubility in benzene, which easily dissolves the addition products. After filtration, partial evaporation, and dilution with ligroin the addition products separated as colorless crystals. By this modified procedure 5,6-benz-1,4,9,10,11,12-hexahydrophenanthrene-11,12-dicarboxylic anhydride[1] and its 2,3-dimethyl derivative[1] were obtained in 87 and 81% yield, respectively.

1,4,11,12,13,14 - Hexahydrochrysene - 13,14 - dicarboxylic anhydride, II (R = H) was obtained as colorless microcrystals, m. p. 143.5–144° from benzene–ligroin, in 67% yield.

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.92; H, 5.30. Found: C, 79.08; H, 5.62.

The yield of the 2,3-dimethyl derivative[1] was 94%.

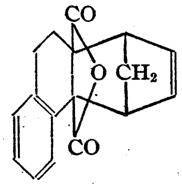
1,4,11,12,13,14 - Hexahydro - 6,7 - acechrysene - 13,14-dicarboxylic anhydride, IX (R = H) formed small colorless needles, m. p. 189–189.3°, from benzene–ligroin; yield 81%.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.97; H, 5.49. Found: C, 79.81; H, 5.49.

The 2,3-dimethyl derivative, IX (R = CH_3) forms prisms, m. p. 187.5–188°; yield 67–73%.

Anal. Calcd. for $C_{24}H_{22}O_3$: C, 80.41; H, 6.19. Found: C, 80.41; H, 6.28.

1,4 - *Endo*methylene - 1,4,9,10,11,12 - hexahydrophenanthrene-11,12-dicarboxylic anhydride was prepared



by heating 5 g. of 1,2-dihydronaphthalene-3,4-dicarboxylic anhydride with 10 g. of cyclopentadiene for twenty-four hours at 100° in a sealed tube. The excess diene and its dimer were removed by distillation in vacuum and the solid residue was crystallized from benzene–ligroin. The pure addition product collected amounted to 3.2 g. and the material from the mother liquor was contaminated with unchanged starting compound. The *endo*methylene compound melts at 158–159° with vigorous evolution of gas; this was found to be due to decomposition into the components by reversal of the Diels–Alder reaction.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.66; H, 5.30. Found: C, 76.55; H, 5.30.

The 2,3-dihydro derivative of the above compound, obtained by hydrogenation in glacial acetic acid solution with Adams catalyst, formed colorless prisms from benzene–ligroin, m. p. 156–156.5° (no decomposition).

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.09; H, 6.02. Found: C, 76.32; H, 6.20.

1,4 - *Endo*dimethylene - 1,4,9,10,11,12 - hexahydrophenanthrene-11,12-dicarboxylic anhydride was obtained in 70% yield by heating 2 g. of the unsaturated anhydride with 4 g. of cyclohexadiene for eight days at 100°. The excess liquid hydrocarbon was eliminated by distillation in vacuum and the residual solid crystallized from benzene–ligroin; colorless prisms, m. p. 137–138°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.11; H, 5.75. Found: C, 77.27; H, 5.46.

The 2,3-dihydro derivative, prepared as above, formed colorless prisms melting at 135–135.5°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.54; H, 6.45. Found: C, 76.42; H, 6.38.

5,6 - Benz - 1,2,3,4,9,10,11, 12 - octahydrophenanthrene-11,12-dicarboxylic anhydride, obtained by the hydrogenation of the previously described addition product in glacial acetic acid, formed colorless needles, m. p. 182.8–183.2°.

Anal. Calcd. for $C_{20}H_{18}O_3$: C, 78.40; H, 5.92. Found: C, 78.26; H, 5.90.

Conversion to Hydrocarbons

Chrysene.—For the elimination of the anhydride group of the butadiene addition product II (R = H) 5 g. of the material was cautiously heated with 8 g. of potassium hydroxide and 8 cc. of water at about 150° in a distilling flask with sealed-on receiver until conversion to the solid potassium salt was complete and then until the water had been largely evaporated. The temperature of the bath was then increased and the flask was connected to a water pump through a trap to catch sublimed material. Decomposition began at about 320–330° and a light yellow oil distilled and soon solidified. The temperature was gradually increased to 380–400°, when no more oil distilled and the residue in the flask carbonized. The yield of product melting over the range 198–204° was 2.6 g. (69%) and similar results were obtained in several other experiments. The crude solid is very readily soluble in benzene and sparingly soluble in alcohol. After six crystallizations from alcohol and one from glacial acetic acid there was obtained 0.2 g. of a constant melting fraction identified as chrysene. No other fractions of constant melting point were observed, and the mother liquor on further working yielded additional small amounts of chrysene apparently arising in the process of crystallization. The picrate of the chief primary constituent was more stable. An alcoholic solution of 1.9 g. of the crude distillate from the alkali fusion on treatment with 2.5 g. of picric acid deposited 2.7 g. of orange needles melting at 142–144°, and the melting point was not altered by further recrystallization. The substance forms lustrous orange needles which become opaque on drying even at room temperature, and it has the composition of a **dihydrochrysene picrate.**

Anal. Calcd. for $C_{18}H_{14} \cdot C_6H_3O_7N_3$: C, 62.73; H, 3.73; N, 9.15. Found: C, 62.42; H, 3.45; N, 9.06.

The hydrocarbon recovered from the purified picrate melted initially at 223–226°, but on repeated crystallization from glacial acetic acid the melting point steadily rose and eventually pure chrysene was again obtained. Chrysene itself was not observed to form a picrate in alcoholic solution, although in benzene clusters of small orange-red needles, m. p. 174–175°, were obtained.

For the production of chrysene 11.3 g. of the crude hydrocarbon from the alkali fusion was heated with 6 g. of selenium at 300–310° for fourteen hours and then, since the material isolated turned slightly purple and evidently was not completely dehydrogenated, 5 g. of selenium was added and the heating continued for forty-eight hours longer. The reaction product was extracted with benzene and the solution refluxed over fresh portions of sodium wire to remove traces of selenium. The process was repeated with more effectiveness when the benzene was replaced by toluene so that the sodium melted. The clarified solution on cooling deposited 7.6 g. of colorless crystals and 1 g. more was obtained from the mother liquor. The first crop was distilled at 2 mm. pressure and reserved for use in the atomic weight work of Professor G. P. Baxter. A sample crystallized from toluene formed colorless plates with a blue fluorescence, m. p. 254.5–255°.

2,3-Dimethylchrysene, III (R = CH_3).—The fusion of the addition product (5.5 g.) was conducted as above and the crude distillate (3.2 g.) was heated with a large excess of selenium for forty hours. The crystallized product (1.8 g.) was purified with sodium, distilled, and further crystallized from benzene, giving colorless plates, m. p. 215–215.3°.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.70; H, 6.30. Found: C, 93.47; H, 6.33.

Oxidation of the hydrocarbon with chromic anhydride in acetic acid solution gave after crystallization a bright red product which appeared from microscopic examination and from the melting range (222–232°) to be a mixture of two ortho quinones.

6,7-Dimethyl-3,4-benzphenanthrene, V (R = CH_3).—On fusing 5 g. of the addition product IV with potassium hydroxide a reaction occurred at a bath temperature of 330–340° but in a few minutes the residue turned black and the distillation of light yellow oil promptly stopped. In several experiments the oily product amounted to 0.5–0.8 g. The combined material from three runs was dehydrogenated as above and since the purified oil obtained did not solidify it was treated with picric acid in alcoholic solution. After removing a small amount of high-melting material which first separated there was obtained 2 g. of fine orange needles of the **picrate.** After further crystallizations this melted at 143–144°.

Anal. Calcd. for $C_{20}H_{16} \cdot C_6H_3O_7N_3$: N, 8.66. Found: N, 8.45.

The hydrocarbon recovered by decomposition of the purified picrate with ammonia solution retained a slight yellow color after crystallization from benzene–petroleum ether. On passing a benzene–ligroin solution through a tower of activated alumina the first fraction was colorless and on partial evaporation deposited colorless plates having a strong blue fluorescence, m. p. 94.5–95°.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.30. Found: C, 93.89; H, 5.94.

2,3-Dimethyl-6,7-acechrysene, X.—The fusion of 4 g. of the anhydride IX (R = CH_3) with potassium hydroxide at 360–380° gave 0.65 g. of solid distillate from which after several crystallizations from glacial acetic acid there was obtained 0.25 g. of colorless plates, m. p. 193.5–194.5°. This appears to be a **dihydro derivative.**

Anal. Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.88; H, 7.42.

The crude distillate served as well for the dehydrogenation as the purified dihydro derivative. From 0.5 g. of the distillate there was obtained after purification as above and final crystallization from benzene–ligroin 0.07 g. of colorless needles of the aromatic hydrocarbon, m. p. 222.6–223.1°.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.26; H, 6.52.

Attempts to Prepare 6,7-Acechrysene.—Two grams of the starting material (IX, R = H) gave 0.2 g. of solid distillate about half of which was obtained on crystallization from benzene–ligroin as fine, colorless needles, m. p. 153.2–153.5°. The analysis corresponds most closely to a **dihydroacechrysene.**

Anal. Calcd. for $C_{20}H_{16}$: C, 93.70; H, 6.30. Found: C, 93.32; H, 6.52.

The crude hydrocarbon distillate (0.5 g.) on treatment with selenium at 300–310° for twenty-six hours gave after purification a substance separating from benzene–ligroin as faintly yellow needles, m. p. 181–182°, and having nearly the same composition as the starting material. The same hydrocarbon was obtained in smaller amount when sulfur was used in place of selenium.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.70; H, 6.30. Found: C, 93.99; H, 6.18.

5,6 - Tetramethylene - 1,2,3,4 - tetrahydro - 8,9-acephenanthrene, VI,[15] was prepared in 77% yield (pure) by the high pressure (3000 lb.) hydrogenation of 5,6-tetramethylene-1-keto-1,2,3,4-tetrahydro-8,9-acephenanthrene[6] with Adkins catalyst No. 37 KAF in alcohol at 200°. The same method gave 72–83% yields in the preparation of one of the intermediates, 1,2,3,4-tetrahydro-8,9-acephenanthrene. The hydrocarbon VI was crystallized from alcohol in which it is sparingly soluble, forming long, stout, colorless needles, m. p. 148.6–149.0°.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.53; H, 8.46. Found: C, 91.48; H, 8.31.

A number of attempts were made to effect the dehydrogenation of the hydrocarbon with selenium, sulfur, and platinum black under a variety of conditions, but the only action noticed was that of complete decomposition.

Summary

γ-Arylbutyric esters derived from naphthalene, acenaphthene, and pyrene can be converted by condensation with oxalic ester and cyclization into unsaturated dicarboxylic anhydrides of the phenanthrene, acephenanthrene, aceanthrene and 1,2-benzpyrene series. The yields usually are good and the products can be aromatized without difficulty, or they can be converted in excellent yield into diene addition products. The conversion of the diene addition compounds into aromatic hydrocarbons is the least satisfactory part of the synthesis, for the results are variable. While chrysene and 2,3-dimethylchrysene were obtained easily by this method, attempts to prepare hydrocarbons of the 3,4-benzphenanthrene and 6,7-acechrysene series were only in part successful and then the yields were poor.

Cambridge, Mass. Received June 18, 1936

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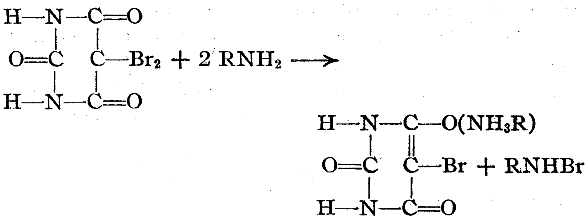
(15) Experiments of E. L. Martin.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MISSOURI]

Phenyl Nitrogen Substitution and Reactivity in the Barbituric Acid Series[1]

BY DOROTHY NIGHTINGALE AND LLOYD C. MORRIS

Dibromobarbituric acid reacts rapidly with primary and secondary amines to form the corresponding amine salt of monobromobarbituric acid.[2] As interpreted by Cope, the reaction may proceed as follows



It reacts with aniline or dimethylaniline to form monobromobarbituric acid and *p*-bromoaniline or *p*-bromodimethylaniline, respectively.[3] With thiourea it forms thiopseudouric acid.[4]

When the halogen derivatives of phenyl nitrogen substituted barbituric acids were used, it was found that the substitution of phenyl groups for hydrogen had a definite effect in the above types of reactions. On the other hand, these nitrogen substituted dibromobarbituric acids both reacted equally well with substituted hydrazines to form hydrazones of the corresponding alloxan, and Macbeth, Nunan and Traill[5] report no difference in the rates of their rapid reaction with hydrazine hydrate.

In the condensation reactions of the methylene group of the barbituric acids with aromatic aldehydes such as cinnamaldehyde and with diphenylformamidine, nitrogen substitution seems to have little if any effect on the rate of the reaction.

Experimental

The 1-phenyl and 1,3-diphenylbarbituric acids and their halogen derivatives were prepared according to the directions of Whiteley[6] and of Macbeth, Nunan and Traill,[5] with some necessary refinements in their procedures. The phosphorus oxychloride and malonyl chloride methods were both used. Even in the malonyl chloride method, by-products soluble in sodium carbonate solution are formed, which are not always completely removed from the barbituric acid by many recrystallizations. This is especially true with 1,3-diphenetylbarbituric acid.

In the preparation of the monohalogen derivatives of these barbituric acids, the acid is suspended in dry chloroform, and the 10% solution of bromine in chloroform must be added very slowly and with stirring. The same precautions must be observed in the preparation of the dihalogen barbituric acids, using glacial acetic acid as the solvent. In either preparation, a gummy product results if the bromine is added too rapidly.

Halogen Barbituric Acids and Aliphatic Amines.—Dibromobarbituric acid reacts rapidly in warm alcohol solution with butylamine to give a 73% yield of the relatively stable butylamine 5-bromobarbiturate. When 1-phenyl-5,5-dibromobarbituric acid was used in warm or cold absolute alcohol solution, a tar was obtained which would not yield crystals. Benzene was found to be a satisfactory solvent for the reaction. The 1-phenyl-5,5-dibromobarbituric acid (3.6 g.) was dissolved in dry benzene and the solution cooled to +10°. The butylamine (1.5 g.) in a little dry benzene was slowly added with stirring. Some tar formed and adhered to the beaker, but when the benzene was poured off and allowed to stand in the cold for several hours, about 1.2 g. of a mixture of butylamine hydrobromide and the amine barbiturate separated. Attempts to purify this mixture resulted in a tar. Decomposition with the formation of a tar took place when the product was heated above 100° or if it was allowed to come in contact with moist air. Kjeldahl analysis indicated a nitrogen content of 10.97%. Butylamine hydrobromide and butylamine 1-phenyl-5-bromobarbiturate contain 9.11 and 11.80% nitrogen, respectively.

The 5-bromo-1-phenylbarbituric acid and butylamine in benzene under the above conditions gave some tar and a 10 to 15% yield of pure butylamine 5-bromo-1-phenylbarbiturate. The salt is unstable and decomposes to form a red tar at elevated temperatures or if exposed to moist air for any length of time. It melts with decomposition around 110–120°. Other aliphatic amines gave similar results.

Anal. Butylamine 1-phenyl-5-bromobarbiturate. Calcd. for $C_{14}H_{18}N_3O_3Br$: total N (Kjeldahl), 11.80; amine N, 3.93. Found: N, 11.73; N, 3.91. The amine nitrogen was determined by the procedure used by Cope.

The butylamine 5-bromo-1-phenylbarbiturate was treated with cold sodium carbonate solution in which it readily dissolved, liberating butylamine. The solution was filtered, acidified with hydrochloric acid, and the precipitate which formed collected on a Büchner funnel. This white solid melted at 213° and did not depress the melting point of a sample of 5-bromo-1-phenylbarbituric acid.

Both the mono and dibromo derivatives of 1,3-diphenylbarbituric acid and butylamine under the above conditions gave some tar on evaporation of the solvent but no crystals

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[1] Abstract of a thesis submitted by Lloyd Clayton Morris in partial fulfilment of the requirements for the degree of Master of Arts at the University of Missouri.

[2] Nightingale and Schaefer, THIS JOURNAL, **54**, 236 (1932); Cope, *ibid.*, **54**, 1251 (1932).

[3] Conrad and Reinbach, *Ber.*, **35**, 522 (1902); Gupta and Thorpe, *J. Chem. Soc.*, **121**, 1896 (1922).

[4] Trzscinski, *Ber.*, **16**, 1057 (1883).

[5] Macbeth, Nunan and Traill, *J. Chem. Soc.*, 1248 (1926).

[6] Whiteley, *ibid.*, **91**, 3135 (1907).

of amine barbiturate, even when heated in a sealed tube with or without a solvent. Solvents such as ethyl alcohol and ether as well as benzene were used but with no better results.

When dibenzylamine reacts with dibromobarbituric acid, the crystals which separate rapidly from the alcohol solution are a mixture of the moderately soluble dibenzylamine hydrobromide and dibenzylamine 5-bromobarbiturate. When 1,3-diphenyl-5,5-dibromobarbituric acid was used, the solution turned a violet-red but no crystals separated. Concentration of the solution gave a small amount of colored crystals which on recrystallization were white and melted at 265°. The melting point of these crystals and dibenzylamine hydrobromide was also 265°. Some amine salt of monobromodiphenylbarbituric acid may be formed but is probably too unstable to isolate.

A comparison of rates of reaction of dibromobarbituric acid and 1-phenyl-5,5-dibromobarbituric acid with butylamine is difficult since they require different experimental conditions. Dibromobarbituric acid is only slightly soluble in hot benzene.

Halogen Barbituric Acids and Aniline.—Aniline reacts immediately in warm alcohol solution with dibromobarbituric acid to give an almost quantitative yield of *p*-bromoaniline and bromobarbituric acid. The 1-phenyl-5,5-dibromobarbituric acid (3.6 g.) was dissolved in hot alcohol and aniline (1 g.) added. There was no immediate reaction noticeable. After standing for several hours, the precipitate of 1-phenyl-5-bromobarbituric acid (m. p. 213°) which gradually separated was collected on a filter. The *p*-bromoaniline (m. p. 66°) was isolated from the filtrate. Yields were nearly quantitative.

The 1,3-diphenyl-5,5-dibromobarbituric acid and aniline formed some tar, but none of the monohalogen acid separated from the solution, even on long standing and evaporation of the solvent.

Halogen Barbituric Acids and Thioureas.—The mono and dibromo derivatives of barbituric acid and of 1-phenylbarbituric acid react rapidly with the thioureas to form the 8-thio-9-R- and 1-phenyl-8-thio-9-R-pseudouric acids, respectively. The halogen barbituric acid (1 mole) in alcohol solution is added to an alcohol solution of the thiourea (1 mole). Heat is evolved and the thiopseudouric acid precipitates rapidly. Yields are nearly quantitative. The thiopseudouric acids are soluble in hot water but insoluble in the common organic solvents, and decompose at their melting points.

8-THIO-9-R-PSEUDOURIC ACIDS

Thiourea used	Formula	°C., dec.	% nitrogen (Kjeldahl) Calcd.	Found
Phenyl	$C_{11}H_{10}N_4O_3S$	240	20.14	19.90
Allyl	$C_8H_{10}N_4O_3S$	270	23.14	23.16
o-Tolyl	$C_{12}H_{12}N_4O_3S$	275	19.18	19.04

1-PHENYL-8-THIO-9-R-PSEUDOURIC ACIDS

Thiourea used	Formula	°C., dec.	% nitrogen (Kjeldahl) Calcd.	Found
Thiourea	$C_{11}H_{10}N_4O_3S$	>300	20.14	20.16
Phenyl	$C_{17}H_{14}N_4O_3S$	280	15.82	15.94
Allyl	$C_{14}H_{14}N_4O_3S$	>300	17.61	17.62

When alcohol solutions of either 5-bromo- or 5,5-dibromo-1,3-diphenylbarbituric acid and the thioureas were mixed, no heat was evolved as with the other halogen barbituric acids, and no crystals separated even after long heating. Evaporation of the solvent gave some crude crystals which, from their nitrogen content and melting points, were apparently mixtures of some of the unchanged halogen barbituric acid and the thiourea. Recrystallization of this material gave the pure thioureas.

α-Naphthylhydrazine and the Dihalogen Barbituric Acids.—An alcohol solution of α-naphthylhydrazine hydrochloride (1 mole) was added to a hot alcohol solution of the nitrogen-substituted dibromobarbituric acid (1 mole). The brick-red hydrazone which separated rapidly was collected on a filter and washed with hot alcohol. These hydrazones are slightly soluble in hot alcohol and insoluble in the other common organic solvents.

	Formula	M. p., °C.	% nitrogen (Dumas) Calcd.	Found
1 - Phenylalloxan α - naphthylhydrazone	$C_{20}H_{14}N_4O_3$	292	15.64	15.49
1,3 - Diphenylalloxan α-naphthylhydrazone	$C_{26}H_{18}N_4O_3$	303	12.90	12.96

There was no observable difference in the rates of these reactions.

Methylene Condensations.—When either cinnamaldehyde or diphenylformamidine was added to a hot alcohol solution of either 1-phenyl- or 1,3-diphenylbarbituric acid, the slightly soluble cinnamylidene and anilinomethylene derivatives separated rapidly and quantitatively. There was no observable difference in the rate of reaction of a series of mono and diaryl nitrogen-substituted barbituric acids with these reagents.[7]

Summary

The replacement of one hydrogen by a phenyl group in dibromobarbituric acid decreases the rate of reaction with aniline and possibly with aliphatic amines. The amine salts of 1-phenyl-5-bromobarbituric acid are less stable than those of 5-bromobarbituric acid.

Amines and thioureas do not react appreciably with 1,3-diphenyl-5,5-dibromobarbituric acid under the conditions described.

Aryl nitrogen substitution seems to have little if any effect on the reactivity of the methylene groups in the aryl nitrogen substituted barbituric acids.

COLUMBIA, MISSOURI RECEIVED MAY 18, 1936

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(7) Nightingale and Alexander, THIS JOURNAL, **58**, 794 (1936).

[CONTRIBUTION NO. 151 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & CO., INC.]

Solvation and the Determination of Molecular Weights by Means of the Svedberg Ultracentrifuge

BY WILLIAM D. LANSING AND ELMER O. KRAEMER

In a recent paper,[1] Professor McBain considers the error due to solvation in molecular weights determined by means of the ultracentrifuge and concludes that the error may amount to "hundreds of per cent." Although Professor McBain is not clear on this point, by emphasizing the dependence of sedimentation on a difference in the partial specific volumes of solvated and unsolvated molecules, he implies that solvation affects in a different manner molecular weights determined by means of the ultracentrifuge and by conventional methods such as osmotic pressure or change in freezing point, boiling point, or vapor pressure.

In contrast to this point of view, we shall show that the effect of solvation is the same for the ultracentrifuge as for conventional methods; that as a matter of fact, the error owing to solvation in binary systems is independent of the partial specific volumes of the components; and that in no case can the error amount to "hundreds of per cent." in a binary system for the reason that the apparent molecular weight, ignoring solvation, is always less than the true molecular weight of the unsolvated molecules, regardless of the values for the partial specific volumes. Furthermore, we shall show that whenever the molecular weight determinations are made in low concentrations, as is generally admitted to be necessary for valid results by any method, enormous solvations lead to a relatively small error. We therefore believe that, in practice, solvation very rarely, if ever, leads to any significant error in ultracentrifuge determinations of molecular weight on binary solutions.

The effect of solvation in a multicomponent system may be considerably more complicated than for a binary solution. Since Professor McBain discusses such systems also, without however presenting any mathematical treatment, we add a brief quantitative discussion of ternary systems in which combination occurs between the sedimenting component and one of the other two.

Solvation in Binary Systems.—Considering a binary solution, in which s grams of component 2 (solvent) combines with one gram of component 1 (solute), the following symbols and definitions may be set up

x_1, x_2 = number of grams of components 1 and 2 in solution.
$y_{12} = (s + 1)x_1$ = grams of compound (solvate) in solution.
$y_2 = x_2 - sx_1$ = grams of free solvent.
v = volume of solution; V = specific volume of solution $= v/(x_1 + x_2)$.
$\overline{V}_1$, $\overline{V}_2$ and $\overline{V}_{12}$ = partial specific volumes of solute, solvent and solvate respectively.

Remembering that $v = f\,(y_{12}, y_2)$, one obtains by partial differentiation

$$\frac{\delta v}{\delta x_1} = \overline{V}_1 = \frac{\delta v}{\delta y_{12}}(s + 1) - \frac{\delta v}{\delta y_2}s \qquad (1)$$

and

$$\frac{\delta v}{\delta x_2} = \overline{V}_2 = \frac{\delta v}{\delta y_2}$$

Combining these, and replacing the differentials by the corresponding specific volume symbols, one finds that

$$(s + 1)\overline{V}_{12} = s\overline{V}_2 + \overline{V}_1 \qquad (2)$$

That is to say, the partial specific volume of the solvate can be calculated only if the degree of solvation s is known.

Turning now to the question of molecular weights, it is apparent that

$$M_{12} = (s + 1)M_1 \qquad (3)$$

where M_1 is the molecular weight of the unsolvated solute and M_{12} is the molecular weight of the solvated solute. Since in calculating molecular weight by the usual equation for sedimentation equilibrium, the partial specific volume of the unsolvated solute is used, an "apparent molecular weight" M' is obtained, which is related to M_{12} and the partial specific volumes by the equation

$$M_{12}(1 - \overline{V}_{12}/V) = M'(1 - \overline{V}_1/V) \qquad (4)$$

Combining equation 4 with equations 2 and 3, and eliminating M_{12} and $\overline{V}_{12}$, we get

$$M_1 = M'\frac{(1 - \overline{V}_1/V)}{(1 - \overline{V}_1/V) + s(1 - \overline{V}_2/V)} \qquad (5)$$

Introduction of the definitions for $\overline{V}_1$ and $\overline{V}_2$ ex-

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[1] J. W. McBain, THIS JOURNAL, **58**, 315 (1936).

pressed in terms of weight fractions, c_1 and c_2, for solute and solvent,[2] namely

$$\bar{V}_1 = V + c_2 \mathrm{d}V/\mathrm{d}c_1 \qquad (6)$$
$$\bar{V}_2 = V - c_1 \mathrm{d}V/\mathrm{d}c_1$$

finally gives

$$M_1 = M' \frac{1 - c_1}{1 - c_1 - sc_1} \qquad (7)$$

It may readily be shown that the same equation describes the effect of solvation on molecular weights by osmotic pressure and other conventional methods. This of course is to be expected in view of the thermodynamic equivalence of osmotic pressure and sedimentation equilibrium.[3]

From eq. 7 it is evident that the error due to solvation is independent of the partial specific volumes of the components for the ultracentrifuge method, as well as for osmotic pressure and related methods. Furthermore, inasmuch as the apparent molecular weight M' is always smaller than the true molecular weight M_1 of the unsolvated solute, the error can never amount to "hundreds of per cent." In fact, since low concentrations should always be used for molecular weight determinations by means of the colligative properties of solutions, quite enormous degrees of solvation have an insignificant effect on molecular weight. For example, from eq. 7, if c_1 is about 0.001, as it commonly has been in our ultracentrifuge work, the solvation would have to be about 990% to make an error of 1% in the molecular weight. We therefore believe that solvation needs never lead to any serious error in ultracentrifuge determinations of molecular weight for binary solutions.

Three-Component Systems with Solvation or Compound Formation.—Three-component systems containing but one sedimenting component and with no combination between the components may be considered as a binary system without solvation. If the sedimenting component combines with the other two components in the same proportions as they exist in the solution, the solution is equivalent to a binary solution with solvation, as treated above. If, however, combination occurs between the sedimenting component and one of the other components, or if the sedimenting component combines with both of the other components in proportions different from those in which they exist in the solution, a new case arises.

Calling the sedimenting or colloidal solute component 1, and considering the case where r grams of component 2 combines with one gram of component 1, we may set up the following definitions

$$y_{12} = (r + 1)x_1$$
$$y_2 = x_2 - rx_1$$
$$y_3 = x_3$$

where y_{12}, y_2, and y_3 are the grams of compound, free component 2, and component 3 in the solution.

By operations entirely similar to those used in the discussion of binary solutions, we obtain an equation which is analogous to eq. 2; namely

$$(r + 1)\bar{V}_{12} = r\bar{V}_2 + \bar{V}_1 \qquad (8)$$

and an equation which is analogous to eq. 5, namely

$$M_1 = M' \frac{(1 - \bar{V}_1/V)}{(1 - \bar{V}_1/V) + r(1 - \bar{V}_2/V)} \qquad (9)$$

In other words, the true molecular weight of component 1 in its uncombined state can be determined only if the component with which the colloidal solute combines, the composition of the compound, and the partial specific volumes of both components of the compound, are known. It may be noted that for this case, as well as for the binary solution, the error in molecular weight is not dependent on the partial specific volume of the compound formed by the colloidal solute.

The partial specific volumes in question are defined by a set of equations analogous to those of eq. 6 and similarly derivable

$$\bar{V}_1 = V + (1 - c_1)\frac{\delta V}{\delta c_1} - c_2 \frac{\delta V}{\delta c_2}$$
$$\bar{V}_2 = V - c_1 \frac{\delta V}{\delta c_1} + (1 - c_2)\frac{\delta V}{\delta c_2} \qquad (10)$$
$$\bar{V}_3 = V - c_1 \frac{\delta V}{\delta c_1} - c_2 \frac{\delta V}{\delta c_2}$$

where the partial derivative with respect to c_1 is taken with c_2 constant, and *vice versa*. Since $c_1 + c_2 + c_3 = 1$, changes in c_3 may be ignored. By substituting the values for $\bar{V}_1$ and $\bar{V}_2$ as given by eq. 10 into eq. 9, one may calculate the error corresponding to various values of r.

Whereas for the binary case, as Professor McBain points out, the partial specific volumes of the colloidal component and its compound with the solvent must necessarily differ if sedimentation is to occur, the same is not in general true for multicomponent systems. Specifically, in a ternary system, it is possible for the colloidal solute and its compound with one of the components to have

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[2] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York City, 1923, p. 38.

[3] A. Tiselius, *Z. physik. Chem.*, **124**, 449 (1926).

the same partial specific volume without eliminating the difference between $\bar{V}_{12}$ and V, which is the condition for sedimentation to occur. In such a case, as shown by eq. 8, $\bar{V}_1 = \bar{V}_2 = \bar{V}_{12}$, and as shown by eq. 9, the molecular weight calculated from ultracentrifugal data is then the true molecular weight of the *compound*. The relationship, under these conditions, between $\bar{V}_{12}$ and V may be shown from eq. 10 to be

$$\bar{V}_{12} = V + c_3(\delta V/\delta c_1) \qquad (11)$$

The question regarding the formation of a compound between the colloidal solute and another component of a solution has concerned us a good deal in connection with our ultracentrifugal studies of cellulose in cuprammonium.[4] Although these solutions contain at least four components, we have assumed that they could be considered as ternary systems with combination occurring between the cellulose and the copper. We know of no entirely satisfactory way of determining directly the composition of the compound or its partial specific volume, so our conclusions concerning the molecular weight of cellulose in cuprammonium involve other considerations. As pointed out above, however, if the partial specific volumes of cellulose and of the compound with copper happen to be the same, a true molecular weight of the compound is obtained. We attempted to give general expression to this thought in our previously cited paper, but unfortunately we did not limit our remark to ternary or more complicated systems, and we are in complete agreement with Professor McBain's criticism of our statement, in so far as binary systems are concerned.

From Professor McBain's remarks concerning "bound water" and its determination in ternary systems, it might be thought that his method offers a direct way of measuring at least the partial specific volume of the cellulose–copper compound. We fear, however, that such is not the case. The partial specific volume of the cellulose is considerably less than the specific volume of the solution. As a result, very considerable amounts of an additional substance with a definitely lower partial specific volume than the cellulose would have to be added to the solution in order to reduce the specific volume of the solution to equality with that of the cellulose–copper compound and thus to prevent sedimentation. Whether the elimination of sedimentation could actually be accomplished in this way we do not know, but if it could be done, we feel that there would in general be very little chance that the partial specific volume of the colloidal solute would remain unchanged, especially if the colloidal component formed a compound with some other component of the system.

However, whenever the partial specific volume of the compound containing the colloidal solute can be determined by Professor McBain's method, one may replace $\bar{V}_{12}$ of eq. 8 with the value of V, substitute the values of $\bar{V}_1$ and $\bar{V}_2$ as given by eq. 10, and calculate r. This assumes, of course, that $\bar{V}_1$, $\bar{V}_2$ and $\bar{V}_{12}$ are not changed by the additional component required to bring V and $\bar{V}_{12}$ into equality, that one knows which component combines with the colloidal solute, and that $\bar{V}_3$ and c_3 refer to the mixture of all components other than the colloidal solute and the component with which it combines.

Summary

For binary solutions the change in partial specific volumes resulting from solvation or compound formation does not affect molecular weights determined by the sedimentation equilibrium method in any way different from that for conventional methods, in spite of the fact that sedimentation equilibrium is dependent on differences in partial specific volumes. Under normal conditions, with a binary solution, solvation is probably rarely if ever great enough to lead to an appreciable error in molecular weights. For ternary and higher order systems, also, the error in molecular weight by the sedimentation equilibrium method may be evaluated quantitatively without considering the partial specific volume of solvates or compounds formed by sedimenting component.

WILMINGTON, DEL. RECEIVED MARCH 14, 1936

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[4] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 165 (1935).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Some Chromous and Chromic Ammines

BY J. H. BALTHIS, JR.,[1] AND JOHN C. BAILAR, JR.

In the course of some work on the stereochemistry of chromium, it has been necessary to know something of the stability of chromous ammines toward water and air. Very few chromous ammines have been studied in this respect; apparently no investigation has been made of the ones in which we are particularly interested—those containing ethylenediamine and its homologs.

Traube and Passarge[2] prepared chromous ammines by the action of hydrazine and of hydrazine sulfate upon chromous salts. These compounds were so stable that they showed no change on standing in the air for several days. Traube, Burmeister and Stahn[3] by treating chromous chloride and chromous formate with pyridine obtained complexes which absorb oxygen from the air, but which are stable, even when wet, if protected from the air. Barbieri and Tettamanzi[4] found that $[\mathrm{Cr\ dip_3}]\ \mathrm{Br_2{\cdot}6H_2O}$ (dip = dipyridyl) oxidizes slowly in the air. The same investigators prepared chromous complexes containing hexamethylenetetramine, and found them to be readily oxidized when wet. Chromous ammonia complexes are stable when dry[5] but when a solution of a chromous salt is treated with ammonium hydroxide and an ammonium salt, hydrogen is evolved and the chromic complex is formed.[6] We have found that ethylenediamine and its homologs behave in this same way, liberating hydrogen very rapidly.

When a solution of chromous chloride in an atmosphere of nitrogen was treated with a solution of ethylenediamine with or without the addition of ethylenediamine hydrochloride a transient blue precipitate formed. This was perhaps a chromous complex. Rapid oxidation to the chromic state prevented its isolation, however. As soon as the solutions were mixed, evolution of hydrogen began, and within an hour and a half the oxidation was practically complete.

The use of chromous acetate instead of the chloride gave essentially the same results. In this case an 80% yield of triethylenediamine chromic bromide $[\mathrm{Cr\ en_3}]\ \mathrm{Br_3{\cdot}3H_2O}$ was obtained by concentrating the solution and adding sodium bromide. A small amount of hexaethylenediamine-hexol-tetrachromic bromide $[\mathrm{Cr_4(OH)_6en_6}]\mathrm{Br_6{\cdot}4H_2O}$[7] was formed, also.

An unstable chromous ammine must have been formed before the oxidation took place, for the chromic ion will not react with ethylenediamine under these conditions. Although the conditions of the experiment were varied in many ways, no chromous compound could be isolated. In the hope of obtaining more stable compounds 1,2-propylenediamine and 2,3-butylenediamine (for which an improved method of preparation was developed) were substituted for the ethylenediamine. Again, only chromic compounds were obtained. Chromous ammines containing bases of this series are apparently too readily oxidized by water to be isolated from aqueous solution. This furnishes a much easier method of preparing the triethylenediamine chromic salts than any which has previously been described. A simplified procedure for this preparation is outlined in the Experimental Part.

We were led by these observations to study briefly the stability of chromous ammines containing bases with nitrogen in the ring. In agreement with the results of Barbieri and Tettamanzi, we found the dipyridyl complex to be quite stable. In the case of the pyridine complex the nitrogen to chromium bond is evidently less stable for the compound which we prepared, $[\mathrm{Cr\ py_2}]\mathrm{Cl_2}$, lost pyridine gradually on standing. Quinoline complexes are still less stable. Chromous chloride and acetate dissolved readily in quinoline to give deeply colored solutions, but the addition of alcohol precipitated the original chromous salt. None of the complex ions containing ring bases were oxidized by water.

Experimental

Most of the experiments were carried out in the apparatus shown in Fig. 1. A novel feature of this device is the combined stirrer-filter B. The shaft of this stirrer is a heavy-walled 8-mm. tube. The lower end is expanded to an

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(1) Abstracted from part of a thesis submitted for the degree of Doctor of Philosophy at the University of Illinois.

(2) Traube and Passarge, *Ber.*, **46**, 1505 (1913).

(3) Traube, Burmeister and Stahn, *Z. anorg. allgem. Chem.*, **147**, 50 (1925).

(4) Barbieri and Tettamanzi, *Atti Accad. Lincei*, **15**, 877 (1932).

(5) These compounds are discussed by Schlesinger and Hammond, THIS JOURNAL, **55**, 3971 (1933).

(6) Asmanow, *Z. anorg. allgem. Chem.*, **160**, 209 (1927).

(7) Pfeiffer, *ibid.*, **58**, 272 (1908).

internal diameter of 10 mm. and is packed with glass wool. A short piece of glass rod is sealed to the shaft just above the expanded portion. During filtration the upper end of the shaft is connected (at C) to the vacuum line by a piece of light rubber tubing; when the device is used for stirring the rubber is disconnected from the vacuum line and closed by a piece of glass rod. By placing B very close to the bottom of the flask, practically all of the liquid can be drawn off. Liquids for washing precipitates are introduced through K and withdrawn through B. The apparatus is convenient and has proved to be very efficient.

Preparation of Chromous Acetate.—Chromic chloride is reduced by zinc and hydrochloric acid in F, the excess hydrogen escaping through the small Erlenmeyer, which is partially filled with water. When the reduction is complete, stopcock D is opened and rubber tube H is closed by a clamp. This forces the liquid in F through the glass wool filter A into the reaction flask G, through which a slow stream of oxygen-free nitrogen is passing. A concentrated solution of sodium acetate (excess) is added through K, and the precipitated chromous acetate is washed by stirring it with small portions of freshly boiled water. If it is to be removed from the apparatus it must be washed with alcohol and ether and dried by the stream of nitrogen. The yield is over 90%.

Chromous Chloride.—Eighteen grams of chromous acetate in the reaction chamber G is dissolved in 60 cc. of ice cold concentrated hydrochloric acid. With the flask immersed in an ice-bath, a steady stream of hydrogen chloride gas is passed into the flask with the nitrogen. (With undiluted hydrogen chloride, there is a tendency for water to be sucked in from flask L.) After about an hour, blue crystals of $CrCl_2 \cdot 4H_2O$ precipitate. The liquid is filtered off and the crystals washed with cold, concentrated hydrochloric acid. The yield is 90%, based on weight of chromous acetate, or 81% based on the weight of chromic chloride used.

Action of Ethylenediamine and its Homologs upon Chromous Chloride.—Solid chromous chloride tetrahydrate (from 15 g. of $CrCl_3 \cdot 6H_2O$) was dissolved in 30 cc. of freshly boiled ice-cold water in an atmosphere of nitrogen, and 30 cc. of an ice-cold saturated solution of ethylenediamine hydrochloride was added. Thirty cubic centimeters of a 65% solution of ethylenediamine was then added gradually with stirring. During the addition a pale blue precipitate formed, but soon redissolved. Even though the solution was kept at 0°, oxidation began at once and was complete in a few hours. Addition of alcohol to the cherry red solution precipitated $[Cr(NH_2CH_2CH_2NH_2)_3]Cl_3 \cdot 3.5H_2O$ as orange crystals. A second crop was obtained by evaporation. The total yield was 16 g. Dehydration over phosphorus pentoxide showed the compound to contain 15.65% water; (calcd., 15.69%). Analysis of the anhydrous material by ignition to Cr_2O_3 showed 15.7% chromium; calcd., 15.4%.

The substitution of 1,2-propylenediamine for ethylenediamine led to similar results, $[Cr(NH_2CH(CH_3)CH_2NH_2)_3]Cl_3 \cdot H_2O$ being obtained. Analysis for chromium: Found, 13.12%. Calcd., 13.05%.

In another experiment, a slight excess of butylenediamine was added to the solid chromous chloride, which had been freed from hydrochloric acid by washing with acetone. The results were the same as with the other bases. After oxidation was complete, the solution was poured into 50 cc. of concentrated hydriodic acid. The iodide precipitated in beautiful orange needles, which are soluble in water, alcohol and acetone, and were recrystallized from water. The loss in weight upon drying at 50° in a vacuum over phosphorus pentoxide was negligible. Analysis for iodide: Found, 54.85%. Calcd. for $[Cr(CH_3CH(NH_2)CH(NH_2)CH_3)_3]I_3$, 54.63%. This is the first member of the butylenediamine series to be described.

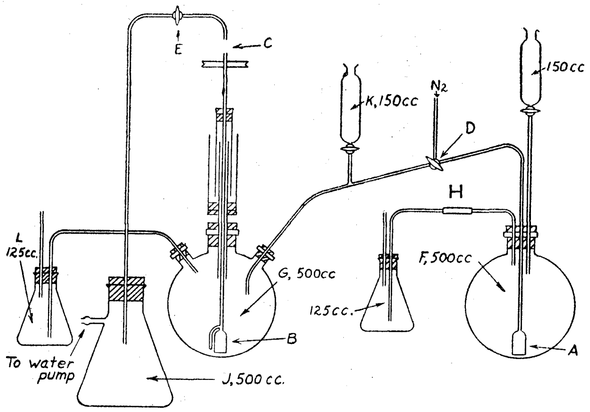

Fig. 1.

Action of Ethylenediamine upon Chromous Acetate.—When chromous acetate was dissolved in 65% ethylenediamine oxidation took place as with the chloride. Addition of sodium bromide followed by evaporation gave triethylenediamine chromic bromide and a small amount of hexaethylenediamine-hexol-tetrachromic bromide, $[Cr_4(OH)_6en_6]Br_6 \cdot 4H_2O$. These were separated through the difference in solubility in water and the tetrachromic salt was identified by analysis. Calcd.: Cr, 16.20; N, 13.8. Found: Cr, 16.13, 16.14; N, 13.7.

Action of Nitrogen Ring Bases upon Chromous Salts.—The directions of Barbieri and Tettamanzi[4] were followed in the preparation of the dipyridyl complex $[Cr\ dip_3]Br_2 \cdot 6H_2O$. In agreement with their report, we find the compound to be fairly stable toward water, and only slowly oxidized by exposure to the atmosphere.

An excess of pyridine was added to chromous chloride dissolved in water. The pale green precipitate which formed was filtered, washed successively with water, alcohol and ether, and dried by heating to 80° in a current of nitrogen. Analysis showed it to be $[Cr\ py_2]Cl_2$. Calcd.: Cr, 18.5; Cl, 25.1. Found: Cr, 18.0; Cl, 25.3. The compound undergoes slow oxidation when exposed to air. It has a faint odor of pyridine and evidently loses pyridine continuously. Since the completion of this work Chatelet[8] has reported the preparation of this compound from anhydrous chromous chloride and pyridine. Traube, Burmeister and Stahn[3] isolated this compound as the dihydrate.

Chromous acetate and chloride were dissolved in wet quinoline in an atmosphere of nitrogen to give deep red solutions. No oxidation was apparent after the solutions had stood for several days. Addition of alcohol to the solution reprecipitated the original chromous salt.

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[8] Chatelet, *Compt. rend.*, **199**, 290 (1934).

Simplified Procedure for the Preparation of $[Cr(NH_2\cdot CH_2\cdot CH_2\cdot NH_2)_3]Br_3\cdot 3H_2O$.—A one-liter flask is equipped with a mercury sealed stirrer, a dropping funnel, an inlet for nitrogen and an outlet for escaping gases. Twenty grams of chromium in small pieces and 400 cc. of water are placed in the flask and the water is boiled to expel dissolved oxygen. Air is swept from the flask by a current of nitrogen. One hundred cubic centimeters of concentrated hydrobromic acid is added over a period of five minutes, followed immediately by 70 cc. of ethylenediamine monohydrate. The solution is allowed to stand with occasional stirring until oxidation is complete (eight to ten hours), is filtered and evaporated. The bromide crystallizes as orange needles. The yield in a typical run was 47 g. or 81% based upon the fact that 5.8 g. of chromium dissolved.

Preparation of 2,3-Butylenediamine.—Angeli[9] has described the preparation of 2,3-butylenediamine by reduction of an alcoholic solution of dimethylglyoxime. This method gives very poor yields, apparently because the sodium salt of dimethylglyoxime is insoluble in alcohol. The substance has been prepared also by the action of ammonia on 2,3-dibromobutane[10] and by the catalytic reduction of dimethylglyoxime dissolved in alcohol.[11] The catalytic reduction gives excellent yields of the base when very dilute solutions are used. Under these conditions it is difficult to obtain the material in large amounts. We have found that it is possible to obtain 2,3-butylenediamine readily by the following modification of Angeli's directions: dimethylglyoxime is acetylated by the method of Biltz.[12] Seventy grams of the diacetate is dissolved in two liters of anhydrous alcohol in a flask fitted with a stirrer and an efficient reflux condenser. One hundred and sixty grams of sodium in lumps the size of marbles is introduced rapidly. When the sodium has dissolved 200 cc. of water is added and the mixture is steam distilled. Most of the amine is obtained in the first three liters of distillate. Addition of a saturated solution of oxalic acid precipitates the oxalate. More of the oxalate can be obtained by concentrating the solution and adding alcohol and ether. The total yield is 27 g. or 40% of the theoretical. This material is pure enough for preparation of the free base. A sample, after recrystallization from water and drying over phosphorus pentoxide, melted at 235°. Angeli[9] reported 238°.

The base is liberated by mixing the oxalate with its own weight of sodium hydroxide in a small amount of water. Distillation gives a nearly quantitative yield of a fuming, somewhat viscous liquid with an odor similar to that of ethylenediamine. The hydrated base boils at 130°.

The major portion of the dimethylglyoxime not accounted for in the yield of diamine may be recovered from the original reaction mixture.

Summary

The stability of chromous ammines has been studied. Ammines containing ethylenediamine, 1,2-propylenediamine and 2,3-butylenediamine could not be isolated from water solution because of rapid oxidation to the chromic state by the water. On the other hand, when the chromous ion is coördinated with dipyridyl, pyridine or quinoline it is stable toward water, and in the case of the dipyridyl at least is somewhat stabilized to atmospheric oxidation.

A new and simple method for the preparation of triethylenediamino chromic salts and similar compounds has been presented.

An improved synthesis of 2,3-butylenediamine is described.

URBANA, ILLINOIS RECEIVED MAY 23, 1936

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[9] Angeli, *Ber.*, **23**, 1357 (1890).

[10] Morgan and Hickinbottom, *J. Soc. Chem. Ind.*, **43**, 307T (1924).

[11] Frejka and Zahlova, *Spisy vydávané Prírodovedeckou Fakultou Masarykovy Univ.*, No. **73**, 3 (1926); Strach and Schwaneberg, *Ber.*, **67**, 1006 (1934).

[12] Biltz, *Ber.*, **41**, 1883 (1908).

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

The Transference Number of Lanthanum Chloride as a Function of the Concentration

BY GRINNELL JONES AND LAURENCE T. PRENDERGAST

Introduction

The purpose of this paper is to test the general validity of several equations which have been proposed for the variation of the transference numbers of electrolytes with the concentration by the use of new data on lanthanum chloride covering a wide range of concentration. Although the old classical theory predicts that transference numbers should be independent of the concentration, it has long been known that variations do occur, especially among salts of polyvalent ions.

In 1924 Drucker and Riethof[1] found that the data for the transference numbers for the chloride ion in hydrochloric acid between 0.01 and 0.1 normal, inclusive, could be expressed by the two parameter equation: $t_- = 0.172(1 - 1/N^{0.51})$; where t_- is the transference number of the anion and N is the moles of water per mole of salt. The figures 0.172 and 0.51 were selected to fit the data, but the figure 0.172 obviously must be the limiting value of t as the concentration approaches

[1] C. Drucker and G. Riethof, *Z. physik. Chem.*, **111**, 20 (1924).

zero. No general validity for this form of equation was claimed and it aroused little interest but has been revived by Drucker[2] in his recent book "Elektrochemie" in the form

$$t_- = t_-^0\ (1 - 1/\sqrt{N})$$

which differs from the original only in the change of the exponent from 0.51 to 0.50. This change was perhaps influenced by the development of the Debye–Hückel theory in the meantime.

Soon after the original proposal of Drucker's equation Scatchard[3] used an equation for potassium chloride which is readily transformable into the form, $t_+ = 0.4975 - 0.014\sqrt{m}$, where m is the molality (moles of salt per 1000 grams of water) and the figure 0.4975 must be the limiting value at zero concentration if this equation is valid. This equation is of essentially the same form as Drucker's revised equation, except that it contains one more arbitrary parameter, namely, the coefficient of the last term. Scatchard regarded this equation as valid for potassium chloride up to 1.25 normal but makes no claim that it has general validity.

In 1929 Jones and Dole[4] found that an equation of the form $t_+ = A/(1 + B\sqrt{c}) - 1$ (where c is moles of salt per liter and A and B are parameters chosen to fit the data) held for barium chlorides solutions over the range of concentration from 0.001 to 1.0. It is evident from the form that if this equation is valid for extrapolation down to zero concentration then $t_+^0 = A - 1$.

In 1931 Jones and Bradshaw[5] found that this equation could be applied to lithium chloride from c = 0.001 to 3.0 normal.

Dole[6] has pointed out that the Jones and Dole equation has the same form as the limiting law derivable from the Onsager conductance equation but that the numerical coefficients are different.

Longsworth[7] has proposed and tested a two parameter equation for the variation of the transference number of uni-univalent salts with the concentration

$$t_+ = t_+^0 - \frac{(1 - 2t_+^0)\,\beta\sqrt{c}}{\Lambda_0 - (\alpha\Lambda_0 + 2\beta)\sqrt{c}} + Ac\left(1 + \frac{2\beta\sqrt{c}}{\Lambda_0 - (\alpha\Lambda_0 + 2\beta)\sqrt{c}}\right)$$

where α and β have a definite known numerical value from the Onsager conductance theory and Λ_0 must be estimated from the data on conductance so that only the limiting value of the transference number and the constant A are selected to fit the data. This equation was shown to be valid for potassium chloride between 0.001 to 0.1 normal and for sodium chloride and lithium chloride and hydrochloric acid between 0.01 and 0.1 normal.

The interionic attraction theory predicts that the variation of ionic mobilities with concentration should be greater for trivalent ions than for univalent or bivalent ions and therefore that the variation of the transference numbers of the ions with the concentration should be larger for a tri-univalent salt than for the simpler types of salts. This is supported by the fragmentary available data.

As Onsager[8] has pointed out, a qualitative prediction as to the sign of the change can be made from the Onsager theory beyond the range of concentration for which the conductance equation is valid. The interionic electric forces decrease the mobilities of the two ions in equal ratios and, therefore, do not affect the transference numbers. On the other hand, the absolute effect of electrophoresis in diminishing the mobility of an ion is proportional to its valence and independent of its mobility. For a 3-1 salt, this means that if the transference number of the trivalent ion at infinite dilution is more than 0.75, the theory predicts that it will increase with increasing concentration; and if it is less than 0.75 it will decrease with increasing concentration.

In order to test the various equations which have been proposed it seemed desirable to secure reliable data on some tri-univalent salt covering a wide range of concentration. Lanthanum chloride was selected because it is less hydrolyzed than any other chloride of a trivalent metal, is sufficiently soluble, and so far as is known does not form complex ions in solution. Moreover, conductance data on this salt have been obtained in this Laboratory.

The only published data known to us on the transference numbers of the ions of lanthanum chloride are by Proskauer.[9] His results are only given to two significant figures and show variations between the results obtained at the anode

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(2) C. Drucker in Teil IV of "Elektrochemie," edited by K. Fajans and E. Schwarz, Akad. Verlagsgesellschaft, Leipzig, 1933, p. 24.

(3) G. Scatchard, THIS JOURNAL, **47**, 705 (1925).

(4) Grinnell Jones and M. Dole, *ibid.*, **51**, 1073 (1929).

(5) Grinnell Jones and B. C. Bradshaw, *ibid.*, **54**, 138 (1932).

(6) M. Dole, *J. Phys. Chem.*, **35**, 3647 (1931).

(7) L. G. Longsworth, THIS JOURNAL, **54**, 2741 (1932); B. B. Owen, *ibid.*, **57**, 2441 (1935).

(8) L. Onsager, *Physik. Z.*, **28**, 277 (1927).

(9) E. Proskauer, Diss., Frankfort am Main, 1933.

and at the cathode of about 5% on the average. A few unpublished measurements have been made in this Laboratory by B. C. Bradshaw which agree well with the new data given below.

Experimental

The lanthanum chloride used in the early part of the work was originally separated from other rare earths by Professor Charles James and purified and dried by C. F. Bickford[10] as described in an earlier paper from this Laboratory. After this supply was used up the material was recovered from the used solutions by precipitation as the oxalate, ignition to the oxide and conversion into the chloride by the procedure used by Bickford. A concentrated solution of the salt gave a *p*H of 6.2 as determined by Phenol Red indicator, showing that the hydrolysis was so slight that even for the most dilute solution investigated the correction to the transference number due to hydrolysis was less than the experimental error.

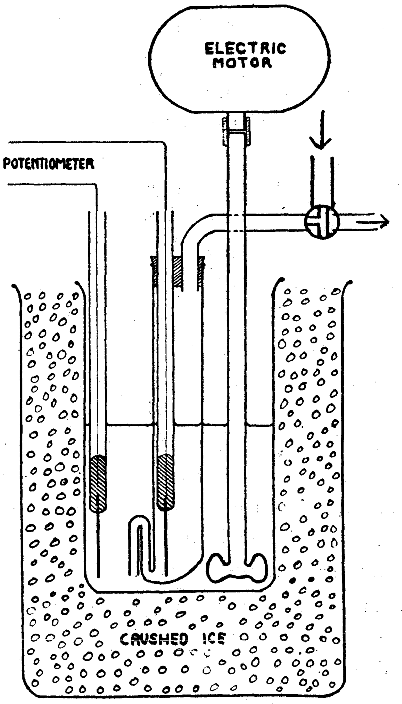

Fig. 1.

The transference numbers were determined by the analytical method using an apparatus of the type devised by Washburn.[11] The other details of the procedure were similar to those used by Jones and Dole, and Jones and Bradshaw with some modifications. The anode for solutions more concentrated than 0.01 normal was a roll of silver gauze, coated with spongy silver. This was made by covering the gauze with a paste of silver oxide in water, drying and heating to a low red heat. For very dilute solutions (0.01 molar and below), a roll of silver gauze without the spongy silver was used. This type of anode was more easily cleaned than the spongy silver type. During electrolysis these electrodes became covered with adherent silver chloride which could be easily washed, dried and weighed without loss. There was no evolution of oxygen or formation of acid at the anode in any of the experiments reported. These electrodes gave entire satisfaction, except that with dilute solutions there is a tendency for the silver chloride to be formed in colloidal suspension instead of adhering to the anode. This limits the current density which can be used and the total permissible transference. The formation of colloidal silver chloride in dilute solution is probably due to the fact that the chloride ions become depleted in the immediate vicinity of the anode so that silver ions may be formed and migrate away from the electrode before they meet a chloride ion and are precipitated. If the potential gradient in the solution is too high (more than 1 volt per centimeter) there may be evolution of oxygen and formation of acid. The anodes after being used could be prepared for reuse by cathodic reduction, followed by washing and drying.

The cathodes were made similar to the anodes and then were thickly coated with silver chloride by electrolysis in hydrochloric acid, thoroughly washed and dried at 105°. The silver chloride and reduced silver formed therefrom by electrolysis were so adherent that there was no loss of weight in handling the electrodes. For the more concentrated solutions, it was necessary to use very large electrodes weighing 30 g.

In order to prevent the formation of hydroxyl ion at the cathode when using these electrodes, it is necessary to remove the oxygen dissolved in the solution. This was done by bubbling oxygen-free nitrogen through the solution before pumping it into the transference cell. Then the cell was sealed with paraffin to exclude oxygen.

The analysis was carried out by differential potentiometric titration, similar to the procedure used by MacInnes and Dole. Our experience confirms the advantages of this method claimed by these authors. For the titration we have used the device shown in Fig. 1 which we have found to be more rapid and positive in its action than the air lift device used by MacInnes and Dole. The solution to be analyzed was added from a weight buret to a beaker immersed in an ice-bath. The sharpness of the end-point is greatly increased by chilling. The electrodes were platinum wires covered with silver by electroplating from a cyanide-bath. One electrode was inside a tube connected with the bath by a narrow gooseneck. A standard solution of silver nitrate was added from a weight buret until the end-point was near and then the titration completed by means of a very dilute solution added from a volumetric buret. After each addition of a drop of silver nitrate the solution in the beaker was thoroughly stirred and the change in potential was observed. The solution around the inner electrode was then mixed with the main body of the solution by making alternate connections with a pressure bottle and the outer air by means of a three-way cock as shown in the diagram. This method of electrometric titration is far more rapid than the gravimetric method and is sufficiently accurate for the purpose. The error in the analysis is probably not more than 0.01% except when applied to solutions less than 0.01 molar when the error increases somewhat.

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[10] Grinnell Jones and C. F. Bickford, THIS JOURNAL, **56**, 604 (1934).

[11] E. W. Washburn, *ibid.*, **31**, 322 (1909).

TABLE I

TRANSFERENCE NUMBER OF THE LANTHANUM ION IN LANTHANUM CHLORIDE SOLUTIONS AT 25°

c, molar	t_+, from anode	t_+, from cathode	t_+, ave.
0.003814	0.4703	0.4689	0.4696
.010407	.4587	.4582	.4585
.010414	.4587	.4581	.4584
.015614	.4514	.4513	.4514
.022803	.4438	.4428	.4433
.051602	.4266	.4262	.4264
.075659	.4181	.4173	.4177
.087366	.4142	.4139	.4140
.087387	.4141	.4132	.4137
.198411	.3873	.3866	.3869
.198441	.3869	.3863	.3866
.40426	.3580	.3571	.3575
.67725	.3268	.3263	.3266
1.01778	.3004	.2997	.3000

Discussion of the Data

The experimental data presented above show that the transference number of the lanthanum ion in lanthanum chloride solutions decreases with the concentration from 0.4696 in 0.0038 molar solution to 0.3000 in 1 molar solution. This is a greater variation than has been observed for any strong electrolyte of the uni-univalent or uni-bivalent types.[12] This case is, therefore, especially well suited to test the general validity of the various proposals which have been made for the variation of transference numbers with the concentration. An important part of the problem is the estimation of the limiting value of the transference number at infinite dilution which requires that some law be assumed to be valid in the dilute range where reliable experimental data are not obtainable.

The results confirm the predictions of the Onsager theory both in regard to the great variability of the transference number with the concentration and to the sign of this variation.

Figure 2 shows a plot of the transference numbers of the lanthanum ion in lanthanum chloride against the square root of the concentration $\sqrt{c}$. This curve, although approximately straight, shows unmistakable positive curvature which makes extrapolation to zero concentration hazardous. Therefore, an equation of the form $t_+ = t_+^0 - A\sqrt{c}$ can only be a rough approximation over the entire range. This curvature is most pronounced in the middle range and tends to disappear in the dilute range and also in the concentrated range (0.2 to 1 molar). The four lowest points (0.0038 to 0.022) are on a straight line within the experimental error. There is no reason, either experimental or theoretical, to suspect that the curve could become more nearly horizontal as it approaches the axis which would require a change in the sign of the curvature at extreme dilution. Therefore, if we extrapolate the curve to zero concentration along the straight line determined by the last four points the result, $t_+^0 = 0.4881$, should be the minimum estimate of the transference number at zero concentration. The equation of this straight line is $t_+ = 0.4881 - 0.2946\sqrt{c}$, which agrees with the data within the experimental error up to $c = 0.022803$ but fails badly at the higher concentrations. This is shown in column 4 of Table II, which gives the difference between the experimental values and the values computed by this equation.

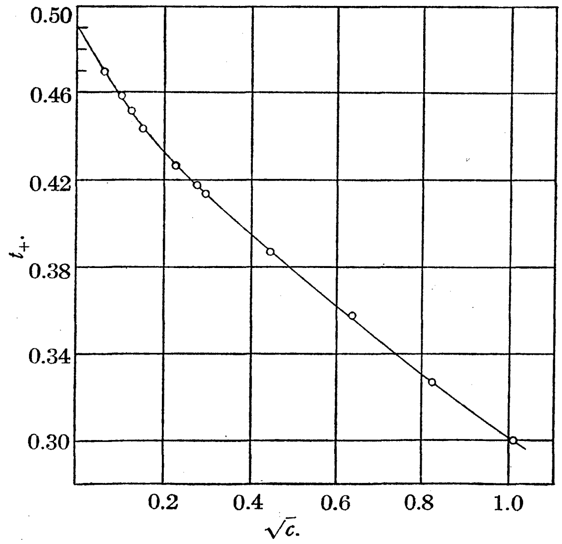

Fig. 2.

If the curve depicted by Fig. 2 has an appreciable curvature below the lowest concentration measured, then the limiting transference number would be higher than 0.4881.

We have tried the effect of adding a term proportional to the concentration, giving an equation of the form $t_+ = t_+^0 - A\sqrt{c} + Bc$, but the result was not satisfactory as it gives too great a curvature.

If we express the composition in terms of moles of salt per thousand grams of water (following Scatchard's suggestion) instead of concentrations,

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(12) Although relatively greater changes in transference numbers have been observed for cadmium bromide and cadmium iodide, there is independent evidence that in the cases of these salts the cadmium is present partly in the form of a complex anion. Since the fraction of the cadmium present in the complex ion varies with the concentration, the decrease in the transference number of the cadmium is due to this cause.

the curvature of this plot is increased rather than decreased, so that there is no advantage for this purpose in this method of expressing the composition.

The Jones and Dole equation has been shown to hold for barium chloride and for lithium chloride over a wide range of concentration. This equation may be written $t_+ = A/(1 + B\sqrt{c}) - 1$; or $\frac{1}{1 + t_+} = \frac{1 + B\sqrt{c}}{A} = \frac{1}{A} + \frac{B\sqrt{c}}{A}$ where it is obvious that $t_+^0 = A - 1$. Figure 3 shows a plot of $1/(t + 1)$ against $\sqrt{c}$ which should give a straight line if the equation is valid. An inspection of this curve shows that a good straight line can be put through the points from $c = 0.05$ to 1.0, but that there appears to be a definite curvature in the more dilute range. The equation of this straight line is $1/(t_+ + 1) = 0.6815 + 0.08728\sqrt{c}$; or $t_+ = 1.4673/(1 + 0.128\sqrt{c}) - 1$.

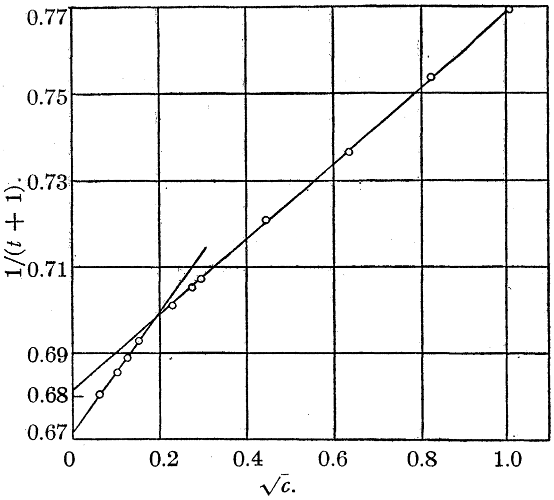

Fig. 3.

The differences between the experimental data and the figures computed by this equation are shown in column 5 of Table II. This is a good interpolation formula for the stronger solutions between the limit $c = 0.05$–1.0, but this equation fails in the dilute range. This equation leads to a value of $t_+^0 = 0.4673$, which is obviously too low since it is less than the observed transference number at $c = 0.0038$.

As is also shown in Fig. 3, we may put a straight line through the four lowest concentrations which gives $\frac{1}{t_+ + 1} = 0.6717 + 0.1388\sqrt{c}$, or $t_+ = 1.4887/(1 + 0.2067\sqrt{c}) - 1$, and hence $t_+^0 = 0.4887$. As will be seen from column 6 of Table II, this equation agrees with the data over the lower range but fails badly in the upper range.

A modified form of the Jones and Dole equation containing one more parameter selected to fit the data would be $t_+ = A/(1 + B\sqrt{c}) - D$. For barium chloride and lithium chloride the constant D was equal to 1, but this might not be generally true of all types of salts. We tried, therefore, evaluating the constant D by the method of least squares but the result was $D = 0.9998$ and there was no significant improvement

TABLE II

SUMMARY OF DEVIATIONS BETWEEN EXPERIMENTAL DATA FOR TRANSFERENCE NUMBERS OF LANTHANUM CHLORIDE AND RESULTS COMPUTED BY VARIOUS EQUATIONS

1 c	2 $c^{1/2}$	3 t_+ obsd.	4	5	6 $\Delta t = t_{\text{obsd.}} - t_{\text{comp.}}$	7	8
0.003814	0.06176	0.4696	−0.0003	+0.0138	−0.0003	−0.0011	+0.0006
.010414	.10205	.4584	+ .0003	+ .0100	+ .0004	+ .0013	+ .0001
.015614	.12496	.4514	+ .0001	+ .0072	+ .0002	+ .0008	+ .0000
.022803	.15101	.4433	− .0003	+ .0038	− .0003	− .0009	− .0016
.051602	.22716	.4264	+ .0052	+ .0006	+ .0045	− .0001	− .0010
.075659	.27506	.4177	+ .0106	+ .0003	+ .0091	+ .0258	+ .0003
.087377	.29559	.4138	+ .0128	.0000	+ .0108	+ .1331	+ .0004
.19843	.44545	.3868	+ .0298	− .0013	+ .0236	− .1304	+ .0004
.40426	.63581	.3575	+ .0567	+ .0007	+ .0417	− .2778	+ .0011
.67725	.82295	.3266	+ .0809	− .0008	+ .0543	− .5047	− .0016
1.01778	1.00885	.3000	+ .1091	+ .0007	+ .0682	− .7261	− .0014

Column 4: $t = 0.4881 - 0.2946\sqrt{c}$

Column 5: $t = 1.4673/(1 + 0.1281\sqrt{c}) - 1$ (Jones and Dole)

Column 6: $t = 1.4887/(1 + 0.2067\sqrt{c}) - 1$ (Jones and Dole)

Column 7: $t = \frac{(0.4972 + 2.5702c)\,(\Lambda' + 880.24\sqrt{c}) - 660.18\sqrt{c}}{\Lambda'}$ (Longsworth)

Column 8: $\frac{1}{t + 1} = \frac{1}{0.4893 + 1} + 0.16563\sqrt{c} - 0.06835c + 0.07457c \log c$

in the agreement between the observed and computed result by replacing the term -1 by -0.9998.

Longsworth has recently proposed a method of extrapolating transference numbers to infinite dilution based on Onsager's limiting law for the variation of the conductance of ions with the concentration. Longsworth only claims that his method is valid for four univalent chlorides but it is of interest to test the method for salts of other valence types. Although Jones and Bickford have shown that Onsager's limiting law is not valid for lanthanum chloride even up to 0.001 molal, nevertheless if the influences which cause the failure of Onsager's law should affect the two ions proportionally a transference equation based on Onsager's law might be valid to much higher concentrations than Onsager's conductance equation. Longsworth's treatment may be readily generalized to apply to salts of any valence type. The mathematical details of this generalization are omitted to save space in printing. A plot prepared according to Longsworth's method was approximately straight up to 0.05 molar only. The corresponding equation is given in Table II and the difference between the experimental values and the values of t computed by this equation is given in column 7 of Table II. The deviations between the observed and computed values are not much greater than the experimental error up to $c = 0.051$, but the equation fails utterly at higher concentrations which indicates that it does not have the proper mathematical form to be regarded as generally valid. The values of t^0_+ are higher than those given by other methods of extrapolation.

Onsager and Fuoss[13] have suggested, without giving detailed mathematical proof, that any property of a solution of an electrolyte can be expressed as a function of the concentration by an equation of the form

$$\mathrm{F}\,(c) = \mathrm{F}\,(o) + A\sqrt{c} + Bc + Dc \log c + \dots$$

We have attempted to fit this equation to our transference data but the result was disappointing. The coefficient D of the $c \log c$ term came out nearly zero, thus reducing the equation to the form $t = t^0 + A\sqrt{c} + Bc$ which had already been found to be unsatisfactory. The next step was to try an equation of the form

$$\frac{1}{t+1} = \frac{1}{t^0+1} + A\sqrt{c} + Bc + Dc \log c$$

which may be regarded as an extension of the Jones and Dole equation since it reduces to the Jones and Dole equation as c approaches zero or if B and D are placed equal to zero. The equation

$$\frac{1}{t+1} = \frac{1}{0.4893+1} + 0.16563\sqrt{c} - 0.06835c + 0.07456c \log c$$

agrees with our data over the entire range better than any other equation known to us. Since this equation contains four parameters, it is to be expected that it can be made to fit better than the simpler forms discussed above. The differences between the experimental values and the values computed from this equation are shown in column 8 of Table II.

The data throw light on the difficult problem of the extrapolation of conductance data discussed by Jones and Bickford. The foregoing discussion makes it seem probable that the limiting value of the transference number must be at least as high as 0.4881 and may be as high as 0.4893. If the limiting value of the conductance of the chloride ion is 76.34 and $t^0_\pm = 0.4881$, then the conductance of lanthanum chloride at infinite dilution would be 447.4, whereas if $t^0_\pm = 0.4893$ then Λ_0 would be 448.4.

Jones and Bickford have found that if the conductance data for lanthanum chloride are extrapolated by the method of Shedlovsky the value for Λ_0 obtained was 432.7, which is much below the estimates based on the transference numbers. If the value 432.7 is correct the value of t^0 would be 0.4707. It seems clear from Fig. 2 that the curve would have to take an extremely improbable course to reach a value of t^0_+ as low as this. The extrapolation of the conductance data by the Jones and Dole conductance equation gives $\Lambda_0 = 442.97$ corresponding to a value of t^0_+ of 0.483. It is evident that these figures agree much better with the estimates based on the transference numbers. This evidence, therefore, indicates that for this case at least the Jones and Dole conductance equation is better than the Onsager or Shedlovsky equations for finding the limiting value of the conductance.

Summary

1. The transference numbers of the lanthanum ion in lanthanum chloride solutions have been determined by the analytical method at 25° at eleven concentrations over a range of 0.0038

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(13) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

to 1.0 molar. The transference number varies from about 0.47 to 0.30 over this range.

2. Several equations purporting to express the transference number as a function of the concentration and the problem of extrapolation of transference numbers to infinite dilution are discussed.

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[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES, HARVARD UNIVERSITY]

Polarization and Dielectric Constant of Liquids

BY JEFFRIES WYMAN, JR.

There is much evidence that the dielectric constant is a linear function of the polarization per unit volume in the case of the more polar liquids for which the Clausius–Mosotti relationship ceases to hold. This appears to be almost the only conceivable interpretation of the strikingly simple behavior of a variety of strongly polar molecules in solvents of high dielectric constant.[1] It is in accord with the temperature variation of the dielectric constant of polar liquids, and the change of dielectric constant with density, under pressure, at constant temperature (see below). If we suppose the linear function to approximate direct proportionality, it offers a ready explanation of such a simple empirical relationship as that submitted by Girard,[2] according to which for water and the aliphatic alcohols the product of molecular weight times the dielectric constant is nearly constant; for in these cases the electric moments and consequently the molecular polarizations are all about the same, and therefore the polarizations per cc. should be inversely proportional to the molecular volumes or, roughly, to the molecular weights.[3] Onsager, in the following paper in THIS JOURNAL, develops a theoretical argument for a linear relation between dielectric constant and polarization in strongly polar media.

The problem of determining the two constants of this inferred linear relationship between dielectric constant and polarization is of course of great interest and the present paper is an attempt to deal with it from a purely empirical point of view.[4] There are of course no cases of polar liquids in which we have exact independent knowledge of the polarization with which to correlate the dielectric constant. We may, however, calculate ideal or hypothetical values of the polarizations per unit volume for such liquids by making use of the values of the electric moments and molar polarizations obtained from measurements on the vapor or on dilute solutions in non-polar solvents and by taking account of the density. Clearly, such ideal, calculated values of the polarization per unit volume cannot be supposed in general to be realized more than approximately, but, nevertheless, apart from special cases of strongly associated liquids such as those forming hydrogen bonds, they may be expected to be fairly representative of the actual values. We may then try the effect of comparing these calculated values of the polarization with the observed values of the dielectric constant, to see whether or not the linear relation shows up. If it does, there is justification of our procedure of making use of the calculated values of the polarization and we may then proceed to determine the magnitude of the two constants. This in fact is what has been done.

By reference to the section of the "International Critical Tables" (Vol. VI) devoted to the dielectric constant of liquids and to the recent extensive table of electric moments and polarizations given in the *Transactions of the Faraday Society*,[5] it was possible to pick out about 140 cases of liquids with a dielectric constant greater than 5 and for which the electric moments and polarizations had been determined. In most of these the dielectric constant is pretty well known, although in some, accompanied in Table I below by a question mark, it has been measured only at very high frequencies, several times 10^8 cycles per second, and the values may be too low, the more so in the case of the larger molecules, owing to anomalous dispersion. On the other hand the

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(1) See J. Wyman, THIS JOURNAL, **56**, 536 (1934).

(2) P. Girard, *Trans. Faraday Soc.*, **30**, 763 (1934).

(3) As a matter of fact Cohn has pointed out that Girard's relationship is improved if we multiply the dielectric constant in each case not by the molecular weight but by the molecular volume. E. J. Cohn, "Annual Review of Biochemistry," Annual Review of Biochemistry, Ltd., Stanford University P. O., California, Vol. IV, 1935, p. 100.

(4) An attempted derivation of the relation based on a modification of the underlying assumptions of the classical theory with regard to the internal field has been suggested but appears far too special.[1]

(5) *Trans. Faraday Soc.*, **30** (1934).

values of the polarizations are much less certain, showing in some cases a twofold variation or more. This appears to be due in part to differences in the conditions under which the measurements were made and in part to experimental discrepancies. From these data were calculated the ideal values of the polarization per cc. for the liquids for comparison with the dielectric constant.

TABLE I

Name	ϵ		p		ϵ + I/8.5	
Water	78.54		4.24		9.34	
Prussic acid	95	116	3.98		11.3	11.9
Formic acid	62		1.08		7.39	
Acetic acid	7.1		0.43	0.96	0.96	
Ethyl formate	8.6		1.21		1.13	
Propyl formate	9.1		1.05		1.19	
Isobutyl formate	8.		0.93		1.06	
Amyl formate	7.7		.78		1.02	
Methyl acetate	7.3		1.03		0.98	
Ethyl acetate	6.4		0.78	1.11	.85	
Propyl acetate	6.3		.82	0.94	.86	
n-Butyl acetate	5.1		.80		.72	
Isobutyl acetate	5.6		.81		.77	
Phenyl acetate	5.3		.68	.77	.75	
Benzyl acetate	5.1		.77		.71	
Ethyl acetoacetate	15.9?		1.87		1.99	
Methyl propionate	5.5?		0.84	.93	0.75	
Ethyl propionate	5.7		.77	.87	.79	
Methyl butyrate	5.6?		.83		.78	
Ethyl butyrate	5.2		.75		.73	
Diethyl oxalate	8.2?		1.18		1.08	
Diethyl malonate	7.9	8.4	1.12		1.05	1.25
Methyl salicylate	9.0?		1.32		1.17	
Ethyl salicylate	8.6		1.55		1.13	
Ethyl cinnamate	6.6		0.95		0.90	
Methyl benzoate	6.9		.87		.93	
Ethyl benzoate	6.2		1.03	.82	.85	
Methyl nitrate	23.9		2.93		2.90	
Ethyl nitrate	19.7		2.4		2.41	
Propyl nitrate	14.2?		2.12		1.79	
Acetonitrile	38.8		4.1	5.21	4.65	
Propionitrile	27.7		3.54	4.37	3.37	
Butyronitrile	20.7?		3.13		2.55	
Benzonitrile	26.5		2.93	3.32	3.23	
Benzyl cyanide	18.3		2.32	2.58	2.27	
o-Tolunitrile	18.8?		2.94		2.23	
Phenyl isocyanate	5.7?	8.9?	1.42	1.32	0.79	1.17
Methyl *n*-thiocyanate	35.9?		4.2		4.31	
Methyl isothiocyanate	19.7?		3.24		2.42	
Ethyl *n*-thiocyanate	29.6		3.48		3.59	
Ethyl isothiocyanate	19.7		2.94		2.41	
Allyl isothiocyanate	17.5?		2.65		2.16	
Phenyl isothiocyanate	10.7?		1.77	2.02	1.37	
Ethyl mercaptan	8.0?		0.81		1.04	
Dimethyl sulfide	6.3?		.83		0.85	
Diethyl sulfide	7.2?		.77		.99	
Acetyl chloride	15.9		2.38		1.98	
Ethylidine chloride	10.9		1.15		1.39	
Ethylene chloride	10.5		0.63	1.12	1.34	
Propyl chloride	7.7?		1.02	1.18	1.02	
Allyl chloride	8.2		1.27		1.06	
Isoamyl chloride	6.4?		0.91		0.87	
t-Amyl chloride	9.5		1.04		1.24	
Benzal chloride	6.9?		1.02		0.93	
Benzyl chloride	7.0		0.94		.94	
Chloroacetone	29.8?		1.58		3.6	
Ethylene chlorohydrin	25.8		1.42	1.63	3.14	
Epichlorohydrin	22.9		1.14		2.79	
Chlorobenzene	5.9		0.74	0.85	0.81	
o-Chlorophenol	6.3	8.2	.69		0.86	1.08
m-Chloroaniline	13.3		2.02	1.76	1.68	
m-Chlorotoluene	5.4		0.81	0.96	0.75	
p-Chlorotoluene	6.2		.89	.97	.85	
Dichloroethylene-*cis*	9.22		1.08	1.28	1.18	
Chloroform	5.05		0.59	0.65	0.70	
Benzotrichloride	7.4?	6.4?	.98		.98	0.67
Ethyl bromide	9.4		1.14	1.50	1.2	
Allyl bromide	7.0		1.13	1.01	0.81	
Propyl bromide	7.2		1.0	1.33	.95	
t-Butyl bromide	8.6?		1.10	1.18	1.10	
Isoamyl bromide	6.1		.90		0.83	
Tertiary amyl bromide	9.1?		1.10		1.19	
Bromobenzene	5.4		0.78	0.90	0.75	
m-Bromoaniline	13?		.173		1.65	
o-Bromotoluene	5.3?		.69		0.74	
1-Bromonaphthalene	5.1		.73		.73	
Ethylene bromide	4.8	6.3	.56	.88	.69	.98
1,2,3-Tribromopropane	6.4?		.74		.85	
Methyl iodide	7.1		1.20		.95	
Ethyl iodide	7.4		1.12		.99	
t-Butyl iodide	6.3?		1.11		.85	
Isoamyl iodide	5.6?		0.83		.78	
t-Amyl iodide	6.9?		1.20		.93	
Methylene iodide	5.5		0.73	1.55	.76	
Nitromethane	39.4		3.82	5.81	4.73	
Nitroethane	30.0?		3.26	4.76	3.63	
Nitrobenzene	36.1		3.05	3.74	4.36	
o-Nitrotoluene	27.4		2.78		3.34	
m-Nitrotoluene	23.8		3.43		2.92	
Methylamine	<10.5		0.68	1.02	<1.35	
Ethylamine	6.3?		.75	0.51	0.85	
Diethylamine	3.7	5.5	.40	.53	.55	.76
Ethylenediamine	16?		1.49		2.0	
Nitrosodimethylamine	54		4.79		6.46	
Formamide	>84		5.84		>10	
Methyl alcohol	33.7		1.26	1.78	4.07	
Ethyl alcohol	25.07		1.28	1.49	3.05	
Propyl alcohol	21.8		1.03		2.66	
Isopropyl alcohol	26		1.15	0.98	3.15	
n-Butyl alcohol	17.8		0.85	.99	2.20	
s-Butyl alcohol	15.5		.95		1.93	
t-Butyl alcohol	11.4		.87		1.45	
Amyl alcohol	15.8		.81		1.97	
Isoamyl alcohol	15.3		0.79	0.95	1.92	
Dimethylethylcarbinol	11.7		.82	.94	1.49	
Heptyl alcohol	6.7		.69		0.91	
Cyclohexanol	15		.88	1.01	1.88	
Benzyl alcohol	13		.96		1.65	
Glycol	41.2		1.17	2.29	4.95	
Propionaldehyde	18.9	14.4	1.92		2.31	1.81
Butyraldehyde	13.4		1.69		1.68	
Benzaldehyde	18		1.87		2.23	
Furfuraldehyde	41.9		3.58		5.04	
Paraldehyde	14.5		0.89		1.82	
Acetone	21.5		2.32	2.62	2.60	
Methyl ethyl ketone	18.5		2.06		2.25	
Methyl propyl ketone	16.8		1.75		2.09	
Mesityl oxide	15.4		1.70		1.93	
Cyclohexanone	18.2		1.75	2.15	2.26	
Methyl *t*-butyl ketone	12.6		1.59		1.60	
n-Dipropyl ketone	12.6		1.37		1.60	
Methyl hexyl ketone	10.4		1.10		1.34	
Acetophenone	18.6		1.83		2.42	
Menthone	9.6?		1.30	1.37	1.24	
Benzophenone	13.3		1.38	1.47	1.68	
Acetyl acetone	23.1	25.9	2.12	1.87	2.83	3.16
Diethyl ketone	17.3		1.75		2.15	
Acetic anhydride	20.5		1.59	1.99	2.50	
o-Cresol	5.8		0.74		0.80	
m-Cresol	5		.84		.71	
p-Cresol	5.6		.87		.78	
Pyridine	12.5		1.46	1.64	1.59	
Aniline	7.25		0.91		0.97	
Methylaniline	6		.86		.82	
o-Toluidine	6.4		.84		.87	
m-Toluidine	6.0		.75		.82	
Quinoline	9.		1.20		1.17	
Phenylhydrazine	7.2		1.04		0.96	
Methyl phenylhydrazine, *asym.*	7.3?		0.95		.98	
Azoxyphenetole	6.8		0.84		.92	

The results of the comparison are given in Table I and are shown graphically in Fig. 1, where the dielectric constant ϵ is plotted against p, the ideal value of the polarization per cc. The full curve at the left, which corresponds to the Clausius–Mosotti relation $p = (\epsilon - 1)/(\epsilon + 2)$ and is asymptotic to $p = 1$, is included for reference. It may be seen from the figure that the majority of the points are consistent with a linear increase of the dielectric constant with p described by the expression

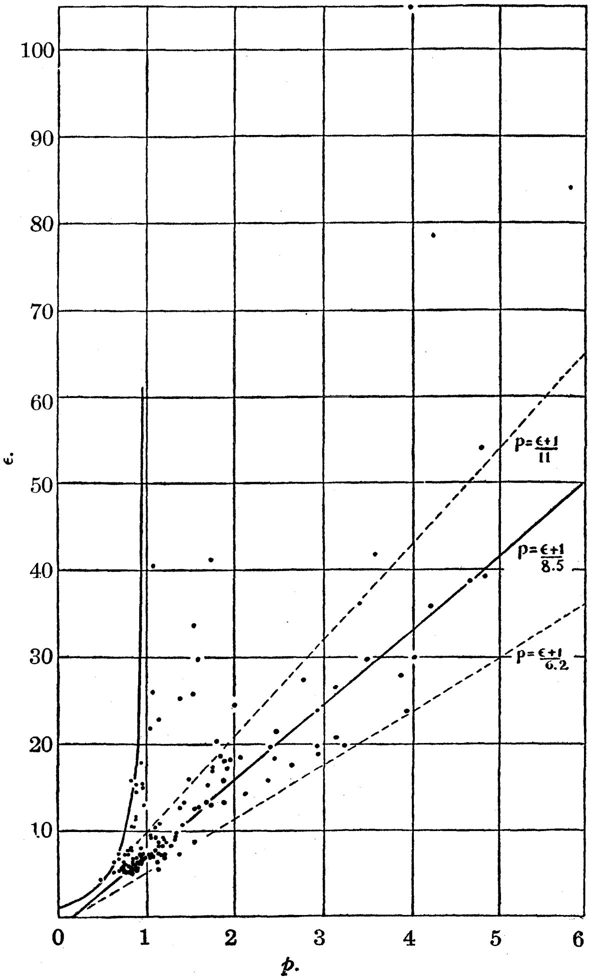

Fig. 1.

$$p = (\epsilon + 1)/8.5 \qquad (1)$$

corresponding to the full straight line. The figures 1 and 8.5 are of course only estimates (compare the dotted straight lines corresponding to a different choice of coördinates). The same thing is seen rather better by comparing columns 3 and 4 in Table I. For the most part the agreement between the two columns is fairly good.

On the other hand, hydrocyanic acid, formic acid, formamide, water, most of the alcohols, and a few other substances have dielectric constants much greater than corresponds to this empirical relation. Most of these will be recognized as liquids which are generally supposed to be strongly associated due to the formation of hydrogen bonds. Kumler has pointed out[6] that such liquids show abnormalities in regard to boiling point and dielctric constant, and it is not surprising that they should be exceptional in the present case. It would simply mean that the actual polarizations for the liquid state are quite different from the ideal values calculated from the moments taken from the literature.

In Fig. 2, values of the polarization per gram, calculated from the relation $p' = (\epsilon + 1)/8.5\rho$, ρ denoting density, are plotted against the reciprocal of the absolute temperature for a number of liquids for which data are available. The result should in each case be a straight line whose intercept on the axis of ordinates gives the sum of the atomic and electronic polarizations per cc. and whose slope gives the electric moment in accordance with the relation

$$\mu = 0.0127\sqrt{M\frac{\mathrm{d}p'}{\mathrm{d}1/T}} \times 10^{-18}\ \text{e. s. u.} \qquad (2)$$

where M is the molecular weight. The straight lines of the figure are in each case so drawn as to fit the data and at the same time give the correct intercept on the axis of ordinates (in accordance with optical or other data). Except for acetone and nitrobenzene, the nine liquids are in moderately good accordance with expectations. If we calculate the moments from the slopes of the lines as drawn we obtain the following values

Substance	μ cal. × 10^{18}	μ literature × 10^{18}
Chloroform	1.22	1.10–1.15
o-Toluidine	1.63	1.44–1.65
Ethylene chloride	1.96	1.12–1.75
Pyridine	2.24	2.11–2.21
Benzyl cyanide	3.27	3.47–3.56
Acetone	2.85	2.61–2.97
Nitrobenzene	4.29	3.66–4.08
Nitromethane	3.40	3.02–3.78
Water	2.77	1.88

The moments calculated in this way are in good agreement with the values from the literature, except for water, which, as was pointed out above, is in all probability much associated.

In the case of the ten liquids studied under

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[6] Kumler, This Journal, 57, 600 (1935).

pressure by Danforth,[7] the variation of dielectric constant with density is very nearly linear and in accordance with the empirical relation presented above, except for the two non-polar liquids, pentane and carbon disulfide, and for ethyl ether and glycerol. For the others the quantity $(\epsilon + 1)/8.5\,\rho$ varies over the whole range by no more than about 3% at most, in some cases much less. This is probably almost within the experimental error. For ether and glycerol the variation is somewhat more than 10%.

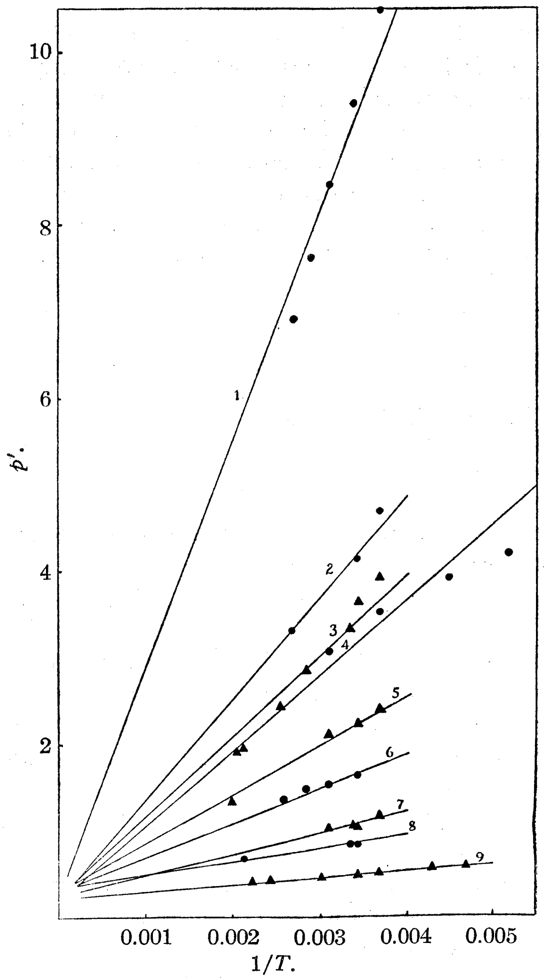

Fig. 2.—1, Water; 2, nitromethane; 3, nitrobenzene; 4, acetone; 5, benzyl cyanide; 6, pyridine; 7, ethylene chloride; 8, *o*-toluidine; 9, chloroform.

It is of interest to consider the meaning of the empirical relation just presented in terms of the internal field F. On the basis of the classical theory

$$F = E + (4/3)\pi I = E + pF \qquad (3)$$

where E is the electric intensity and I the electric moment per unit volume. Hence

$$F/E = 1/(1 - p) \qquad (4)$$

On the other hand, if the dielectric constant be linear in p

$$\epsilon = ap + b \qquad (5)$$

where a and b are constants.

But from the fundamental theory

$$E(\epsilon - 1) = 4\pi I = 3pF \qquad (6)$$

whence

$$\frac{F}{E} = \frac{1}{3}\left(a + \frac{b-1}{p}\right) \qquad (7)$$

The graphs of these two expressions are shown in Fig. 3 (b is taken as -1 and a as 8.5 in accordance with what we have found). Both curves are hyperbolas and we must suppose that the transition from one to the other occurs somewhat as shown by the dotted line, between $p = 0.3$ and $p = 1.3$ or between $\epsilon \cong 3$ and $\epsilon \cong 10$. It is of course always possible to calculate p from ϵ if F/E is known by means of the relation

$$p = \frac{E}{F}\frac{(\epsilon - 1)}{3} \qquad (8)$$

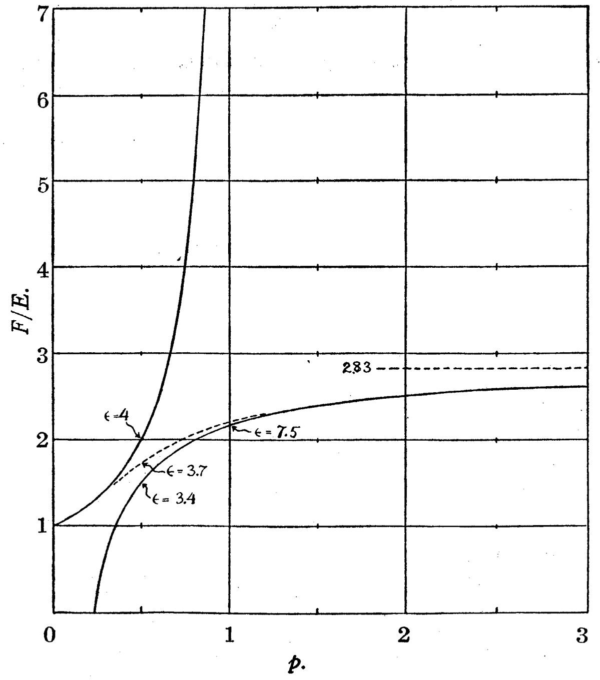

Fig. 3.—F/E, the ratio of the internal field to the electric intensity, as a function of the polarization per cc. (a) in accordance with the Clausius-Mosotti relation (left-hand full curve), (b) on the basis of the empirical equation 1 (right-hand full curve). The right-hand curve approaches $F/E = 2.83$ asymptotically.

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[7] Danforth, *Phys. Rev.*, **38**, 1224 (1931).

which is general.[8]

It is of interest also to consider the moment of glycine calculated from the relation given above. On the basis of the observations in water at 25° the polarization is 3060 cc. and the moment 12.2 × 10^{-18} e. s. u. This would correspond to a dipole distance of 2.55 Å. Recent calculations based on a model proposed by Kirkwood[9] give a value of 3.17 Å. for this distance, or a moment of 15.2 × 10^{-18} e. s. u.

Summary

A correlation of the dielectric constant of a large number of polar liquids with assumed values of the polarization per cc. calculated by ascribing to the molecules in the liquid state the electric moments obtained from measurements on the vapor and on dilute solutions in non-polar solvents suggests an empirical relation between polarization and dielectric constant: $p = (\epsilon + 1)/8.5$. This relation is fairly satisfactory when applied to the variation of dielectric constant with temperature and with pressure in the case of a number of polar liquids for which data are available. The meaning of such a relation in terms of the internal field in the liquid is discussed.

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[8] It may also be worth mentioning the implication of *any* linear relation between polarization and dielectric constant in the case of anomalous dispersion. According to the Debye treatment, based on the Clausius–Mosotti equation, the absorption index reaches a maximum at a frequency given by

$$2\pi\nu = \frac{1}{\tau}\,\frac{\epsilon_0 + 2}{\epsilon_1 + 2}\sqrt{\frac{\epsilon_1}{\epsilon_0}}$$

where τ is the relaxation time, ϵ_0 the dielectric constant at low frequencies and ϵ_1 the dielectric constant at frequencies above the region of dispersion. On the other hand, if the Clausius–Mosotti relation be replaced by any linear relation, the same for both ϵ_0 and ϵ_1, this expression reduces to

$$2\pi\nu = \frac{1}{\tau}\sqrt{\frac{\epsilon_1}{\epsilon_0}}$$

(see Debye, "Polar Molecules," Chemical Catalog Co., New York City, 1929).

[9] J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

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Electric Moments of Molecules in Liquids

BY LARS ONSAGER

In its original, still generally accepted, form Debye's dipole theory[1] accounts quantitatively for the dielectric properties of gases, and qualitatively for those of liquids. In view of the extensive and consistent evidence the fundamental hypothesis of molecules possessing permanent electric moments is not in doubt.

When the theory is applied to liquids (and solids), the interaction of a molecule with its environment must be taken into account. For this purpose, Debye borrowed the theory of "internal field" which was developed by Clausius and Mosotti, one that has been applied universally and with remarkable success to aggregates of polarizable molecules. According to this theory, the "internal field" which polarizes a molecule in the dielectric equals the external field, augmented by $(4\pi/3)$ times the electric moment induced in a unit volume of the dielectric. Debye's implicit assumption is that the force-couple which tends to orient an electrically asymmetric molecule in a polarized dielectric is proportional to the same "internal field." This assumption leads to Debye's well-known formula for the dielectric constant (ϵ)

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3}\sum N\left(\alpha + \frac{\mu^2}{3kT}\right) \qquad (1)$$

where α denotes the polarizability of the molecule, μ its permanent electric moment, kT the energy of thermal agitation, and N the concentration (molecules/cc.), and the summation is extended over all species of molecules present.

Formula (1) can be tested in a number of ways. When only a single species of molecules is present, one can compute the dipole moment μ, with the aid of Eq. 1, from the observed dielectric constant, and the test is whether the dipole moments computed for the liquid state or in liquid mixtures with a non-polar component remain the same as that observed in the vapor state. A more thorough analysis of the problem shows that one should not expect the dipole moment to remain quite constant, because all real molecules have a positive polarizability α. The polarization of the dielectric in the electric field of the molecule itself gives rise to a *reaction field*, which tends to enhance the electrical asymmetry.

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[1] P. Debye, *Physik. Z.*, **13**, 97 (1912).

When Eq. 1 is compared with experience, one finds in general that for dilute solutions of polar substances in non-polar liquids the moments inferred with the aid of the formula come out approximately the same as in the vapor state, although with a systematic tendency for μ to decrease with increasing dielectric constant of the environment.[2] For pure polar liquids one computes very small moments; the discrepancy is more pronounced the higher the dielectric constant of the liquid. The reason for this remarkable result is the nature of the function $(\epsilon - 1)/(\epsilon + 2)$, which cannot exceed unity. Accordingly, Eq. 1 requires for any dielectric

$$(4\pi/3)\left(\alpha + \frac{\mu^2}{3kT}\right) \leqq \text{molecular volume}$$

The point of equality is known as the "Curie point"; it is characterized by an infinite dielectric constant. Beyond the Curie point, the theory predicts a stable state of permanent electric polarization, like the familiar permanent magnetic polarization of iron. Some bodies are actually capable of existing in such a "ferroelectric" state; the best known example is perhaps that of Rochelle salt, a solid. Nevertheless, the phenomenon is quite rare and certainly not, as one should expect from Eq. 1, a common occurrence with polar substances.

According to Eq. 1, a polar liquid with a high dielectric constant should necessarily be close to its Curie point, and, in this region its dielectric constant should be very sensitive to variations of all pertinent factors (temperature, pressure, field intensity), as seen from the formula

$$\Delta\epsilon = \frac{(\epsilon + 2)^2}{3}\,\Delta\left(\frac{\epsilon - 1}{\epsilon + 2}\right)$$

Like the Curie point, this predicted instability always fails to materialize; the observed variations of the electric susceptibility with temperature, pressure, volume and field intensity are of a smaller order of magnitude than those predicted by the theory.

This rather brief outline may suffice for a perspective of the difficulties which the original theory has encountered. Many authors have resigned themselves to the view that the consistent discrepancies were due to "association"; in other words, the forces between the polar molecules were so strong that their effects would not admit of any simple description.

J. Wyman[3] has shown that certain simple, general relations are approximately fulfilled by a large class of polar liquids, for example

$$(\epsilon - 1)\,T \sim \text{constant} \qquad (2)$$

Such a discovery belies the pessimistic expectations of the "association theory," and indicates that our theoretical understanding of polar liquids is capable of great advancement.

Without reference to any particular theory, by straightforward thermodynamic reasoning, Wyman's relation (2) implies quite simply that the polarization of the dielectric (by orientation) involves practically no change of the internal energy. According to Debye's theory, the polarization should be greatly enhanced by the internal field, and the consequent reduction of the energy should often be much greater than the work required to accomplish the polarization.

Analysis of the Internal Field

We shall show presently that the original Mosotti theory of the internal field is not applicable to permanent dipoles, in that only a certain part of it, which we might call the *cavity field*, contributes to the orienting force-couple. The remaining part of the internal field, the *reaction field*, is parallel to the dipole moment; it has therefore the very different effect of enhancing both the permanent and the induced dipole moments, in a ratio given by the polarizability of the molecule.

For cases where the electric polarization by orientation is but a small fraction of the whole, the modification of the theory involves the underlying picture more than the predicted results. For cases where the polarization is mainly due to orientation, the predictions of the new theory are very different; for example, no Curie point is expected.

Our molecular model will be the same as that of the Debye theory. While the shape of the molecules will affect the result, in the present article our concern shall be limited to spheres, whose radius will be denoted by a. Further pertinent characteristics of a molecule are its polarizability, α, related to an "internal refractive index" n as follows

$$\alpha = \frac{n^2 - 1}{n^2 + 2}\,a^3 \qquad (3)$$

and a permanent electric moment μ_0 (*in vacuo*). In an electric field, **F**, the total electric moment,

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[2] H. Mueller, *Physik. Z.*, **34**, 689 (1933).

[3] Wyman, THIS JOURNAL, **58**, 1482 (1936).

is the vector sum of the permanent and the induced dipole moments

$$\mathbf{m} = \mu_0\mathbf{u} + \alpha\mathbf{F} \tag{4}$$

where **u** denotes a unit vector in the direction of the dipole axis. The statistical *a priori* expectation of **u** is isotropic.

First, let us consider an unpolarized medium of dielectric constant, ϵ, and introduce a rigid dipole of moment m into a cavity of radius a. For simplicity, let the dipole be a point singularity of the electric field, situated in the center of the spherical cavity. The potential ψ has to satisfy Laplace's equation

$$\Delta\psi = 0 \tag{5a}$$

and the formulation of the boundary conditions in polar coördinates is

$$\psi(r,\theta) - \frac{m\cos\theta}{r^2} = \text{continuous} < \infty \tag{5b}$$

$$\left(\frac{\partial\psi}{\partial r}\right)_{r = a - 0} = \epsilon\left(\frac{\partial\psi}{\partial r}\right)_{r = a + 0} \tag{5c}$$

The solution of this problem is

$$\begin{aligned} \psi &= \frac{m\cos\theta}{r^2} - Rr\cos\theta,\ (r < a) \\ \psi &= \frac{m^*\cos\theta}{\epsilon r^2},\ (r > a) \end{aligned} \tag{6}$$

whereby the coefficients m^* and R must equal

$$\begin{aligned} m^* &= \frac{3\epsilon}{2\epsilon + 1}\, m \\ R &= \frac{2(\epsilon - 1)}{2\epsilon + 1}\,\frac{m}{a^3} \end{aligned} \tag{7}$$

The former may be called the *external moment* of the immersed dipole; it determines the force (modified by the intervening medium), which the dipole will exert upon a distant charge in the dielectric. The coefficient R measures the electric field which acts upon the dipole as a result of electric displacements induced by its own presence, we shall refer to it as the *reaction field.*

For a neutral, spherical molecule with an arbitrary distribution of charges the above relations between m, m^* and R still maintain. In this more general case m is the actual dipole moment of the molecule, while m^* measures the dipole part of its external field, and R the homogeneous part of the reaction field. This important rule, that m^* and R are determined by m alone, independently of higher electric moments, admits of generalization to ellipsoidal molecules, whereby the coefficients naturally depend on the axes ($2a$, $2b$, $2c$) of the ellipsoid.

As a complement to this consideration of an immersed dipole in the absence of an external field, let us recall the familiar results for the modification of a homogeneous field E by an empty spherical cavity. The mathematical problem is the same as before, except that (5b) is replaced by

$$\psi(r,\theta) + Er\cos\theta = \text{continuous} < \infty \tag{8b}$$

and the solution is

$$\begin{aligned} \psi &= -Er\cos\theta - (M/r^2)\cos\theta,\ (r > a) \\ \psi &= -Gr\cos\theta \qquad\qquad\qquad\ ,\ (r < a) \end{aligned} \tag{9}$$

with the coefficients

$$\begin{aligned} M &= \frac{\epsilon - 1}{2\epsilon + 1}\, Ea^3 \\ G &= \frac{3\epsilon}{2\epsilon + 1}\, E \end{aligned} \tag{10}$$

In passing, we observe a reciprocal relation between this case and Eq. 7, namely

$$G/E = m^*/m = 3\epsilon/(2\epsilon + 1) \tag{11}$$

By combining the results (7) and (10) we now find the total field F which acts upon a spherical molecule in a polarized dielectric

$$\mathbf{F} = \mathbf{G} + \mathbf{R} = \frac{3\epsilon}{2\epsilon + 1}\,\mathbf{E} + \frac{2(\epsilon - 1)}{(2\epsilon + 1)a^3}\,\mathbf{m} \tag{12}$$

This equation formulates the conditions for equilibrium *in the environment of the molecule.* The condition for internal equilibrium of the molecule is given by our model

$$\mathbf{m} = \mu_0\mathbf{u} + \alpha\mathbf{F} \tag{4}$$

Accordingly, for a given instantaneous direction **u** of the "permanent dipole" axis the total electric moment of the molecule is given by the formula

$$\left(1 - \frac{2(\epsilon - 1)}{(2\epsilon + 1)}\frac{\alpha}{a^3}\right)\mathbf{m} = \mu_0\mathbf{u} + \frac{3\epsilon}{(2\epsilon + 1)}\,\alpha\mathbf{E} \tag{13}$$

When we introduce the "internal dielectric constant" n^2 according to Eq. 3, we obtain a convenient explicit formula as follows

$$\begin{aligned} \mathbf{m} &= \frac{(n^2 + 2)(2\epsilon + 1)}{3(2\epsilon + n^2)}\,\mu_0\,\mathbf{u} + \frac{\epsilon(n^2 - 1)}{(2\epsilon + n^2)}\,a^3\mathbf{E} \\ &= \mu\mathbf{u} + \frac{\epsilon(n^2 + 2)}{(2\epsilon + n^2)}\,\alpha\,\mathbf{E} \end{aligned} \tag{14}$$

In the same notation, the explicit formula for the internal field becomes

$$\mathbf{E} + \mathbf{I} = \mathbf{F} = \left(1 + \frac{n^2(\epsilon - 1)}{(2\epsilon + n^2)}\right)\mathbf{E} + \frac{2(\epsilon - 1)}{(2\epsilon + 1)}\frac{\mu}{a^3}\mathbf{u} \tag{15}$$

As regards the induced moment in the **E** direction, this formula does not differ greatly from that of Clausius and Mosotti, which is

$$\mathbf{I} = \mathbf{E}(\epsilon - 1)/3$$

while with $\mu = 0$, Eq. 15 gives

$$\mathbf{I} = \mathbf{E}n^2(\epsilon - 1)/(2\epsilon + n^2)$$

For a non-polar liquid we have $\epsilon = n^2$, and the two formulas are identical. In application to mixtures of non-polar liquids, Eq. 15 yields slightly higher values of ϵ.

Nevertheless, in applying the same formulas to polar liquids we shall presently derive results which are very different from those previously accepted. The problem before us is to compute the effective energy of interaction between the molecule and the field, and the consequent average orientation of the molecule.

For this purpose it is not admissible, as Debye did, to assume that the orienting force is proportional to the time average of $\mathbf{F}$. Since $\mathbf{F}$ depends on the orientation, we must compute the orienting force-couple for each individual direction of $\mathbf{u}$; the *work* involved in the process of orientation is then the potential of this orienting force.[4] The force-couple equals the vector product of $\mathbf{F}$ and $\mathbf{m}$. We can use either of the expressions for $\mathbf{F}$ given by Eqs. 12 and 15; the former represents a more instructive decomposition of the vector

$$\begin{gathered}\mathbf{F} = \mathbf{G} + \mathbf{R}\\ \mathbf{G} = \mathbf{E} \times 3\epsilon/(2\epsilon + 1)\\ a^3\mathbf{R} = \mathbf{m} \times 2(\epsilon - 1)(2\epsilon + 1)\end{gathered}$$

The force-couple equals

$$\mathbf{M} = \mathbf{F} \times \mathbf{m} = \mathbf{G} \times \mathbf{m} = (3\epsilon/(2\epsilon + 1))\,\mathbf{E} \times \mathbf{m} \qquad (16)$$

We observe that *the reaction-field* $\mathbf{R}$*, being parallel to the dipole* $\mathbf{m}$*, does not contribute to the orienting force-couple.* The calculation is easily completed with the aid of Eq. 14; this time only the part parallel to $\mathbf{u}$ matters, because $\mathbf{G} \times \mathbf{E}$ vanishes

$$\mathbf{M} = \mu\,\mathbf{G} \times \mathbf{u} = \mu^*\,\mathbf{E} \times \mathbf{u} \qquad (17)$$

Here, in accord with the notation of Eq. 7

$$\mu^* = \mu\,3\epsilon/(2\epsilon + 1) \qquad (18)$$

stands for the "external" characteristic moment of the molecule, while the actual electric moment μ will depend on the dielectric constant of the environment according to Eq. 14

$$\left.\begin{aligned}\mu &= \frac{(n^2 + 2)(2\epsilon + 1)}{3(2\epsilon + n^2)}\,\mu_0\\ \mu^* &= \frac{\epsilon(n^2 + 2)}{(2\epsilon + n^2)}\,\mu_0\end{aligned}\right. \qquad (19)$$

Dropping the vector notation, Eq. 17 may be written

$$M = \mu^*\,E \sin\theta$$

then the work of orientation, w, is given by

$$\left.\begin{aligned}\partial w/\partial\theta &= M;\\ w &= -\,\mu^*\,E\cos\theta\end{aligned}\right. \qquad (20)$$

This extremely simple result suggests the possibility of an equally simple derivation; for this purpose, it is convenient to invert the problem. Let us keep the orientation of the molecule fixed, and find out how the work of creating a field of a certain intensity E in a given direction depends on the angle θ between this direction and the dipole axis of the molecule. The most elementary derivation is obtained if we assume that the external field is due to a charge of the magnitude $-r_1^2E$ at some point (r_1, θ, φ) on a large sphere of radius r_1. In order to change the direction of the field at constant intensity, we move the charge to another point on the sphere. The work involved is given by the potential

$$\psi = \mu^* \cos\theta/\epsilon r^2$$

(*cf.* Eq. 6), of the field due to the molecule, and Eq. 20 obviously results. This alternative computation of w exhibits the reciprocal character of Eq. 11.

The mean orientation of the molecules in the field is given by Boltzmann's formula

$$\overline{\cos\theta} = \int \cos\theta\, e^{-w/kT} \sin\theta\, d\theta\, d\varphi \Bigg/ \int e^{-w/kT}$$
$$\mathit{sin}\,\theta\, d\theta\, d\varphi = L(\mu^*E/kT) = \coth(\mu^*E/kT) - (kT/\mu^*E) = (\mu^*E/3kT) - O(E^3)$$

Thus, for low field intensities E, we have[5]

$$\overline{\cos\theta} = \mu^*E/3kT \qquad (21)$$

and we can compute the polarization per unit volume from Eq. 14, as follows

$$\mathbf{P} = N\overline{\mathbf{m}} = N\left(\frac{\mu\mu^*}{3kT} + \frac{\epsilon(n^2 + 2)}{(2\epsilon + n^2)}\,\alpha\right)\mathbf{E} \qquad (22)$$

Dielectric Constants of Pure Polar Liquids

In computing the dielectric constant, we shall assume that the volume of the liquid equals the sum of the volumes of the molecules; accordingly

$$N \times 4\pi a^3/3 = 1 \qquad (23)$$

With the notation expressed by Eq. 3, we then obtain

$$4\pi N(n^2 + 2)\,\alpha = 4\pi N(n^2 - 1)a^3 = 3(n^2 - 1) \qquad (24)$$

Now the fundamental electrostatic formula

$$(\epsilon - 1)\,\mathbf{E} = 4\pi\mathbf{P} \qquad (25)$$

yields in combination with Eqs. 22 and 24 the following implicit formula for the dielectric constant

$$\epsilon - 1 = 4\pi N\,\frac{\mu\mu^*}{3kT} + \frac{3\epsilon(n^2 - 1)}{2\epsilon + n^2}$$

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[4] In a polar medium, the field fluctuates with the rotation of the neighboring molecules. In such a case, the *average force* is the important quantity [(L. Onsager, *Chem. Rev.*, **13**, 73 (1933))]. An alternative procedure is to compute the work of charging a dipole in a given direction **u**.

[5] The given formula is not in general applicable to strong fields, *i. e.*, saturation; because its derivation involves the assumption of an isotropic environment.

which may be written more compactly

$$\frac{(2\epsilon + 1)(\epsilon - n^2)}{(2\epsilon + n^2)} = 4\pi N \frac{\mu\mu^*}{3kT} \qquad (26)$$

or in view of Eq. 18

$$3\epsilon(\epsilon - n^2)/(2\epsilon + n^2) = 4\pi N(\mu^*)^2/3kT \qquad (27)$$

Here, μ and μ^* still depend on ϵ according to Eq. 19. We obtain after elimination

$$(\epsilon - n^2)(2\epsilon + n^2)/\epsilon(n^2 + 2)^2 = 4\pi N\mu_0^2/9kT \qquad (28)$$

When ϵ is large, the left member is very nearly equal to

$$2\epsilon/(n^2 + 2)^2 \sim 4\pi N\mu_0^2/9kT \qquad (29)$$

One of the reasons for this simple limiting law is that μ and μ^* approach limits as ϵ increases. With the notation

$$\mu_\infty = \mu_0(n^2 + 2)/3 \qquad (30)$$

(*cf.* Eq. 19), we can write Eq. 28 in the alternative form

$$(2\epsilon + n^2)(\epsilon - n^2)/\epsilon = 4\pi N\mu_\infty^2/kT \qquad (31)$$

On the other hand, when only a small fraction of the electric susceptibility is due to orientation of the molecules, that is, whenever

$$\epsilon - n^2 \ll n^2$$

Eq. 27 agrees in the first approximation with the formula of Clausius and Mosotti. We readily derive from Eq. 27

$$\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} = \frac{3\epsilon(n^2 + 2)}{(2\epsilon + n^2)(\epsilon + 2)} \frac{4\pi N\mu_0^2}{9kT} = \frac{4\pi N\mu_0^2}{9kT} f(\epsilon, n^2) \qquad (32)$$

Fig. 1 indicates the range where the approximation of Clausius and Mosotti is good.

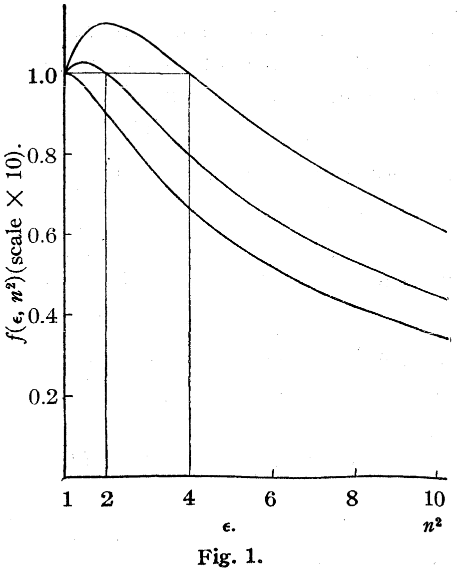

Fig. 1.

Dielectric Constants of Solutions

We shall consider a solution which contains in a unit volume $N_1, \ldots N_i, \ldots$ spherical molecules of different species, with radii $a_1, \ldots a_i, \ldots$, polarizabilities $\alpha_1, \ldots \alpha_i, \ldots$ and dipole moments $\mu_1, \ldots \mu_i, \ldots$, respectively. We introduce the individual refractive indices $n_1, \ldots n_i, \ldots$ by the relation

$$\alpha_i = a_i^3(n_i^2 - 1)/(n_i^2 + 2) \qquad (33)$$

and we shall denote the volume fractions by

$$\vartheta_i = N_i \times 4\pi a_i^3/3 \qquad (34)$$

The dipole moments will depend on the dielectric constant of the environment according to Eq. 19; the moments *in vacuo* will be denoted by μ_{0i}.

The fundamental electrostatic relation

$$(\epsilon - 1)\,\mathbf{E} = 4\pi\,\mathbf{P} \qquad (25)$$

yields in conjunction with Eqs. 22, 24 and 34

$$\epsilon - 1 = 4\pi \sum N_i \left(\frac{\epsilon(n_i^2 + 2)}{\epsilon + n_i^2}\alpha_i + \frac{\mu_i\mu_i^*}{3kT}\right) = \sum \vartheta_i \frac{3\epsilon(n_i^2 - 1)}{n_i^2 + 2\epsilon} + 4\pi \sum N_i \frac{\mu_i\mu_i^*}{3kT} \qquad (35)$$

Making use of the identity

$$3\epsilon(n_i^2 - 1) = (2\epsilon + n_i^2)(\epsilon - 1) - (2\epsilon + 1)(\epsilon - n_i^2)$$

we can rearrange Eq. 35 in the form

$$(1 - \Sigma\vartheta_i)(\epsilon - 1) + (2\epsilon + 1)\Sigma\vartheta_i(\epsilon - n_i^2)/(2\epsilon + n_i^2) = 4\pi\Sigma\, N_i\mu_i\mu_i^*/3kT \qquad (36)$$

Now if we assume that the entire space is occupied by the molecules

$$\Sigma\vartheta_i = 1 \qquad (37)$$

the first term in the member of Eq. 36 vanishes. Then in view of Eq. 18, Eq. 36 may be written

$$\Sigma\vartheta_i(\epsilon - n_i^2)3\epsilon/(2\epsilon + n_i^2) = 4\pi\Sigma\, N_i(\mu_i^*)^2/3kT \qquad (38)$$

which furnishes the generalization of Eq. 27 to the case of several molecular species. The right member of Eq. 38 depends on the dielectric constant according to Eq. 19:

$$\mu_i^* = \frac{\epsilon(n_i^2 + 2)}{(2\epsilon + n_i^2)}\mu_{0i} = \frac{2\epsilon}{(2\epsilon + n_i^2)}\mu^*_{\infty i} = \frac{3\epsilon}{(2\epsilon + n_i^2)}\mu_{\infty i} \qquad (39)$$

In the limit of high dielectric constants

$$\epsilon \gg n_i^2, (i = 1,2, \ldots)$$

Eq. 38 becomes

$$\epsilon = O(n^2) + 4\pi\Sigma N_i\mu_{i\infty}\mu^*_{i\infty}/3kT = O(n^2) + \sum \frac{(n_i^2 + 2)^2}{2} \frac{4\pi}{3} N_i \frac{\mu_{0i}^2}{3kT} \qquad (40)$$

We observe that in this limit, the dielectric constants of solutions are nearly additive.

The opposite extreme is a dilute solution of polar molecules in a non-polar medium. In the following, the index *m* will refer to the non-polar solvent, the index *s* to a polar solute present in small concentration, so that

$$\begin{aligned} \epsilon_m &= n_m^2 \gg \epsilon - \epsilon_m \\ \vartheta_m &\gg 1 - \vartheta_m = \vartheta_s \end{aligned} \qquad (41)$$

Neglecting terms of higher order in the concentration (N_s), we obtain for the dielectric constant of the solution

$$\epsilon = n^2 + \frac{4\pi(\mu^*)^2}{3kT} N_s \qquad (42)$$

here the "refractive index" of the solution differs from that of the solvent by the amount

$$n^2 - n_m^2 = \vartheta_s \frac{3n_m^2}{2n_m^2 + n_s^2} (n_s^2 - n_m^2) \qquad (43)$$

and the (external) dipole moment depends on the dielectric constant of the non-polar solvent according to Eq. 19

$$\mu^* = \frac{3n_m^2}{2n_m^2 + 1} \mu = \frac{n_m^2(n_s^2 + 2)}{2n_m^2 + n_s^2} \mu_0 \qquad (44)$$

For comparison, the Clausius-Mosotti formula yields (on our restrictive assumption of additive volumes)

$$\frac{\epsilon - 1}{\epsilon + 2} = \vartheta_m \frac{\epsilon_m - 1}{\epsilon_m + 2} + \vartheta_s \frac{n_s^2 - 1}{n_s^2 + 2} + \frac{4\pi}{3} N_s \frac{\mu_0^2}{3kT} \qquad (45)$$

and by neglecting terms of higher order we obtain the analogs of Eqs. 42 and 43

$$\epsilon = n^2 + 4\pi N_s((n_m^2 + 2)\,\mu_0/3)^2/3kT \qquad (46)$$

$$n^2 = n_m^2 + \vartheta_s \frac{(n_m^2 + 2)}{(n_s^2 + 2)} (n_s^2 - n_m^2) \qquad (47)$$

These formulas are seen to agree with Eqs. 42–44 in two cases: when $n_m = 1$ and when $n_m = n_s$. For values of n_m between these limits, Eqs. 42–44 predict larger increments of the "refractive index" and of the dielectric constant than does the classical theory. On the other hand, for $n_m > n_s$, the new formulas predict a *smaller decrement* of the refractive index, n, and a *smaller increment* of $\epsilon - n^2$, the susceptibility due to orientation. The quantitative relations between the two theories can be summarized as follows

$$\begin{aligned} &(n^2 - n_m^2)_{\text{new}}/(n^2 - n_m^2)_{\text{old}} = f \\ &(\epsilon - n^2)_{\text{new}}/(\epsilon - n^2)_{\text{old}} = f^2 = (\mu_{\text{app}}/\mu_0)^2 \\ &f = f(\epsilon_m, n_s^2) = 3\epsilon_m(n_s^2 + 2)/(2\epsilon_m + n_s^2)(\epsilon_m + 2) \end{aligned} \qquad (48)$$

Here, $\mu_{\text{app.}}$ denotes the "electric moment" computed by means of the classical formula, Eq. 1, from the dielectric constant of a solution which conforms to the present theory. The function $f(\epsilon, n^2)$ is represented in Fig. 1. Some of its important properties are

$$\begin{aligned} f(\epsilon, n^2) - 1 &= 2(\epsilon - n^2)(\epsilon - 1)/(2\epsilon + n^2)(\epsilon + 2) \\ f(1, n^2) &= f(n^2, n^2) = 1 \\ f(\epsilon, n^2) &\leqq f(n, n^2) = 1 + 2((n - 1)/(n + 2))^2 \\ f(\epsilon, n^2) &= f((n^2/\epsilon), n^2) \end{aligned} \qquad (49)$$

Discussion

The present development of the theory is by no means complete. One open question is the proper choice of the molecular "radius" *a*. The assumption that the molecules fill the whole volume of the liquid (Eqs. 23, 37), is a makeshift; and its application to the extreme case of a gas would be quite absurd. Assuming that our molecular model is adequate, it would appear better to find a suitable basis for the determination of constant "*a*." Then in order to allow for changes of volume due to thermal expansion or other causes it would only be necessary to consider the "void" as a constituent of a mixture. This point of view is in perfect accord with our Eq. 36, where the "void," of dielectric constant unity, enters quite symmetrically with the other constituents. Nevertheless, it appears that the development of the theory along these lines will involve careful consideration of molecular arrangements, and probably some arbitrary exercise of judgment.

Similar questions would arise in a generalization of the present theory to molecules of shapes other than spherical, in which case the ratios μ/μ_0, μ^*/μ_0 and μ^*/μ will be greater the shorter the dipole axis compared to other dimensions of the molecule. As far as dilute solutions in non-polar solvents are concerned, it is only necessary to compute the ratio μ^*/μ_0 as a function of ϵ_m; then μ^* determines the increment of the dielectric constant according to Eq. 38. On the other hand, for an imaginary polar liquid of refractive index unity the electric susceptibility must be proportional to the product $\mu\mu^*$, rather than to $(\mu^*)^2$. Fortunately, the difference between the two results is not in general very large. The paradox which it represents is capable of solution, but only by taking into account the reciprocity of neighborhood relations between non-spherical molecules!

The computation of the molecular radius (a) from the total volume of the liquid should lead to an underestimate of the dielectric constant for the given molecular model. The error ought not to be very large, except when a liquid is considered close to its critical point. The assumption of spherical molecules can cause positive or negative errors, perhaps about equally often. With this in mind we should inquire whether the present theory can furnish a reasonably good description for the *average* dielectric behavior of polar liquids and their solutions.

As regards the former, we have available Wyman's analysis[3] of an extensive material which he has compiled without apparent prejudice and without any knowledge of the theory to be tested. Wyman has summarized his conclusions in the formula

$$p = (\epsilon + 1)/A$$

where p measures the total "polarization" per unit volume, in our notation

$$p = \frac{4\pi}{3} \sum N\left(\alpha + \frac{\mu_0^2}{3kT}\right)$$

The value of the factor A is derived from measurements of ϵ together with measurements of μ_0 in the vapor in non-polar solvents. For a great number of liquids Wyman finds $A \sim 8.5$, with a certain spread given by the limits $A = 6.2$ and 11.

Wyman's formula is practically the same as our Eq. 29

$$\epsilon/A = 2\epsilon/(n^2 + 2)^2 \sim 4\pi N\mu_0^2/9kT \qquad (29)$$

We obtain $A = (n^2 + 2)^2/2$, and Wyman's typical value $A = 8.5$ corresponds to a refractive index

$$n = 1.46$$

which is very reasonable indeed. The range

$$6.2 < A < 11$$

corresponds to

$$1.275 < n < 1.64$$

A comparison with individual refractive indices has not been attempted; it would hardly be significant without allowance for molecular shape. Incidentally, our "refractive index" should include the "atomic polarization" due to elastic displacement of the atomic nuclei by the electric field.

According to Wyman's analysis, one group of liquid dielectrics deviates very markedly from the rest, in that they exhibit much larger dielectric constants than they ought to have. This group includes water, alcohols and ammonia; on the whole, it coincides with the liquids which on the basis of unusual thermodynamic behavior have long been considered as "associated."

There is good cause for the view that we are dealing here with a type of molecular interaction which does not admit of adequate description in terms of permanent and induced dipoles. A promising scheme for coördination of the phenomena is the "proton bond" theory,[6] which has recently been given considerable attention by Hildebrand[7] and by Pauling.[8]

If the dielectric behavior of the substances in question is to be explained along these lines, then an important part of the present theory may still be applicable. As a starting point, Eq. 26 can hardly be far from the truth; its derivation is almost phenomenological. Moreover, it is not likely that in a liquid like water, the ratio μ^*/μ will differ much from its normal value of 3/2; in order to account for the large anomalies in question, it would have to equal 3. Thus we are led to abandon Eq. 19, and that involves only a quite reasonable addition to the basic hypothesis of the proton bond theory: *The formation of a "hydrogen bond" increases the electric moment of the group which carries the hydrogen.*

On the basis of this general picture, we can estimate that a water molecule in the liquid has a dipole moment of the order $\mu \sim 3 \times 10^{-18}$ e. s. u., with $\mu^*/\mu \sim 3/2$. The increment from $\mu_0 = 1.8 \times 10^{-18}$ in the vapor could hardly be accounted for by ordinary homogeneous induction. The properties of water as a solvent for electrolytes appear to harmonize well with our assumption of a large electric moment.

This explanation for the anomaly of "proton bond" liquids differs from the "association theory" in the assumption of a large ratio μ/μ_0, while the "association theory" would call for an anomalous ratio μ^*/μ.

For dilute solutions of polar substances in nonpolar solvents, the present theory expects in accordance with experience that the "apparent" dipole moments computed on the basis of the Clausius–Mosotti equation should not in general differ much from those found in vapors of the same substances.

An important theoretical advance is the reconciliation of this empirical rule with the expectation of increased dipole moments in solutions; in our picture $\mu_{\text{app.}}$ is only a fictitious quantity with a complicated meaning.

According to Eq. 18, the apparent electric moments of a given molecule should be somewhat dependent on the solvent, so as to decrease with increasing dielectric constant of the environment. The researches of H. Mueller[2,9] have shown that

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(6) Latimer and Rodebush, THIS JOURNAL, **42**, 1419 (1920).

(7) Hildebrand, *Science*, **83**, 21 (1936).

(8) Pauling, THIS JOURNAL, **57**, 2680 (1935); *ibid.*, **58**, 94 (1936).

(9) H. Mueller, *Physik. Z.*, **35**, 346 (1934).

in spite of occasional irregularities, a general effect of this type exists. The effect is of the expected order of magnitude. Mueller's results[9] for the temperature dependence of $\mu_{\text{app.}}$ in solutions support the view that the "radius" a should be treated as a molecular constant. It is worth pointing out that the present theory gives a precise interpretation for the dielectric constants of dilute solutions: except for the susceptibility due to elastic polarization (refractive index), the increment of the dielectric constant is a measure for $(\mu^*)^2$, as given by our Eq. 42. We should also mention that the recent calculations by R. M. Fuoss[10] of the dielectric properties and of molecular interaction of salt molecules in non-polar solvents are in accord with the present theory, if only his electric moments, which he denotes by μ, are identified with our "external" electric moments μ^*.

As regards the electrostatic interaction of polar molecules in dilute solutions, Fuoss' computations are carried to a higher degree of approximation. A comparison with his results shows that in cases of extremely strong molecular interaction, the predictions of the present, simpler theory are subject to considerable modification. This disagreement should be taken as a warning against uncritical application of the present theory, which purports to be no more than a first approach to the complete description of dielectrics.

In our computations, the neighborhood of a molecule is considered as a continuum, thus neglecting its actual discrete structure. Moreover, the polarization of the neighboring liquid by a given molecule was considered as proportional to the field, while actually this relation might be modified by compression and by some sort of dielectric saturation. In spite of these shortcomings, the theory apparently accounts for a considerable field of experience, and there is some indication that an outstanding class of discrepancies are due to the physical assumptions involved in the conventional molecular model, and not to the mathematical approximations.

Summary

1. The dipole theory of dielectrics, as originally developed with the aid of Mosotti's formula for the "internal field," leads to the expectation of electrical Curie points, with attendant instability for liquids of high dielectric constants. This prediction is not verified by experience.

2. The field which acts upon a molecule in a polarized dielectric may be decomposed into a *cavity field* **G**, given by the shape of the molecule and proportional to the external field intensity, and a *reaction field* **R**, which is proportional to the total electric moment, and depends on the instantaneous orientation of the molecule.

3. The mean orientation of a molecule is determined by the orienting force-couple exerted by the cavity field **G** upon the electric moment of the molecule. The earlier naïve application of the Mosotti formula is equivalent to the assumption that the effective orienting field equals the average of $(\mathbf{G} + \mathbf{R})$, and incorrect because **R** never exerts a torque upon the molecule.

4. Since all real molecules are electrically deformable, the reaction field **R** will cause an enhancement of the electric moment of any molecule immersed in a dielectric. The induced moment due to the cavity field **G** will be similarly enhanced by the corresponding component of **R**.

5. The electric moment μ of a spherical molecule is computed as a function of the dielectric constant ϵ of the environment. In addition, it is convenient to consider an "external" electric moment μ^*, which determines the interaction of the molecule with all distant charges and long range fields in the dielectric. For spherical molecules, the ratio μ^*/μ increases from unity to 3/2 as the dielectric constant of the environment increases from 1 to ∞. Both μ and μ^* approach limits, which depend on the deformability of the molecule, for $\epsilon \longrightarrow \infty$. Accordingly, no Curie point is expected.

6. For simplicity, the computations are restricted to spherical molecules. The resulting formulas for the dielectric constants of pure polar liquids are similar to those proposed on empirical grounds by Wyman. For solutions of polar molecules in non-polar liquids the predictions of the earlier theory are largely upheld, but with certain minor modifications which are in qualitative agreement with the experiments of Horst Mueller.

NEW HAVEN, CONN. RECEIVED JUNE 1, 1936

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[10] R. M. Fuoss, THIS JOURNAL, **56**, 1027, 1031 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Separation and Determination of Tungsten and Molybdenum

BY HERMAN YAGODA[1] AND HAROLD A. FALES

The precise analysis of materials containing tungsten and molybdenum is complicated by the fact that in separating tungstic acid the precipitate is always contaminated by appreciable quantities of molybdenum,[2] and that in the formation of molybdenum sulfide, a considerable amount of tungsten is precipitated with it. The problem of the separation of molybdenum, both from tungsten and the other metals, is further complicated in that molybdenum sulfide is seldom precipitated quantitatively in one operation, its complete removal demanding two or more repetitions of the treatment with hydrogen sulfide.

A bibliography of the literature on the methods of analysis for tungsten and molybdenum up to the year 1923 is available in the bulletin by Moore.[3] Since that time, new methods for the determination of these elements have appeared making use of organic precipitants, but none of the reagents is suitable for separating the two metals. Among the organic compounds proposed for these determinations are, 8-hydroxyquinoline[4] which forms stable compounds having the composition, $WO_2(C_9H_6ON)_2$[5] and $MoO_2(C_9H_6ON)_2$[6]; and α-benzoin oxime which is serviceable for the direct determination of molybdenum in steels.[7]

The methods for the separation of tungsten and molybdenum come under two general headings. In the first grouping, one of the constituents of the mixture is removed by extraction with a suitable solvent. In this class come the methods of Ruegenberg and Smith,[8] who employed concentrated sulfuric acid to separate the molybdenum from a mixture of hydrated tungstic and molybdic acids; also, the procedure of Merrill,[9] who effected a like separation through the use of selenium oxychloride as the solvent. Under the second classification come precipitation reactions, the mechanism of which, in general, lends itself to more exact separations than are possible by extraction methods. Unfortunately, the properties of the two ions in question are very similar, so that with the exception of the sulfides, salts of the two elements have not been discovered that have a sufficient difference in solubility to effect a quantitative separation of one metal from the other.

The disadvantage of the separation by means of hydrogen sulfide is that the precipitation of molybdenum sulfide is usually incomplete owing to the reduction of part of the molybdenum by the reagent to lower valency states in which the ions can no longer form insoluble sulfides.[2] A further inconvenience of the method is that the subsequent removal of the large quantities of tartaric acid, whose presence is essential for a sharp separation of the two elements, is a very difficult and time consuming operation.

The present investigations were initiated in order to circumvent the described difficulties in the quantitative precipitation of pure molybdenum sulfide. Examination of the law of mass action for the reaction between the hexavalent molybdenum ion and the hydrogen sulfide in an acid medium, reveals that the complete precipitation of the molybdenum sulfide is favored by a low hydrogen-ion concentration and a high concentration of hydrosulfide ion

$$Mo^{6+} + 3HS^- \rightleftharpoons MoS_3 + 3H^+ \qquad (1)$$

$$[Mo^{6+}] = [MoS_3][H^+]^3/k[HS^-]^3 \qquad (2)$$

The hydrogen-ion concentration can be reduced only over a narrow range as, in alkaline media, soluble sulfomolybdates are formed. The concentration of hydrogen sulfide can be increased by conducting the precipitation in a pressure bottle at an elevated temperature. The efficiency of this procedure is doubtful, for the pressure effect is probably nullified by the increased reducing action of the reagent at elevated temperatures.[10]

It occurred to the writers that another means of increasing the concentration of the hydrogen

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[1] J. T. Baker Chemical Co. Research Fellow in Analytical Chemistry, 1935–36.

[2] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, pp. 246–247.

[3] R. B. Moore and collaborators, "Analytic Methods for Certain Metals," *Bur. Mines Bulletin* 212, Washington, D. C., 1923, pp. 125 and 167.

[4] G. Banalescu, *Ann. chim. anal.*, **12**, 259 (1930).

[5] S. Halberstadt, *Z. anal. Chem.*, **92**, 86 (1933).

[6] H. R. Fleck and A. M. Ward, *Analyst*, **58**, 388 (1933).

[7] H. B. Knowles, *Bur. Stds. J. Res.*, **9**, 1 (1932).

[8] M. J. Ruegenberg and E. F. Smith, THIS JOURNAL, **22**, 772 (1900).

[9] H. B. Merrill, *ibid.*, **43**, 2383 (1921).

[10] W. Werz, *Z. anal. Chem.*, **100**, 241 (1935); "Applied Inorganic Analysis," p. 55.

sulfide in the system is to take advantage of the increased solubility of the gas in water at low temperatures. At 0° the solubility of hydrogen sulfide is 7.1 g. per liter, which is more than twice that at 25°.[11] As the concentration of the hydrosulfide ion enters as a cube in equation 2, doubling the concentration of the hydrogen sulfide tends to make an eight-fold effect in diminishing the molybdenum-ion concentration. Also, as the reaction is conducted at a low temperature, the reducing action of the reagent is considerably diminished, a factor which favors the quantitative separation of the sulfide. Experimental investigations revealed that this method was eminently suitable for the separation of molybdenum from tungsten.

Purification of Standards

$Na_2WO_4 \cdot 2H_2O$.—The purification of sodium tungstate was effected by following the procedure developed by Folin.[12] The final product was tested for traces of molybdenum by means of potassium ethyl xanthate.[13] By applying the spot test technique, described by Feigl[14] to solutions of the purified salt to which were added known quantities of sodium molybdate, it was found that the red coloration characteristic of the element was discernible in a mixture containing 0.005% of sodium molybdate. As the solution of the purified salt did not give any visible reaction, the sodium tungstate employed in these investigations probably contained not more than 0.005% of sodium molybdate. Analysis of the product for water of crystallization[15] and tungstic oxide[16] showed that the salt contained 10.91 ± 0.02% water and 70.27 ± 0.02% WO_3, which compares favorably with the theoretical amounts 10.92 and 70.30%, respectively.

$Na_2MoO_4 \cdot 2H_2O$.—This salt was purified by dissolving 50 g. of the best obtainable sodium molybdate in 300 cc. of water; to the solution was added 600 cc. of 95% alcohol. A small crop of crystals separated at this point, these were filtered off after a period of one hour and discarded. The clear filtrate was again treated with 600 cc. of alcohol, the small crystals of sodium molybdate were filtered, washed with 100 cc. of 95% alcohol and permitted to dry at room temperature. The product, weighing 25 g., consists of small pearly-lustered crystals that are completely water soluble.

There is no chemical test for tungsten sufficiently delicate to establish the presence of traces of the element as an impurity in sodium molybdate. Spectrographic examination of the purified salt showed a very faint line in the position where the most persistent line of the arc spectrum of tungsten is located. But, as the other characteristic lines of the optical spectrum of tungsten were not recorded on the plate, appreciable amounts of the element probably are not present in the sample. This is further evident from the chemical analysis in which it was found that the salt contained 14.91 ± 0.01% water[15] and 59.49 ± 0.02% MoO_3,[17] the values closely agreeing with the calculated percentages, 14.89 and 59.50, respectively.

Preparation of Reagents

0° Hydrogen Sulfide Water.—This solution can be prepared by bubbling a stream of the purified gas through a column of water that has been chilled in an ice-bath to 0°. Several methods for preparing this solution were investigated with the object of obtaining rapid saturation and economy in the use of the gas. It was found most convenient to pass the gas through a porous sphere of "Aloxite."[18] This produces an ascending stream of numerous minute bubbles that are almost entirely absorbed by the column of water before they reach the surface. The standard 61 cm. (2-ft.) Kipp gas generators do not supply sufficient pressure to overcome the internal resistance of the porous sphere and the hydrostatic pressure of the column of water above it. The pressure can be augmented easily by compressing the air in the head of the Kipp with the help of an atomizer bulb. Small tanks of liquid hydrogen sulfide, substituted for the Kipp generator, serve the purpose admirably well.

The length of time required to reach the saturation point depends upon the volume of water, its initial temperature and the rate of influx of the gas. The relative rate of absorption, under constant gas pressure, by a column of water at the freezing point is recorded in Table I.

TABLE I

RATE OF ABSORPTION OF HYDROGEN SULFIDE

Volume of water at 0°, 750 cc. Diameter of "Aloxite" sphere, 25 mm. Influx of gas, 150 bubbles per min., as counted in the wash bottle having a conducting tube of 4 mm. inside bore.

Time, min.	10	20	30	45	60	120
G. H_2S/l. sol.[19]	0.863	2.12	3.53	5.21	6.12	6.59
Molarity	0.0253	0.062	0.104	0.153	0.180	0.193

The point of near saturation can be ascertained visually when it is noted that large bubbles reach the surface of the solution. In one experiment on the absorption of hydrogen sulfide, the undissolved gas was collected, dried over calcium chloride, and its weight ascertained by measuring the increase in weight of a U-tube filled with sodium hy-

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[11] L. W. Winkler, *Math. és Termeszettu-dományi Eresitō*, **25**, 86 (1907).

[12] Otto Folin, *J. Biol. Chem.*, **106**, 311 (1934).

[13] S. L. Malowan, *Z. anal. Chem.*, **79**, 201 (1929).

[14] F. Feigl, "Qualitative Analyse mit Hilfe von Tüpfelreaktionen," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1931, p. 176.

[15] The water content was determined by drying 1-g. samples of the salt at 120° for several hours in a platinum crucible. To make sure of the complete removal of the water, the anhydrous salt was heated to the point of fusion.

[16] The tungstic oxide was determined by the standard cinchonine-hydrochloric acid method.

[17] The molybdic oxide content was determined by precipitating and weighing lead molybdate.

[18] These aerator stones are manufactured by the Carborundum Company, Niagara Falls.

[19] The concentration of the hydrogen sulfide was determined by transferring a 10-cc. sample to a solution of lead acetate and weighing the resultant lead sulfide.

droxide pellets connected to the train. It was found that in the process of saturating 750 cc. of water only 0.42% of the total hydrogen sulfide escaped absorption.

Formic Acid.—The acid employed in these investigations was a standard product of analyzed purity, of 85–90% strength. Analysis of the material showed that its concentration was 23.7 molar. Dilute 2 *M* formic acid was prepared by diluting 80 cc. of the concentrated acid to one liter.

Ammonium Formate.—A 50% solution of the salt was prepared by dissolving 250 g. of the J. T. Baker Chemical Co. analyzed product in 150 cc. of water, warming the mixture until the crystals dissolved, filtering and diluting to 500 cc. The solution should have a *p*H of 6.7 using bromo cresol purple as the indicator.

Tartaric Acid.—A 50% solution of the acid was prepared from an analyzed grade product. After the procedure for the separation of the two metals was developed, it was found more convenient to use a 30% solution of the acid.

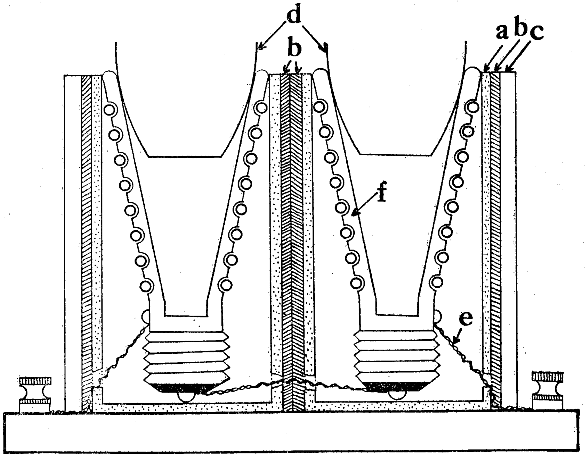

Fig. 1.—Crucible furnace for igniting MoS_3: a, porous clay cup 11 cm. high and 5.5 cm. diam. (inside meas.); b, a 3-mm. layer of thin asbestos paper; c, a 5-mm. layer of heavy asbestos paper; d, protective nickel crucibles; e, connecting wires of standard nichrome; f, 660-watt conical heating units.

Quantitative Precipitation of Molybdenum Sulfide

Molybdenum sulfide can be precipitated from solutions acidified with hydrochloric, sulfuric or formic acid. If the filtrate is to be reserved for the analysis of tungsten, it is desirable that the acidifying agent be readily volatile. Complete precipitation in hydrochloric acid media is a difficult matter[2]; it was therefore decided to investigate the claims of Sterba-Böhm[20] concerning the precipitation of molybdenum sulfide in solutions acidified with formic acid, who concludes that the sulfide can be precipitated completely over a range of acidity varying from 5–20% of the acid. To check this, six samples of sodium molybdate were each dissolved in 125 cc. of 10% formic acid and the solutions were saturated at room temperature with hydrogen sulfide. On examination of the filtrates, all were found to contain minute amounts of molybdenum, averaging 0.10 ± 0.03 mg. of the metal.[21]

A series of analyses was then made using hydrogen sulfide water saturated at 0° as the precipitant. The sodium molybdate was dissolved in 10 cc. of water, 100 cc. of the hydrogen sulfide reagent was added to each sample and the solutions were acidified with measured volumes of 24 *M* formic acid. The mixtures were heated on a hot-plate; when the temperature reached 36° the molybdenum sulfide coagulated, and settled to the bottom of the beakers in the form of bulky deep black precipitates. After digestion for thirty minutes at 40–50° the sulfides were filtered and washed with 5% formic acid. All the filtrates were colorless and perfectly clear[22] and on analysis were found to contain only traces of molybdenum. The results from twelve experiments showed that on the average only 0.04 to 0.01 mg. of the metal failed to be precipitated by following this procedure. This loss is entirely negligible in the gravimetric determination of the element.

Determination of Molybdenum as Molybdic Oxide

After the molybdenum is separated as the sulfide, it is convenient to convert the molybdic sulfide to molybdic oxide and weigh the element in that form. The early investigators of this process[3] concluded that it was difficult to roast the sulfide to the oxide owing to the volatile nature of molybdic oxide. Recent work by Brinton,[23] Hartmann[24] and Knowles[7] proves that the moist sulfide can be converted to the oxide, at temperatures below 600°, without any appreciable loss; and that the process is quite rapid at temperatures above 500°. As the temperatures must be carefully controlled, it is best to ignite the molybdenum sulfide in an electric furnace. The simple heating unit described in Fig. 1, which can be readily assembled from standard laboratory stock, proved to be very useful in executing this process.

The improvised furnace reaches thermal equilibrium in about thirty minutes. With two 660-watt conical heating coils connected in series and insulated as shown in the diagram, the surfaces of the nickel crucibles reach a maximum temperature of 550°. At this temperature the furnace draws a current of 2.75 amp. at 120 volts. By removing part of the wiring from the heating coils, the temperature reaches 750° and the unit can then be employed for igniting precipitates of tungstic acid to the oxide. It is recommended that the crucible containing the precipitate be protected by a nickel crucible, as shown in the figure, in order to prevent its being scratched by the rough walls of the cone shaped heater.

During the progress of the work on the quantitative conversion of molybdenum sulfide to oxide, it was found

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(20) Sterba-Böhm and J. Vostrebal, *Z. anorg. allgem. Chem.*, **110**, 81 (1920).

(21) The molybdenum content was determined colorimetrically by evaporating the solution to dryness and testing the residue by the thiocyanate reaction: L. C. Hurd and H. O. Allen, *Ind. Eng. Chem., Anal. Ed.*, **7**, 396 (1935).

(22) As the solutions warm up to room temperature, the excess hydrogen sulfide escapes from solution. The resultant gas bubbles probably play an important part in flocculating the molybdenum sulfide. See Henry Bassett, "Theory of Quantitative Analysis," New York, 1925, p. 102.

(23) P. H. Brinton and A. E. Stoppel, This Journal, **46**, 2454 (1924).

(24) W. Hartmann, *Z. anal. Chem.*, **67**, 152 (1926).

that the most concordant results were obtained when the sulfide was filtered through Gooch or porous bottom porcelain crucibles. Under these conditions the sulfide is deposited in a layer that is quite uniform in depth, and this promotes rapid conversion to the oxide. It was also noted that during the roasting process there was at times mechanical loss of oxide due to the sputtering of the burning sulfur. It is possible to avoid this loss and make the oxidation process quiescent by mixing the precipitate with a small amount of ashless filter paper fibers before conducting the filtration. In general, it takes fifteen to twenty minutes to convert 150 mg. of molybdic sulfide to the oxide. It was found by experiment that a sample of the oxide weighing 120 mg. could be heated for one hour at 550° without any detectable loss in weight. When the temperature was increased to 750°, 0.0036 g. was volatilized during a period of thirty minutes.

The results recorded in Table II show that the oxidation process is suitable for the quantitative determination of molybdenum. The sulfide was precipitated from solutions containing weighed samples of sodium molybdate, by the method previously described, using 100 cc. of the hydrogen sulfide reagent and 10 cc. of 24 *M* formic acid as the acidifying agent.

TABLE II

DETERMINATION OF MOLYBDENUM AS MoO_3

Grams of $Na_2MoO_4 \cdot 2H_2O$	Weight of molybdic oxide Recov.	Calcd.	Diff.
0.2547	0.1513	0.1515	−0.0002
.2030	.1203	.1208	− .0005
.1543	.0920	.0918	+ .0002
.1515	.0899	.0901	− .0002
.1208	.0721	.0719	+ .0002
.1021	.0605	.0608	− .0003

If facilities are lacking for igniting the sulfide by the described method, then it is preferable to determine the element by precipitating and weighing lead molybdate.[25] Solution of molybdenum sulfide can be effected by the action of nitric acid and bromine,[26] or a mixture of ammonium hydroxide and hydrogen peroxide.[27] These solvents oxidize the sulfide, producing appreciable amounts of sulfuric acid, so that it is necessary to separate the lead molybdate in the presence of ammonium acetate in order to prevent the precipitation of lead sulfate.[2] The recent work by McCay[28] shows that molybdates can be precipitated quantitatively by silver nitrate and the molybdenum determined by weighing the silver molybdate. The presence of sulfate ion does not interfere with this reaction and the method should prove useful under the present circumstances.

The Precipitation of Molybdenum Sulfide in the Presence of Tungsten

When a solution of sodium tungstate is treated with hydrogen sulfide and then acidified with dilute acid, no insoluble sulfide is formed. However, when molybdenum sulfide separates from a solution containing both metals it carries down with it part of the tungsten. The degree of contamination varies with the amount of molybdic sulfide formed, the concentration of tungsten in the solution and with the acidity of the medium. Koppel[29] claims that in the presence of formic acid the molybdenum sulfide separates free from tungsten; the writers have not been able to duplicate these results.

Table III is a compilation of analyses of sodium tungstate and molybdate in which the sulfide was separated from solutions containing different concentrations of formic acid. Experiments 2 and 3 correspond to the conditions recommended by Koppel for the separation of the two elements. The results obtained show that the molybdenum sulfide carries down with it large quantities of tungsten, the degree of contamination increasing with the acidity of the solution.

The next matter investigated was whether the results obtained in dilute formic acid media could be improved upon by decreasing the hydrogen-ion concentration of the solution by means of the buffer action of ammonium formate. Under these conditions it was found that a brown colored variety of molybdenum sulfide separated from the solution in a finely divided granular form. After digesting the mixture at 50–60° for one hour the brown sulfide darkens in color, and is then capable of being filtered and washed without encountering any difficulties.

The precipitation of molybdenum sulfide was studied in buffered systems over a range of *p*H from 5.0 to 3.0. As the *p*H increased, the sulfide precipitated in purer form, and it was found that tungsten did not co-precipitate when the *p*H of the solution exceeded 4.5. Under these conditions, however, the hydrogen-ion concentration of the solution is not sufficient to decompose all of the soluble sulfomolybdate, with the result that part of the molybdenum remains unprecipitated. The data obtained from these experiments are summarized in Table IV.

A further attempt was made to render the above processes quantitative by precipitating the molybdenum sulfide in two stages, the idea being to precipitate the bulk of the sulfide in a pure form at a *p*H of 5.0, and then to complete the precipitation by a secondary addition of formic acid. Since the quantity of tungsten that coprecipitates is proportionate to the amount of molybdenum sulfide formed, the mechanism suggested that only a negligibly small amount of the metal would be carried down during the formation of the residual molybdic sulfide upon further acidification.

The experimental data assembled in Table V were obtained by dissolving the weighed salts in 10 cc. of water, 10 cc. of 50% ammonium formate and 100 cc. of hydrogen sulfide water saturated at 0°. Precipitation was initiated in solutions 1–5 by the addition of 5 cc. of 2 *M* formic acid and digesting the mixtures at 60° for one hour. The decomposition of the sulfomolybdate was completed by the further addition of 10 cc. of 2 *M* formic acid. The treatment given to samples 6 and 7 differed from that received from the others only in that the dilute and concentrated formic acids were added at approximately the same time. Comparison of the results obtained in experiments 4 and 5 with those from 6 and 7 shows that though the two-stage decomposition of the ammonium sulfo-

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[25] T. M. Chatard, *Am. J. Sci.*, [3] **1**, 416 (1871).

[26] J. C. Evans, *Western Chemist and Metallurgist*, **3**, 218 (1907).

[27] C. A. Mitchell, "Recent Advances in Analytical Chemistry," Philadelphia, 1931, Vol. II, p. 287.

[28] LeRoy W. McCay, THIS JOURNAL, **56**, 2548 (1934).

[29] I. Koppel, *Chem.-Z.*, **48**, 801 (1924).

TABLE III

SEPARATION OF MOLYBDENUM SULFIDE FROM TUNGSTEN IN FORMIC ACID MEDIA

Expt. no.	Mol. of soln.	$Na_2MoO_4 \cdot 2H_2O$	$Na_2WO_4 \cdot 2H_2O$	Molybdic oxide			Tungstic oxide		
				Recov.	Calcd.	Diff.	Recov.	Calcd.	Diff.
1	0.27	0.1003	0.1000	0.0749	0.0597	+0.0152	0.0528	0.0703	−0.0175
2	1.1	.1008	.1003	.0778	.0600	+ .0178	.0543	.0705	− .0162
3	1.1	.1052	.1512	.0839	.0626	+ .0213	.0873	.1063	− .0190
4	1.8	.1054	.1004	.1107	.0627	+ .0480	.0253	.0706	− .0453
5	1.8	.0533	.3014	.0928	.0317	+ .0611	.1495	.2119	− .0624

TABLE IV

SEPARATION OF MOLYBDENUM SULFIDE FROM TUNGSTEN IN BUFFERED MEDIA

System A: 25 cc. of 50% $HCOONH_4$, 100 cc. H_2S and 10 cc. of 2 *M* formic acid.
System B: 10 cc. of 50% $HCOONH_4$, 100 cc. H_2S and 10 cc. of 2 *M* formic acid.
System C: 5 cc. of 50% $HCOONH_4$, 100 cc. H_2S and 10 cc. of 2 *M* formic acid.
System D: 5 cc. of 50% $HCOONH_4$, 100 cc. H_2S and 25 cc. of 2 *M* formic acid.

System	*p*H[30]	$Na_2MoO_4 \cdot 2H_2O$	$Na_2WO_4 \cdot 2H_2O$	Molybdic oxide			
				Recov.	Calcd.	Diff.	Color
A	5.0	0.2032	....	0.1087	0.1209	−0.0122	White
		.3006	0.3020	.1677	.1789	− .0112	White
B	4.5	.0524	....	.0272	.0312	− .0040	White
		.2029	.2040	.1272	.1207	+ .0065	Faint yellow
		.2011	.2027	.1283	.1197	+ .0086	Faint yellow
C	3.9	.2030	....	.1203	.1208	− .0005	White
		.2008	.2022	.1324	.1195	+ .0129	Yellow
		.1990	.1034	.1279	.1184	+ .0095	Yellow
		.1012	.1030	.0621	.0602	+ .0019	Faint yellow
D	3.5	.2484	....	.1475	.1478	− .0003	White
		.2488	.3017	.1662	.1480	+ .0182	Yellow

TABLE V

TWO-STAGE SEPARATION OF MOLYBDENUM SULFIDE

Expt.	$Na_2MoO_4 \cdot 4H_2O$	$Na_2WO_4 \cdot 2H_2O$	Molybdic oxide		
			Recov.	Calcd.	Diff.
1	0.1592	....	0.0947	0.0947	0.0000
2	.0558	....	.0330	.0332	− .0002
3	.1252	.3086	.0906	.0745	+ .0161
4	.1700	.4000	.1198	.1012	+ .0186
5	.1694	.4000	.1193	.1008	+ .0185
6	.1710	.4000	.1376	.1017	+ .0359
7	.1703	.4000	.1398	.1013	+ .0385

molybdate produces a less contaminated sulfide than that precipitated from a solution whose *p*H is adjusted to 3.0 from the very beginning of the reaction, the mechanism is not able to produce a quantitative separation of the two elements.

Since molybdenum sulfide can be precipitated free from tungsten in solutions containing tartaric acid,[31] experiments were made to determine whether the amount of tartaric acid required for the quantitative separation of the two metals could be diminished by conducting the reaction in solutions buffered by ammonium formate.

Weighed samples of sodium molybdate, of approximately the same mass, were dissolved in 10 cc. of a standardized solution of sodium tungstate containing 4 g. of $Na_2WO_4 \cdot 2H_2O$ per 100 cc. To these solutions were added varying volumes of 50% tartaric acid and 50% ammonium formate, 100 cc. of hydrogen sulfide reagent and 10 cc. of 24 *M* formic acid. The mixtures were kept at 60° for ninety minutes, a small quantity of filter paper pulp was added, the precipitates were permitted to settle, and then filtered through porous bottom porcelain crucibles. The sulfides were washed with five 10-cc. portions of a solution consisting of 5 cc. of 50% ammonium formate, 5 cc. of 24 *M* formic acid and 100 cc. of water; then ignited to oxides at 550° and weighed. The difference between the weights of the recovered oxides and the theoretical weight of molybdic oxide equivalent to the sodium molybdate put into the solution is a measure of the amount of tungstic oxide carried down by the molybdenum sulfide. The degree of co-precipitation can also be judged from the color of the resultant oxide. Pure molybdic oxide is white, and when it is contaminated, it is colored yellow by the tungstic oxide. The yellow coloration becomes quite pronounced when the impure oxide contains more than 4% of tungsten.

The results obtained from these experiments, recorded graphically in Fig. 2 show that in the absence of ammonium formate the molybdenum sulfide carries down with it appreciable amounts of tungsten even though the solution contains a high concentration of tartaric acid. The sulfide that separates under these conditions is black and non-crystalline, and filters and washes with great difficulty. Hence, part of the error observed in experiments 1–8 may be due to the presence of sulfotungstate in the incompletely washed precipitate, as is also indicated by the erratic disposition of the points in curve A of Fig. 2. In solutions buffered with ammonium formate, the tartaric acid is more effective in producing a complete separation

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[30] The *p*H values of the solutions were estimated by the use of suitable indicators and standard buffer mixtures. Because of the bleaching action of the hydrogen sulfide, the measurements had to be made on independent systems in which an equal volume of water was substituted for the 100 cc. of the hydrogen sulfide reagent.

[31] Heinrich Rose, "Ausführliches Handbuch der analytischen Chemie," Vol. I, Part 2 (1851), pp. 356–357.

of the molybdenum sulfide from the tungsten, as can be seen by comparing the curves in Fig. 2.

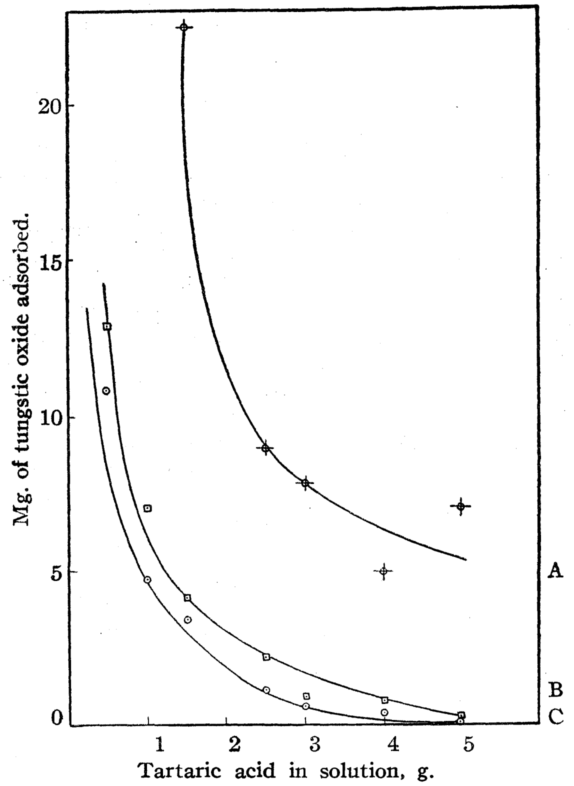

Fig. 2.—Contamination of MoS_3 by tungsten: ⊕, ammonium formate absent; ⊡, 2.5 g. of ammonium formate; ⊙, 5.0 g. of ammonium formate.

On the basis of the evidence presented in Table V and Fig. 2 the following procedure was developed for the separation and determination of molybdenum in the presence of tungsten.

Procedure A.—Dissolve the two salts in 10–15 cc. of water in a 250-cc. Erlenmeyer flask, add 10 cc. of 50% ammonium formate, 10 cc. of 30% tartaric acid, 100 cc. of hydrogen sulfide water saturated at 0° and 10 cc. of 2 *M* formic acid.[32] Heat the mixture on a water-bath to 60° and maintain the temperature for one hour. At the end of the digestion, add a small quantity of filter paper pulp, suspended in about 10 cc. of water, and complete the precipitation of the molybdenum sulfide by adding 10 cc. of 24 *M* formic acid. Keep the mixture in the water-bath for a period of thirty minutes, allow the precipitate to settle, and filter through a porous bottom or a Gooch crucible which has been heated to about 500°. Wash the precipitate with five 10-cc. portions of a solution made by diluting 5 cc. of 50% ammonium formate and 5 cc. of 24 *M* formic acid with 100 cc. of water. Ignite the precipitate in the oven described in Fig. 1 for twenty to thirty minutes until conversion to the oxide is complete; cool and weigh. Reheat the crucible over fifteen-minute intervals until it attains constant weight. Usually the conversion is complete at the end of the first ignition.

TABLE VI

SEPARATION OF MoS_3 FROM TUNGSTEN

Expt.	$Na_2MoO_4 \cdot 2H_2O$	$Na_2WO_4 \cdot 2H_2O$	White molybdic oxide Recov.	Calcd.	Diff.
1	0.0513	....	0.0304	0.0305	−0.0001
2	.0516	0.0516	.0300	.0307	− .0007
3	.0509	.5013	.0298	.0303	− .0005
4	.0524	.5031	.0303	.0312	− .0009
5	.1698	....	.1013	.1010	+ .0003
6	.1704	.2026	.1012	.1014	− .0002

The results obtained following this procedure are recorded in Table VI. The small differences between the calculated and the observed values, together with the white color of the oxides, indicates that a fairly sharp separation of the two elements has been effected.

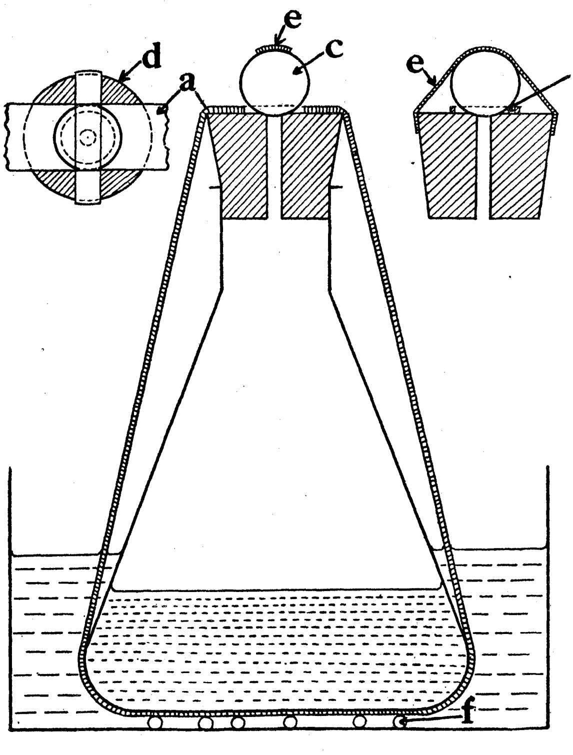

Fig. 3.—Safety pressure flask: a, large endless rubber band 1.4 mm. thick, 1.6 mm. wide and 25 cm. peripheral length at rest; b, 1.3 cm. diam. hole in rubber band; c, 1.6 cm. diam. sphere of glass or "marble"; d, semi-hard rubber stopper with 3-mm. hole in center; e, rubber band 6.4 mm. wide and 0.8 mm. thick; f, glass beads.

During the progress of this work recourse was made to the precipitation of molybdenum sulfide in pressure bottles. Difficulty was encountered in transferring the precipitate quantitatively from the pressure bottle of usual design owing to its narrow mouth and the dangling of the capping device when pouring the contents. Efforts were therefore made to convert Erlenmeyer flasks into pressure

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[32] At this point the solution has a *p*H of 3.9; after the addition of the concentrated formic acid the *p*H drops to 2.9. Crystals of ammonium hydrogen tartrate may separate on the addition of the cold hydrogen sulfide solution, but these redissolve during the subsequent warming of the mixture.

bottles by closing the neck with a rubber stopper, the latter being kept in place by stretching rubber bands around it and the base of the flask. On warming the hydrogen sulfide mixture to 60°, the pressure developed by the liberated gases usually popped the stopper and on two occasions broke the bottom out of the flask.

To prevent such accidents, the safety pressure flask illustrated in Fig. 3 was designed. When the pressure inside the flask becomes sufficiently high, the sphere covering the opening in the stopper loosens and permits some of the gas to escape until the restoring force of the rubber band that keeps it in position is sufficient to balance the internal pressure. The equilibrium pressure varies with the tension in the band supporting the sphere. By closing a suction flask with these valves, maximum pressures above atmospheric of 46–80 cm. of mercury were recorded on a manometer attached to the side-arm.

The construction of the stoppering device is apparent from the figure. The accessory rubber bands are secured to the stopper by means of rubber cement. The band holding the sphere in place is best made by cutting the necessary length from a piece of 6-mm. rubber tubing. The semi-circular cross section of the tubing hugs the surface of the sphere and prevents side slippage.

TABLE VII

PRECIPITATION OF MOLYBDIC SULFIDE UNDER PRESSURE

Pressure, atm.	$Na_2MoO_4\cdot 2H_2O$	$Na_2WO_4\cdot 2H_2O$	White molybdic oxide		
			Recov.	Calcd.	Diff.
1.0	0.1693	....	0.1007	0.1007	0.0000
1.5[33]	.1709	....	.1017	.1017	.0000
1.0	.0534	....	.0314	.0318	− .0004
1.5	.0498	....	.0295	.0296	− .0001
1.0	.0498	....	.0290	.0296	− .0006
1.5	.0498	....	.0295	.0296	− .0001
1.0	.0523	0.5019	.0308	.0311	− .0003
1.5	.0501	.5022	.0296	.0298	− .0002

The results obtained by conducting the precipitation of the molybdenum sulfide in the safety pressure flasks, recorded in Table VII, show that the negative errors in the determination of molybdenum are slightly decreased. In general, little advantage is gained by conducting the precipitation under pressure. The use of the pressure flasks is recommended when the sample of tungsten contains only small amounts of molybdenum, or in the absence of adequate ventilation, to minimize the odor of the gas in the laboratory during the long digestion period.

The Determination of Tungsten

The filtrate and washings resulting from the separation of the molybdenum sulfide contains the tungsten in solution combined as a tartaro complex, together with the excess hydrogen sulfide, ammonium formate and formic acid. Evaporating the solution down to near dryness effects the removal of the hydrogen sulfide, formic acid and part of the ammonium formate. Treatment of the residue with 12 *M* hydrochloric acid and cinchonine precipitates after prolonged boiling the greater part of the tungstic acid in the form of a hard crystalline mass that adheres tenaciously to the surface of the beaker. The yield is not quantitative, as shown by the figures below.

$Na_2WO_4\cdot 2H_2O$	Tungstic oxide		
	Recov.	Calcd.	Diff.
0.2033	0.1385	0.1429	−0.0044
.1013	.0488	.0712	− .0224

Procedure B.—Treatment of the concentrated filtrate with 25 cc. of 16 *M* nitric acid produces a much better recovery of the tungsten. The acid facilitates the completion of the reaction by the removal of the ammonium salts, the presence of which retards the precipitation of tungstic acid,[2] (pp. 119 and 552), and also in that the simultaneous evolution of gases during the decomposition prevents the precipitate from adhering to the walls of the vessel. When the removal of the ammonium salts is completed the mixture is diluted with 100 cc. of water and 5 cc. of cinchonine reagent,[34] digested on a hot-plate for two hours and then filtered through an ashless filter paper. The precipitate is washed, ignited at 750° and the tungstic oxide weighed. The results obtained by following this procedure are not strictly quantitative except when only a small quantity of tartaric acid is present. For a given amount of tartaric acid the amount of tungsten remaining unprecipitated is remarkably constant, and by applying the necessary correction factor, the method is recommended for rapid routine analyses.

TABLE VIII

SEPARATION OF TUNGSTEN IN THE PRESENCE OF TARTARIC ACID USING 16 *M* NITRIC ACID

Tart. acid, g.	$Na_2WO_4\cdot 2H_2O$[34]	Tungstic oxide		
		Recov.	Calcd.	Diff.
3.0	0.5046	0.3489	0.3547	−0.0058
3.0	.2081	.1406	.1463	− .0057
3.0	.2026	.1366	.1424	− .0058
3.0	.2004	.1352	.1409	− .0057
3.0	.1032	.0668	.0726	− .0058
3.0	.0559	.0334	.0393	− .0059
1.0	.2033	.1418	.1429	− .0011
1.0	.2014	.1403	.1416	− .0013
0.52	.2137	.1497	.1502	− .0005
.51	.2031	.1425	.1428	− .0003
...	.2020	.1417	.1420	− .0003

The precise determination of tungsten in the filtrate resulting from the separation of the molybdenum sulfide

TABLE IX

SOLUBILITY OF AMMONIUM HYDROGEN TARTRATE AT 29°

Ratio water: alcohol	95% alcohol by volume	$NH_4HC_4H_4O_6$ per cc. of solution, g.	Equiv. tart. acid, g. per cc.
1:0	...	0.0343	0.0308
1:1	50.0	.0048	.0043
1:2	66.7	.0018	.0016
0:1	100.0	.00005	.000045

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[33] This pressure is small compared with the total pressure obtainable by heating the mixture in a standard pressure flask at 100°. The partial pressure of the hydrogen sulfide, however, is probably comparable in both cases.

[34] The samples were dissolved in 100 cc. of water, to which was added the weighed quantities of tartaric acid, 10 cc. of 50% ammonium formate and 10 cc. of 24 *M* formic acid. These solutions were evaporated to 15 cc., and when cool, 25 cc. of 16 *M* nitric acid was added. The precipitate was then further treated as described in procedure B.

TABLE X

SEPARATION AND DETERMINATION OF TUNGSTEN AND MOLYBDENUM

$Na_2MoO_4·2H_2O$	$Na_2WO_4·2H_2O$	Molybdic oxide Recov.	Molybdic oxide Calcd.	Molybdic oxide Diff.	Tungstic oxide Recov.	Tungstic oxide Calcd.	Tungstic oxide Diff.
0.1703	....	0.1010	0.1013	−0.0003	0.0004	0.0000	+0.0004
....	0.5018	.0002	.0000	+ .0002	.3522	.3528	− .0006
.1725	.1718	.1031	.1026	+ .0005	.1210	.1207	+ .0003
.0539	.0531	.0320	.0321	− .0001	.0365	.0373	− .0008
.0505	.3020	.0300	.0301	− .0001	.2118	.2123	− .0005

necessitates the removal of the greater part of the tartaric acid contained in it. Treatment with oxidizing acids is not recommended, as the process requires many repetitions in order to complete the destruction of the organic matter, and is subject to loss of material due to spattering.

During the later stages of the evaporation of the filtrate, ammonium hydrogen tartrate crystallizes from the solution. The greater part of the organic matter can be removed by taking advantage of the small solubility of this salt in mixtures of alcohol and water.

The solubility of ammonium hydrogen tartrate in water–alcohol systems was approximated by evaporating measured volumes of the saturated solutions and weighing the dry residues. From the solubility data in Table IX it can be seen that by evaporating the filtrate down to a volume of about 25 cc. and adding 50 cc. of alcohol to the concentrate, only about 120 mg. of tartaric acid will remain in solution. This small amount of tartrate no longer interferes with the quantitative separation of tungstic acid, as is demonstrated by the preceding experiments in Table VIII. After being washed with 50% alcohol, the crystals still occlude small quantities of tungsten. This is readily recovered by charring the filter paper containing the ammonium hydrogen tartrate in a platinum crucible containing about 500 mg. of sodium carbonate[2] (p. 61), extracting the residue with water, filtering off any carbonaceous matter, and adding the filtrate to the solution containing the bulk of the tungsten. The resultant solution is evaporated to a small volume to effect the removal of the alcohol, and the tungstic acid is precipitated by the addition of 25 cc. of 16 *M* nitric acid. From this point the precipitate is treated as described in procedure B.

In the table above are recorded the results of several analyses of mixtures of sodium tungstate and molybdate, arrived at by following procedure A for the separation of the sulfides in the presence of ammonium formate, tartaric and formic acids. The close agreement between the recovered and theoretical weights of the oxides shows that the method is satisfactory for the separation of the two metals in the absence of interfering elements. The application of these methods to the analysis of steels and minerals containing tungsten and molybdenum is in the process of investigation.

Acknowledgment.—The writer wishes to express his gratitude to the J. T. Baker Chemical Company whose grant of the 1935–36 Eastern Research Fellowship made these studies possible.

Summary

A new technique is described for precipitating metallic sulfides, using a saturated solution of hydrogen sulfide in water at 0° as the reagent. Molybdenum sulfide can be precipitated quantitatively in formic acid media by initiating the reaction at a low temperature and maintaining a high concentration of hydrogen sulfide in the solution. A quantitative separation of the sulfide in the presence of tungsten can be effected in a solution whose *p*H is adjusted to 2.9 by a buffer mixture consisting of ammonium formate, tartaric and formic acids. The article contains descriptions of a simple electric furnace for igniting precipitates at a constant temperature, and of an improved pressure bottle.

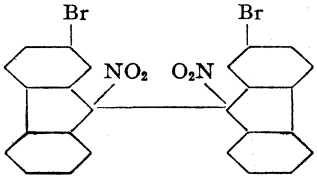
NEW YORK, N. Y. RECEIVED JUNE 10, 1936

NOTES

2-Bromo-9-Nitrofluorene and 1,1-Dinitro-3,3'-dibromo-bifluorenyl

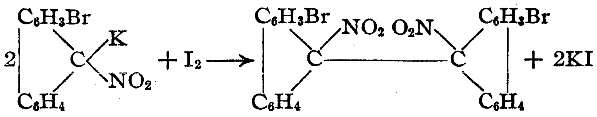
By C. Dale[1] and R. L. Shriner

Recently a compound melting at 170° was described as being 2-bromo-9-nitrofluorene.[2] It is very unusual for a normal nitro compound to melt higher than its aci-form (m. p. 132°). Moreover, the compound decomposes on heating and liberates oxides of nitrogen and forms 2-bromofluorenone. The alkali insolubility of the compound and failure to form a salt of the aci-form, even with potassium methoxide, indicate that it is probably the bimolecular oxidation product with the structure (I) analogous to the product obtained by Nenitzescu[3] in his study of aci-9-nitrofluorene.



I

A reëxamination of this compound has shown that it may be obtained in small amounts by boiling an alcoholic solution of the aci-form, or in good yields by treating the potassium salt of 2-bromo-9-nitrofluorene with one mole of iodine. The product of this reaction is a yellow powder which shrinks and decomposes over a considerable range of temperature (130–140°). By careful fractionation from methyl acetate, colorless crystals of the compound were obtained. They melted at 172.5° (175° corr.).


$$2\,(C_6H_3Br)(C_6H_4)C(K)NO_2 + I_2 \longrightarrow (C_6H_3Br)(C_6H_4)C(NO_2)-C(NO_2)(C_6H_3Br)(C_6H_4) + 2KI$$

The analyses for bromine and nitrogen previously given[2] are correct, but, of course, would check very closely the theoretical values for either the monomolecular or bimolecular structure. A combustion gave the following results: Calcd. for $C_{13}H_8O_2NBr$: C, 53.81; H, 2.76. Calcd. for $C_{26}H_{14}O_4N_2Br_2$: C, 54.00; H, 2.42. Found: C, 54.04; H, 2.51.

The molecular weight was determined by the micro boiling point method, using acetone and benzene as solvents. In acetone a molecular weight of 593 was obtained, and in benzene a value of 554 resulted. The calculated value for I, $C_{26}H_{14}O_4N_2Br_2$, is 578, whereas the molecular weight of $C_{13}H_8BrNO_2$ is 290. It is evident that the compound is the bimolecular oxidation product with the structure I.

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Received May 14, 1936

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[1] University of Rochester, Rochester, New York.

[2] Thurston and Shriner, This Journal, **57**, 2163 (1935).

[3] Nenitzescu, *Ber.*, **62**, 2669 (1929); **63**, 2484 (1930).

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p-Phenylphenacyl Esters of Organic Acids

By T. Leonard Kelly and Eugene A. Morisani

During the course of a research the following *p*-phenylphenacyl esters were prepared which do not appear in the literature. Since the melting points of these may be an aid in the identification of acids they are of value.

They were prepared according to the method of Drake and co-workers[1] and were recrystallized to constant melting point. All melting points are

p-Phenylphenacyl Esters

Acid	M. p., °C.		Halogen, % Calcd.	Found
m-Bromobenzoic	155[a]		20.25	20.13
p-Bromobenzoic	160		20.25	20.16
o-Chlorobenzoic	123		10.12	10.09
m-Chlorobenzoic	154[b]		10.12	10.18
p-Chlorobenzoic	160		10.12	10.19
o-Iodobenzoic	143		28.74	28.38
m-Iodobenzoic	147		28.74	29.21
p-Iodobenzoic	171 (Closed tube)		28.74	28.20
			Nitrogen, %	
o-Nitrobenzoic	140		3.87	3.70
m-Nitrobenzoic	153		3.87	3.95
o-Nitrocinnamic	146		3.61	3.72
m-Nitrocinnamic	193[c]		3.61	3.66
p-Nitrocinnamic	192		3.61	3.94
p-Cyanobenzoic	165		4.10	4.26
Diphenylacetic	111	C,	82.75	82.98
		H,	5.41	5.66

[a] Mixed m. p. with *m*-bromobenzoic acid 127–128°.
[b] Mixed m. p. with *m*-chlorobenzoic acid 130–132°.
[c] Mixed m. p. with *m*-nitrocinnamic acid 180–183°.

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[1] Drake and co-workers, This Journal, **52**, 3715 (1930); *ibid.*, **54**, 2059 (1932).

uncorrected but were taken in a Fisher melting point apparatus with a set of Anschütz thermometers which gave correct melting points with various pure reagents.

DEPARTMENT OF CHEMISTRY
HOLY CROSS COLLEGE
WORCESTER, MASSACHUSETTS

RECEIVED JUNE 1, 1936

COMMUNICATIONS TO THE EDITOR

SYNTHETIC SUBSTRATES FOR PROTEIN-DIGESTING ENZYMES

Sir:

Knowledge regarding the specificity of those enzymes which hydrolyze intact proteins (peptic, tryptic and catheptic proteinases) is meager. In general it is assumed that these enzymes react exclusively on high molecular substrates.

Recently it has been possible to study the specificity of proteinases with the aid of synthetic substrates. Such substrates have been found in this Laboratory for the catheptic enzymes, papain, liver-cathepsin and bromelin. The authors have now observed the splitting of α-hippuryl-lysine-amide by tryptic proteinase.

α-Hippuryl-ε-carbobenzoxy-lysine methyl ester was converted into α-hippuryl-ε-carbobenzoxy-lysine amide, m. p. 212°, with the aid of methanolic ammonia. *Anal.* Calcd. for $C_{23}H_{28}N_4O_5$: C, 62.7; H, 6.4; N, 12.7. Found: C, 62.6; H, 6.7; N, 12.8. This amide was hydrogenated catalytically, yielding α-hippuryl-lysine-amide which was isolated as the strongly hygroscopic hydrochloride, m. p. 248°. *Anal.* Calcd. for $C_{15}H_{23}N_4O_3Cl$: C, 52.5; H, 6.8; N, 16.3. Found: C, 52.0; H, 7.0; N, 15.9.

The tryptic proteinase was prepared according to E. Waldschmidt-Leitz and A. Purr [*Ber.*, **62**, 2217 (1929)]. The preparation contained no dipeptidase, aminopeptidase, and no carboxypeptidase; however, protaminase probably was present (Table I).

TABLE I

ENZYMIC HYDROLYSIS OF α-HIPPURYL-LYSINE-AMIDE AT 40°

(Titration of liberated carboxyl groups)

Enzyme	Time, hrs.	Hydrolysis in % of one peptide bond
Tryptic proteinase, *p*H 8.8	22	123
	72	200
Tryptic proteinase, *p*H 8.8	18	121
	42	175
HCN-Papain, *p*H 5.0	5	58
	24	80
	49	85

In contrast to HCN-papain, which splits only one peptide bond, tryptic proteinase splits two. After a complete splitting, hippuric acid was isolated from the digest (over 70% of the theoretical amount). Therefore, the splitting also must have liberated lysine and ammonia. That the free ε-amino group is an essential condition for the enzymic hydrolysis is shown by the fact that the above mentioned α-hippuryl-ε-carbobenzoxy-lysine amide is not hydrolyzed under the conditions of our experiments. The hydrolysis of our substrate by tryptic proteinase is remarkable since tryptic proteinase is supposed to react exclusively on anionic substrates.

It is intended to continue this research by studying the action of pure tryptic proteinases.

THE LABORATORIES OF
THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N. Y.

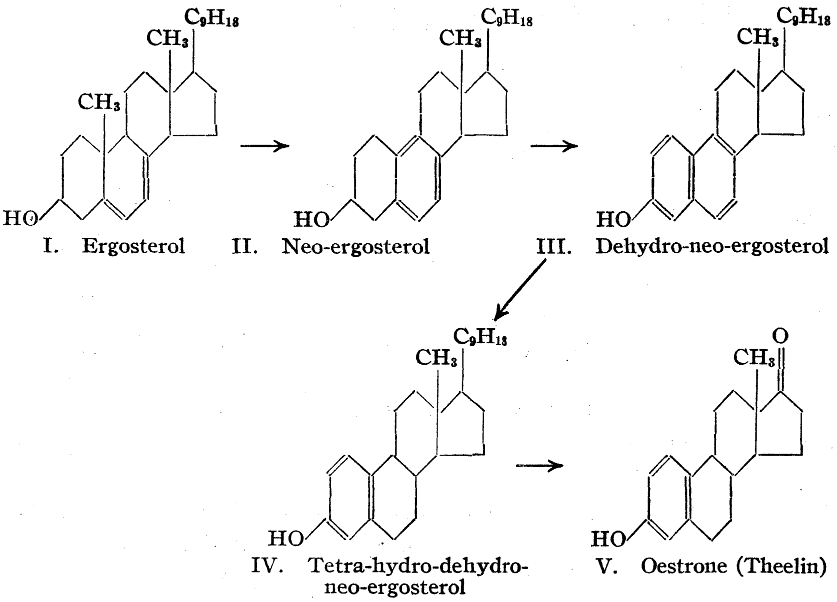
MAX BERGMANN
WILLIAM F. ROSS

RECEIVED JULY 10, 1936

STEROLS. VI. SYNTHETIC PREPARATION OF OESTRONE (THEELIN)

Sir:

The evidence for the accepted structure of oestrone has recently been reviewed [L. F. Fieser, "Chemistry of Natural Products Related to Phenanthrene," A. C. S. Monograph Series, No. 70]. We have been able to prepare a well crystallized compound from ergosterol which by analysis, derivatives and mixed melting points, is identical with oestrone isolated from pregnancy urine. It has been previously shown that ergosterol may be converted into 3-hydroxy-nor-allo-cholanic acid [Chuang, *Ann.*, **500**, 270 (1933); Fernholz and Chakravarty, *Ber.*, **67,** 2021 (1934)] which is also obtainable from dihydro-cholesterol. This acid can give rise to isoandrosterone which differs from androsterone only in configuration of the hydroxyl group in the 3-position. Therefore, with the preparation of oestrone from ergosterol, a complete connection between the hormones, male and female, has been established.



I. Ergosterol II. Neo-ergosterol III. Dehydro-neo-ergosterol

IV. Tetra-hydro-dehydro-neo-ergosterol V. Oestrone (Theelin)

In the present work, dehydro-neo-ergosterol, III, was prepared from ergosterol by the method of Windaus [Windaus and Borgeaud, *Ann.*, **520,** 235, 460 (1928)], Inhoffen [Inhoffen, *ibid.*, **497,** 130 (1932)], and Honigmann [Honigmann, *ibid.*, **511,** 292 (1934)]. Taking advantage of the fact that naphthalene derivatives may be reduced to tetrahydro derivatives with sodium and amyl alcohol, dehydro-neo-ergosterol, III, m. p. 147–150°, was reduced to give tetrahydro-dehydro-neo-ergosterol, IV, m. p. 170.5–171.5°. This substance is phenolic and forms sodium salts.

Anal. Calcd. for $C_{27}H_{41}O$: C, 85.1; H, 10.8. Found: C, 85.7; H, 10.8.

The tetrahydro-dehydro-neo-ergosterol was then acetylated and this product oxidized with chromic acid. The total neutral oxidation product was hydrolyzed with alcoholic sodium hydroxide and then treated with semicarbazide acetate. The crude semicarbazone was hydrolyzed with alcoholic sulfuric acid to the free ketone, which was then distilled at 200° under high vacuum. The sublimate was crystallized from 95% alcohol to give a white crystalline compound m. p. 259–261.5° (uncorr.). This gave no depression in melting point with a sample of natural oestrone of m. p. 255°. It is soluble in alkali. It gave a rotation of $[\alpha]^{32}_D$ +159° in alcohol, c = 514 mg. per 100 cc.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.9; H, 8.3. Found: C, 79.4; H, 8.4.

The product gave a benzoate by the Schotten–Baumann reaction, m. p. 205–207° (uncorr.), which gave no depression to a sample of natural oestrone benzoate m. p. 205° (uncorr.).

Anal. Calcd. for $C_{25}H_{26}O_3$: C, 80.2; H, 7.0. Found: C, 80.6; H, 7.2.

It gave a semicarbazone of m. p. 252–253° (uncorr.). From the analysis this semicarbazone calculates to have one-half molecule of water of crystallization. Butenandt [*Z. physiol. Chem.*, **208,** 129 (1932); **208,** 149 (1932)] observed the same thing on the preparation of the semicarbazone from natural oestrone.

Anal. Calcd. for $(C_{19}H_{25}O_2N_3)_2 \cdot H_2O$: C, 67.9; H, 7.9. Found: C, 68.1; H, 8.2.

This synthesis was repeated independently by two of us. We wish to thank Dr. George H. Fleming of this Laboratory for the micro-analyses reported in this paper.

SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PA.
THE PARKE, DAVIS & CO. RESEARCH LABORATORIES
DETROIT, MICH.

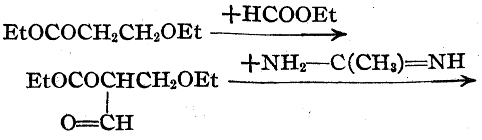
RUSSELL E. MARKER
OLIVER KAMM
THOMAS S. OAKWOOD
JOSEPH F. LAUCIUS

RECEIVED JULY 20, 1936

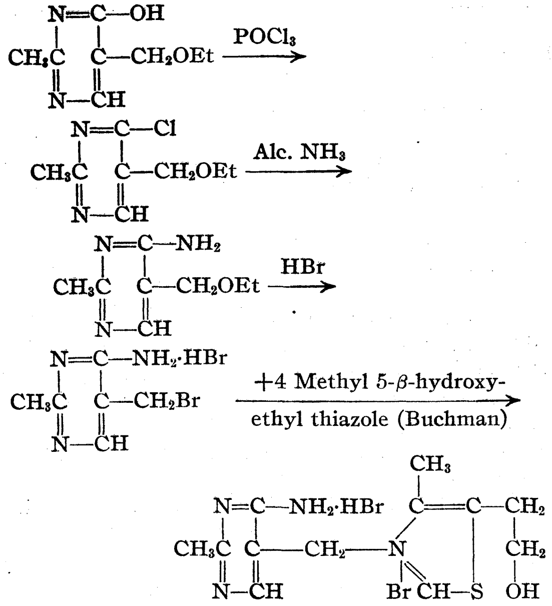
SYNTHESIS OF VITAMIN B_1

Sir:

As foreshadowed in a recent communication [THIS JOURNAL, **58,** 1063 (1936)] we have effected a synthesis of the vitamin by the following route.



$$EtOCOCH_2CH_2OEt \xrightarrow{+HCOOEt} \underset{\displaystyle O{=}CH}{EtOCO\underset{|}{C}HCH_2OEt} \xrightarrow{+NH_2{-}C(CH_3){=}NH}$$



The resulting bromide agreed in molecular absorption with the natural vitamin and when air dried analyzed for the composition $C_{12}H_{17}N_4SOBr \cdot HBr \cdot {}^1/_2H_2O$. The curative dose for polyneuritic rats is $6\ \gamma \pm 1\ \gamma$.

Converted into the chloride, it was found identical with the natural in composition (5 elements) ultraviolet absorption and antineuritic potency (5 γ). Comparing melting points led us to observe two crystal forms in varying proportions in the natural chloride and especially in the picrolonate; the synthetic chloride and picrolonate respectively correspond in appearance to one of these forms. The synthetic chloride melts at 232–234°; our present specimen of natural at 246°; mixed melting point is 242–244°. Kinnersley, O'Brien and Peters have called attention to a variably low melting antineuritic chloride [*Biochem. J.*, **27,** 232 (1933)] and it seems probable that the natural as isolated is often a mixture of two stereoisomers [*cis-trans* on 5 C of pyrimidine? Nishikawa, *T. Mem. Ryojun Coll. Eng.*, **3,** 277 (1931)] of equal potency and that in our synthetic material the low form predominates in higher degree.

The details of structural evidence and of the method of synthesis will appear in forthcoming papers.

In making this announcement the writers wish to express their indebtedness to all those who have participated in the work and whose names have appeared in the authorship of the current series of papers "Studies of Crystalline Vitamin B_1." Mention should also be made of Mr. Jacob Finkelstein, who has performed many syntheses of both known and new compounds.

The senior author is grateful to Dr. E. R. Buchman, who continued to participate in the work when financial support was lacking during the greater part of 1935 and to Mr. R. E. Waterman who joined the writer in meeting this emergency. Through the kindness of Dr. Walter H. Eddy, laboratory space was provided at Teachers College during this as well as earlier phases of the undertaking. More recently funds and facilities have been provided by Merck & Co., Inc., under the auspices of the Research Corporation of New York. Grateful acknowledgment is made to Dr. Eddy and to both of these corporations.

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY
TEACHERS COLLEGE, COLUMBIA UNIVERSITY
NEW YORK, AND
RESEARCH LABORATORY R. R. WILLIAMS
MERCK & CO., INC. J. K. CLINE
RAHWAY, N. J.

RECEIVED JULY 23, 1936

NEW BOOKS

Physical Chemistry for Colleges. A Course of Instruction Based upon the Fundamental Laws of Chemistry. By E. B. MILLARD, Professor of Physical Chemistry, Massachusetts Institute of Technology. Fourth edition. McGraw-Hill Book Company, Inc., 330 West 42d Street, New York, N. Y., 1936. ix + 524 pp. 73 figs. 14.5 × 21 cm. Price, $3.75.

The present edition of this well-known text is a revision of the third edition with the size and character remaining virtually unchanged. The revision has involved greater clarity of presentation of certain topics, substitution of new concepts for older ones, and substitution of many new problems for old problems. Portions of four or five of the chapters have been partially rewritten, notably the chapters on equilibrium, kinetics of reaction and atomic structure. The chapter on "Physical Properties and Molecular Structure" has been omitted and a new chapter on "Free Energy of Chemical Changes" has been added. The changes which have been made, while not extensive, serve to maintain the up-to-date character of this meritorious book.

F. E. BARTELL

Textbook of Quantitative Inorganic Analysis. By I. M. KOLTHOFF and E. B. SANDELL, University of Minnesota. The Macmillan Company, 60 Fifth Avenue, New York, N. Y., 1936. 749 pp.

It requires only a cursory examination of this book to dispel the feeling of satiety with which one is apt to greet the appearance of a new textbook of analytical chemistry. The reader soon realizes that this text enters a new field and satisfies a need which is not met by other English books. To the advanced student of quantitative analysis the book offers a thorough treatment of the fundamental principles upon which the subject rests, a comprehensive discussion of the apparatus, reagents and practical technique employed in analysis and a valuable key to the literature of analytical chemistry. It should prove invaluable in the training of analytical chemists as contrasted with chemical analysts.

Sections of the book are devoted to gravimetric analysis, volumetric analysis, physico-chemical methods, and analyses of complex materials. In the first two of these sections theoretical parts precede parts given over to practical details and specific directions. The outstanding characteristic of this book is the thoroughness with which the theoretical fundamentals of the subject are treated. The authors justify their remark, "The theory of analytical chemistry does not constitute a special branch of chemistry; rather it comprises the application of our entire scientific knowledge to the particular purpose." The phenomena of precipitation and coprecipitation are given particularly extensive treatment.

In the practical and specific parts the same logical completeness is maintained. Thus nine pages of small print are devoted to the precipitation of barium sulfate. There is no falling away into the cookbook style sometimes found in elementary texts. Particularly pleasing are the ample references given to the original literature. These as well as the methods treated in the text are thoroughly up-to-date.

In the third section upon physico-chemical methods a wide variety of general methods are briefly explained. Colorimetry is treated in some detail. Here again the student is given an excellent start in the literature. In the final section upon the analyses of complex materials, directions are given for the analyses of brass, steel and silicate rocks.

The book is set in three sizes of type to facilitate its use in elementary courses, material of a more advanced nature being in small type. Problems with answers are given at the end of the chapters. It is a book to be recommended for serious students.

CHARLES H. GREENE

Der Aufbau der Zweistofflegierungen. Eine kritische Zusammenfassung. (The Constitution of Binary Alloy Systems. A Critical Compilation.) By M. HANSEN. Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1936. xv + 1100 pp. 456 figs. Price, RM. 87.

This book adequately fills a long felt need in metallurgical research. The available data for each binary system are critically discussed and where possible a probable equilibrium diagram is chosen. An exhaustive bibliography follows each discussion, including most 1935 and even some 1936 references. In all, 828 systems are treated, although a few of these receive very brief notice indeed. The longest is the 18-page discussion and 3-page bibliography devoted to the copper–zinc system.

The only comparable work is the set of diagrams in the "International Critical Tables." But these deal with only 200 odd systems and omit discussion. Since there are points of doubt about nearly all the diagrams, discussion is a necessity.

Practically all the important facts one could glean from an extensive survey of the literature seem to be listed under each alloy system. The discussions might be improved by adopting a standardized order of presentation. Suitable subheadings such as liquidus, solidus, miscibility, intermediate phases, etc., might well be common to all systems extensively discussed.

Since experimental data on solid transformations are often meager, contradictory, or subject to varying interpretations, it is not to be expected that the author's chosen equilibrium diagrams will be final or complete. But no general criticism can be made of his selections.

Naturally it is possible to criticize details. For example, the equilibrium diagrams of cobalt do not show the high temperature transformation to hexagonal cobalt discovered in 1930 by Hendricks, Jefferson and Shultz and since abundantly verified. In the Fe-Ni system the author states that it is impossible to detect superstructures by x-ray diffraction because of the nearly equal atomic numbers. However, Jette and Foote recently pointed out that in this and some other cases it is possible to take advantage of critical absorption limits. Nickel radiation is largely absorbed by Fe atoms, leaving the Ni atoms as the only effective scatterers, so that superstructures could be detected.

Such criticisms could be multiplied without altering the fact that the book contains an essentially complete summary of all the experimental data on binary metallic systems. Alloys of nitrogen, sulfur, carbon, phosphorus, and other nonmetals which form metallic alloys are also included.

The systems are printed in the order of the initial letter of the chemical symbol and so can be found rapidly without referring to the index. An anthor index is lacking. The book is beautifully printed and bound.

RALPH HULTGREN
ALDEN B. GRENINGER

Organic Chemistry. A Brief Introductory Course. By JAMES BRYANT CONANT, President of Harvard University, Formerly Sheldon Emory Professor of Organic Chemistry, Harvard University. Revised, with the assistance of MAX TISHLER, Ph.D. The Macmillan Company, New York, 1936. ix + 293 pp. 27 figs. 14.5 × 22 cm. Price, $2.60.

This brief text is intended primarily for students in pre-medical, biological, and general science curricula. It gives an excellent presentation of the fundamental notions of organic chemistry and their relations to biology and to industry. The 1928 edition[1] has been revised thoroughly—some changes have been made in the arrangement of material and new sections have been added. The additions include a chapter on unsaturated alcohols and acids, and on compounds of biological interest. The subject of geometrical isomerism, which was not covered in the first edition, is given a brief but adequate discussion. The revision retains a novel feature of the first edition, namely, the introduction to the subject by way of the alcohols. This book is so arranged that a teacher who prefers to start in the more orthodox fashion, with the hydrocarbons, may do so with little difficulty.

The revision includes reference to newer industrial processes and products such as the synthesis of higher alcohols from olefins, *n*-butyl alcohol from acetaldehyde, chloroprene from acetylene, and fluorine derivatives of methane. The traditional exposition of degradation through the series, $R—CH_2OH \longrightarrow R—CO_2H \longrightarrow RCONH_2 \longrightarrow R—NH_2 \longrightarrow ROH$, has been abandoned for reasons of scientific integrity. In the last step rearrangements occur so frequently and are sometimes so complete as to render this method valueless in the determination of structure. Unfortunately no suitable substitute can be offered in a book of this scope.

It is pleasing to note that the idea of structural units has been introduced in dealing with the natural polymers, rubber and cellulose. It would have been possible to extend a similar treatment to the proteins.

The present volume differs from the author's larger book[2] in the omission of mechanisms and theoretical interpretations. The brief text is unusually adequate and differs from many similar books in that a sound exposition of the principles of organic chemistry has not been sacrificed for the sake of brevity, and no undue emphasis has been given to fields of the author's special interests.

JOHN R. JOHNSON

Invisible Radiations of Organisms. By OTTO RAHN, Professor of Bacteriology, Cornell University. With an Introduction to the Physics of Radiation, by Sidney W. Barnes, Research Associate in Physics, University of Rochester. Verlag von Gebrüder Borntraeger, Koester-Ufer 17, Berlin W 35, Germany, 1936. x + 215 pp. 52 figs. 15 × 22.5 cm. Price, RM. 13.20.

This book is a very clear and precise presentation of the problem of mitogenetic radiation. It is extremely well written and the subject matter is arranged in a logical order.

The work has been written primarily to awake the interest of biologists. Hence, the introductory chapter (30 pages) gives an elementary description of the physics of radiation. The results of the electromagnetic and quantum theory of light are presented in a somewhat popular style and the various methods of intensity and frequency measurements are discussed with special emphasis on the limitations of the physical methods. The second and third chapters discuss the spectra of the light emitted by chemical and biochemical reactions and the effects of radiation on such reactions and on living cells.

Chapters IV, V and VI give a lucid account of the work on mitogenetic radiation and the proposed explanations of the mitogenetic effect. The investigations of Gurwitsch and Reiter and Gabor on onion roots, of Baron, Siebert, Tuthill and Rahn on yeast cells, and the use of bacteria and larger organisms as detectors are discussed in considerable detail. Against the negative results of Moissejewa the author quotes the investigations of Paul. The work with physical and physico-chemical detectors is considered to be inconclusive. Chapter IV ends with a short account of other radiations of biological importance, injurious human radiations, necrobiotic rays, infra-red and beta radiations. The peculiar properties of mitogenetic radiations, the effect of intermittent irradiation, production of secondary radiation and retardation of mitosis by an overdose are discussed in Chapter V. In Chapter VI the various interpretations of the mitogenetic effects are compared with the experimental facts. The author concludes that a cell is susceptible to mitogenetic radiation only when it is in a particularly physiological state.

The concluding chapter, VII, deals with the radiation from nerves, tissues and blood and connects the problem of mitogenetic radiation with the problems of growth, healing of wounds and cancer.

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[1] Reviewed by W. H. Hunter, THIS JOURNAL, 51, 1619 (1929).

[2] J. B. Conant, "The Chemistry of Organic Compounds. A Year's Course in Organic Chemistry," The Macmillan Company, New York, 1933. x + 623 pp.

This monograph can be highly recommended to biologists as well as to chemists and physicists. It is written with great ability and remarkable fairness. Dr. Rahn is convinced, from his own experiences, that mitogenetic radiations exist, but he very frankly admits the occasional failure of the experiments and the contradictory nature of some results. In pointing out the mistakes of the mitogeneticists and their opponents, he has succeeded in giving a valuable guide for further research, which is needed before the proof of existence of the mitogenetic effect can be accepted.

HANS MUELLER

Die Korrosion metallischer Werkstoffe. (The Corrosion of Metallic Materials.) Vol. I. **Die Korrosion des Eisens und seiner Legierungen. (Corrosion of Iron and its Alloys.)** By OSWALD BAUER, OTTO KRÖHNKE and GEORG MASING, Editors. Verlag von S. Hirzel, Königstrasse 2, Leipzig, Germany, 1936. 560 pp. 219 figs. Price, RM. 37.50; bound, RM. 39.

This, the first of a series of four volumes, deals only with iron and iron alloy corrosion. Three additional volumes are in preparation. The second will cover the corrosion of non-metals, the third corrosion prevention, and the fourth will discuss important technical corrosion problems.

The first chapter, theoretical (by G. Masing), pp. 31–126, discusses: A—Corrosion of metals in electrolytes, under the headings, fundamental electrochemical phenomena, inhibited electrode phenomena, solution of metals accompanied by formation of hydrogen, corrosion accompanied by electrochemical consumption of oxygen, protective films, passivity, electrochemical behavior of alloys; B—Corrosion of metals by gases, under the headings, general, optical determination of the thickness of films, oxidation of metals, thick films. A short appendix on the behavior of metals with liquid non-electrolytes is included. The second chapter, the corrosion of iron (by C. Carius and E. H. Schulz), pp. 127–407, deals with corrosion as a physical chemical phenomenon, formation of galvanic cells, formation of rust, corrosion in natural waters and aqueous salt solutions, and atmospheric corrosion. In discussing the corrosion of commercial irons they include the effect of composition, heat treatment, surface condition, method of working, corroding media including chemicals, the effect of stresses, etc. There is a chapter on highly corrosive steels (by K. Daeves), pp. 408–429, and a chapter on acid and scale resistant iron alloys (by E. Houdremont and H. Schottky), pp. 430–529. This last chapter discusses: A—Iron-chromium alloys under phase diagrams, heat treatment and strength, other physical qualities, corrosion resistance with extensive tables, commercial requirements of heat resistant alloys, technical behavior, possibilities for utilization, and discussion; B—A short section on iron–nickel; and C—Iron–silicon alloys is included. Two pages of corrections and a well arranged name and subject index are included.

The present book is a compilation of published and unpublished data. Most of the material is critically reviewed. The authors are apparently unfamiliar with much of the literature, especially that outside of Germany. They refer to the first edition only of Speller's "Corrosion, Causes and Prevention." Of the four English and two German bibliographies mentioned by Speller they refer only to that of Rabald. The reviewer has checked many of the articles mentioned in Speller's (second edition) selected bibliography and finds only a few of those dealing with the topics which one would expect to find mentioned by the authors in Volume I. One finds no mention of the extensive work on soil corrosion, very little mention of the principles and methods of corrosion testing. On the whole, however, the present work is a valuable, well-prepared addition to the literature on the important subject of corrosion.

MERLE RANDALL

Introduction to Quantum Mechanics with Applications to Chemistry. By LINUS PAULING, Ph.D., Sc.D., Professor of Chemistry, California Institute of Technology, and E. BRIGHT WILSON, JR., Ph.D., Society of Fellows, Harvard University. McGraw-Hill Book Company, Inc., 330 West 42d Street, New York City, 1935. xiii + 468 pp. 15.5 × 23.5 cm. Price, $5.00.

In spite of the many introductions to quantum mechanics which have appeared in the last few years, there would still seem to be room for a book on this subject addressed to the chemist and emphasizing the aspects of particular interest to him; this niche is admirably filled by the volume under review. It begins with a survey of classical mechanics and the old quantum theory. Then the Schrödinger wave equation is introduced, and its properties and the physical significance of its solutions are discussed. The hydrogen atom is discussed in great detail, and tables of eigenfunctions for a number of the lower energy levels are given; these should be convenient for reference for anyone who is making calculations with hydrogen-like functions. A great deal of the book is devoted to perturbation theory and its application to the electronic structure of atoms and molecules and to the binding energies of molecules, topics of great importance to the chemist, presented in detail and in easily comprehensible form. An elementary account of electron spin, sufficient for the purposes of the book, is given in an early chapter. There are also chapters on the variation method (with applications also in later chapters), the rotation and vibration of molecules, absorption and emission of radiation, some miscellaneous applications, and the general theory, including matrix mechanics and the uncertainty principle. Some useful mathematical material is given in appendices. Some topics usually treated in elementary books on wave mechanics are omitted as of little immediate use to the chemist. The reviewer cannot agree with the authors that this ground for omission holds in the case of aperiodic processes, but the inclusion of this subject would undoubtedly have required considerably more space, and in general the topics are well selected to fulfill the purposes for which the book is intended. Detailed application of the theoretical development to experimental material is confined for the most part to a few of the simplest cases, such as the hydrogen atom, the helium atom, the hydrogen molecule, and the hydrogen molecule-ion (in which cases great detail is given). Inclusion of more material of this sort probably would have been desirable, but again would have lengthened the book, and enough of the theory is given to make reference to the original literature sufficiently easy.

The wave equation is introduced in an early chapter as a fundamental hypothesis. This course is quite as satisfactory as any other from a purely logical point of view, though the reviewer believes that some preliminary discussion of the relation between wave and corpuscle aspects of radiation and matter, designed to show the reasonableness of this hypothesis, would have made matters easier for the beginner. The first two chapters on classical mechanics and the old quantum theory do not quite seem to take the place of such a discussion. However, in general, the book is clearly and carefully written, so as to reduce the mathematical difficulties to a minimum. A reviewer's opinion of the clarity of an exposition of a subject with which he is already acquainted is perhaps to be questioned; in this case the reviewer's judgment on this matter has been corroborated by conversation with people who have been reading the volume with the purpose of learning the subject. He believes, therefore, that there is no doubt that this book will prove extremely valuable to those studying the subject for the first time. But, also, its later chapters constitute an excellent reference work for investigators doing research in this field, especially useful for the detailed accounts given of many important subjects.

O. K. RICE

Die Thermodynamik einheitlicher Stoffe und binärer Gemische, mit Anwendungen auf Verschiedene physikalisch-chemische Probleme. (**The Thermodynamics of Simple Substances and Binary Mixtures,** with Application to Various Physico-chemical Problems.) By DR. J. J. VAN LAAR. G. E. Stechert, New York, or P. Noordhoff N. V., Groningen und Batavia, 1936. 279 pp. Price, $8.00; bound, $9.00.

The first 145 pages are devoted to the chemical elements. Here the equation of state is developed in detail and the various constants entering into the thermodynamic equations are presented in tabular form. In the second part of the book there is a chapter on Gibbs' thermodynamic potential and the application of the theorem of homogeneous functions to the study of mixtures. The complexities of the equilibrium between phases of binary mixtures are treated in considerable detail. The book may find some use as a reference source for data and for the equations of classical thermodynamics, but it certainly will not prove of any value as a textbook in America. One looks in vain for the numerous experimental and theoretical advances which have been made in this country and abroad in recent years. The reviewer could locate nothing on the third law or the modern applications of statistics. Two pages are devoted to Debye's electrolyte theory which is followed by a page on Ghosh's theory. Both presentations were very disappointing. The activity concept is dismissed as "ein leeres Wort." There are very few data in the book which have been obtained since 1920. The entire presentation is not only mathematically formidable, but appears to be unduly complicated and terrifying.

VICTOR K. LA MER

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. Meyer. **Aluminium-legierungen.** Patentsammlung geordnet nach Legierungs-systemen. (Aluminium Alloys. A Collection of Patents.) Parts I–II. By A. Grützner with the Collaboration of G. Apel. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany, 1936. 342 + 526 pp. Price, RM. 35 + 40.50.

This collection of patents on aluminum alloys is published as an Appendix to the volumes on Aluminum (Part A) of Gmelin's Handbook of Inorganic Chemistry, 8th Edition. The Introduction states that it covers completely the patent literature on these alloys from 1887 to May, 1935. The patents are arranged in a continuous table. The constituent elements of each alloy are listed serially in alphabetical order and the alloys thus characterized are themselves also arranged in alphabetical order. This makes it possible to find out quickly and easily whether an alloy of any given composition is protected by patents, and the very laborious and time-consuming search through the patent literature of all countries which would otherwise be required, is thus avoided.

This volume does not attempt to cover at all the literature dealing with aluminum alloys published in scientific journals, etc., since this information is available in the volumes on Aluminum (Part A) of the Gmelin Handbook.

ARTHUR B. LAMB

Dynamics of Rigid Bodies. By WILLIAM DUNCAN MACMILLAN, A.M., Ph.D., Sc.D., Professor of Astronomy, The University of Chicago. McGraw-Hill Book Company, Inc., 330 West 42d Street, New York, N. Y., 1936. xiii + 478 pp. 80 figs. 16 × 23.5 cm. Price, $6.00.

This book is the third of a series on theoretical mechanics by the same author, the first two being "Statics and the Dynamics of a Particle" and "The Theory of the Potential." The present volume is independent of the first two, however, and contains a good deal of general dynamical theory besides the specialized applications to rigid bodies. Thus, the algebra of vectors, systems of free particles, impulsive forces, Lagrange's and Hamilton's equations are treated quite fully, in addition to a wide variety of problems involving rigid bodies.

Although this work covers a difficult field and will be especially useful to advanced students, the presentation is in general clear and complete, so that any reader with a knowledge of elementary physics and the usual undergraduate courses in differential equations should find it very profitable reading. A number of mathematical concepts are described in the text in connection with their application to dynamical problems; for example, the algebra of matrices, which is used in the last chapter in the discussion of the method of periodic solutions.

The index is satisfactory, and in general the mechanical details, such as choice of type, page arrangement, printing and binding are of the usual high standard maintained by the publisher. Very few misprints were noticed.

This reviewer regrets that the conventional method of defining the Eulerian angles was used, since it seems much simpler to call θ and φ the ordinary polar coördinates of the moving ζ-axis and then to define the third angle as usual (wave mechanicians would appreciate in addition the use of some other symbol besides ψ).

Except for the above trifling criticism, this reviewer found considerable pleasure and profit in reading the book and recommends it to anyone who is interested in dynamics.

E. BRIGHT WILSON, JR.

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June 15, 1936–July 15, 1936

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MARCEL MATHIEU. (1) "Réactions Topochimiques. Généralités." (2) "La Nitration de la Cellulose. Réaction Topochimique." (3) "La Gélatinisation des Nitrocelluloses. Réaction Topochimique." Hermann et Cie., 6 Rue de la Sorbonne, Paris, France. (1) 57 pp. Fr. 12. (2) 65 pp. Fr. 12. (3) 73 pp. Fr. 12.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WEST VIRGINIA AGRICULTURAL EXPERIMENT STATION]

The Anthocyanin Pigment of the Winesap Apple[1]

BY IRA J. DUNCAN AND R. B. DUSTMAN

It is known that the coloration of fruits is affected by a number of factors including light, temperature, supply of nitrogen and moisture from the soil, concentration of carbohydrates and organic acids in the cells and perhaps by other factors. Due to the commercial importance of apple-growing in West Virginia and due to the desirability of high color on apples in the market, it was deemed advisable to undertake an investigation of the red pigment of the apple at this station. The first logical step in an investigation of this type involves a determination of the nature of the substance in question. The present work deals with the isolation, purification, identification and determination of the chemical nature of this pigment.

Historical

During the past fifty years considerable work has been done on the chemistry of the natural coloring matter of flowers, fruits and berries. Willstätter and his co-workers were pioneers in these investigations. In their work on the cornflower Willstätter and Everest[1a] cleared up many experimental difficulties encountered in the investigation of plant pigments. They also introduced a rapid test to distinguish glucoside from non-glucoside pigments. The work of Robinson,[2] Karrer,[3] Anderson[4] and many others during recent years has contributed much information to our knowledge of anthocyanin pigments.

These pigments occur in plants as glucosides, accompanied in a few instances by a small amount of sugar-free pigment. In the substances so far reported the sugar occurring in combination with the non-glucoside fraction is glucose, galactose or rhamnose, but by far the most common is glucose.

Robinson and Robinson[2] developed a rapid method for testing qualitatively the anthocyanins occurring in leaves, flowers and fruits. In this method the pigments are characterized by observing their color reactions with alkalies and ferric chloride, and considerable use is made of their distribution between immiscible solvents. The work of these investigators indicated that the skins of the Winesap and Jonathan apples contain the pigment cyanidin 3-monoside. The work of these and other investigators indicates that in the monoglucosides the sugar molecule is attached to the number three carbon atom.

Experimental

From time to time during the fall of 1933 and 1934 quantities of Winesap apples ranging from 7 to 25 bushels were procured and efforts were made to isolate the red pigment

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[1] Published with the approval of the Director of the West Virginia Agricultural Experiment Station as Scientific Paper No. 162.

[1a] Willstätter and Everest, *Ann.*, **401**, 189 (1913).

[2] (a) MacDowell, Robinson, and Todd, *J. Chem. Soc.*, 806 (1934); (b) Murakami, Robertson and Robinson, *ibid.*, 2665 (1931); (c) Robinson, *Chem. & Ind.*, 737 (1933); (d) Robinson and Robinson, *Biochem. J.*, **25**, 1687 (1931).

[3] (a) Klein, "Handbuch der Pflanzenanalyse" (Anthocyane Von P. Karrer) 111/2, Julius Springer, Wien, 1932, p. 941; (b) Karrer and Meuron, *Helv. Chim. Acta*, **15**, 1212 (1932); rev. in *C. A.* **27**, 302 (1933).

[4] (a) Anderson, New York Agr. Expt. Sta., Tech. Bull. 96; (b) Anderson and Nebenhauer, *ibid.*, Tech. Bull., 146; (c) Shriver and Anderson, *ibid.*, Tech. Bull., 152.

from the skins by using various methods[4b,5] described for the preparation of the pigment of the grape, cranberry and certain flowers. These methods failed to give satisfactory yields of apple pigment. The difficulty was probably due to the relatively low percentage of red pigment in the skins as they were removed. Extracting a given weight of skins even when a minimum volume of extracting liquid is employed results in a relatively dilute solution of the pigment and a high concentration of sugars, waxes, gums and other impurities.

Finally, the method of Willstätter and Burdick[6] used for the isolation of asterin and callistephin from the flowers of the purple-red aster, with some modifications, was found to give fair results. Consequently the skins from fifteen bushels of apples were placed in two-gallon, wide-mouthed jars, and the red pigment was extracted with ethyl alcohol containing 0.1% hydrochloric acid. After twenty-four hours the alcoholic solution was filtered and the coloring matter in the filtrate was precipitated with neutral lead acetate solution. After standing for twelve hours the green gelatinous precipitate of the lead salt was filtered, washed with cold water and allowed to remain on the filter until practically air-dry. The precipitate on the filter was then treated with glacial acetic acid. This dissolved the coloring matter completely and left many colorless impurities undissolved. The pigment was precipitated from the dark-red acetic acid filtrate with two volumes of ether. The lead salt thus obtained was filtered and decomposed on the filter with a mixture of propyl alcohol and methyl alcohol containing 25% hydrochloric acid in the ratio of 10 to 1 by volume. This process left still other impurities undissolved. On treating the alcoholic filtrate with 3 or 4 volumes of ether the coloring matter was precipitated as the chloride salt. This precipitate was filtered, washed with ether and then dissolved in ethyl alcohol containing 0.1% hydrochloric acid. The lead salt was again formed by treating the alcoholic solution with neutral lead acetate solution. After filtering, washing and drying the entire purification process was repeated by resolution in acetic acid, precipitation with ether, decomposition of this precipitate with the propyl alcohol–methyl alcoholic hydrochloric acid mixture, and precipitation finally of the chloride salt with ether. The chloride salt was converted to the picrate by dissolving in warm water and treating the solution with warm picric acid solution. The picrate was again converted to the chloride by solution in methyl alcohol containing 5% hydrochloric acid and treating the acid alcoholic solution with 4 or 5 volumes of dry ether. The chloride precipitated as a red amorphous powder. Crystallization by slow evaporation of the alcohol from a mixture of aqueous hydrochloric acid and ethyl alcohol yielded long needle crystals having a bronze metallic luster. Five additional crystallizations yielded a product free from amorphous material and apparently pure.

A small amount of the chloride salt was again converted to the picrate and the picrate recrystallized from warm water. Fine brownish-red needles were formed. The picrate gave a cherry-red solution in ethyl alcohol and an orange-red solution in water. When a drop of the latter solution was placed on a filter paper it produced a spot with a violet center and yellow exterior. This is the result of hydrolytic dissociation according to Willstätter and Mallison.[5] The picrate is partially decomposed when an aqueous solution is heated above 70°.

The anthocyanin chloride is very soluble in water giving a brownish-red solution which assumes a bluish tinge when greatly diluted. The color does not fade entirely on standing, and a faint red color remains even after boiling. The salt is soluble in ethyl and methyl alcohols producing bluish-red solutions; it is soluble also in very dilute hydrochloric acid but in 7% hydrochloric acid it is almost insoluble. A number of color reactions with inorganic salts were observed. An aqueous solution of the glucoside, previously acidified slightly to prevent decolorization, gave a purplish-red color with a solution of sodium acetate, while sodium carbonate gave a violet color. Sodium or potassium hydroxide gave at first a blue color which changed to green and then to yellow. The red color was not restored on acidification, showing decomposition had taken place with these alkalies. The pigment is precipitated by neutral lead acetate from both alcoholic and aqueous solution, giving blue and purple lead salts, respectively. One drop of very dilute ferric chloride solution gave a deep purple color when added to an aqueous solution of the pigment and a blue color when added to an alcoholic solution.

The bronze luster of the air-dried chloride salt changed to a green color when the salt was dried over sulfuric acid but the bronze color returned on exposure to the atmosphere for a short time. The dry salt melted with decomposition at 210–212°. Apparently the glucoside loses all of its water of crystallization when dried over sulfuric acid at room temperature in a vacuum desiccator at one mm. pressure for forty-eight hours, since no further loss occurred when it was heated at 108° for an additional twenty-four hours in a vacuum of one to five mm. pressure.

Analyses of the air-dried chloride salt of the pigment gave C, 47.31; H, 4.88; Cl, 6.69; O, 41.12 (by difference); and H_2O, 8.58, respectively. Calculation of the empirical formula gave $C_{21}H_{21}O_{11}Cl \cdot 2.5H_2O$, which requires C, 47.58; H, 4.95; Cl, 6.70; O, 40.78 and H_2O, 8.51, respectively. No methoxy groups are present in the molecule. C, H, Cl and methoxy groups were determined by Pregl's micro methods.[7] The analytical values given are averages of triplicate determinations throughout the paper.

Calculation of the percentage composition of the water-free glucoside from the experimental values gave: C, 51.75; H, 4.30; Cl, 7.33; and O, 36.62 (by difference). $C_{21}H_{21}O_{11}Cl$ requires C, 52.01; H, 4.33; Cl, 7.32; and O, 36.44.

The analyses, the physical and chemical properties and the color reactions of the pigment of the Winesap apple agree closely with those of idaein chloride isolated from the cranberry by Willstätter and Mallison.[5]

Quantitative Hydrolysis of the Glucoside

The glucoside pigment, presumably idaein chloride, 0.2591 g., was hydrolyzed by dissolving in 10 cc. of water, adding 10 cc. of concentrated hydrochloric acid and boiling

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(5) (a) Willstätter and Mallison, *Ann.*, **408**, 15 (1915); (b) Willstätter and Miegs, *ibid.*, **408**, 122 (1915).

(6) Willstätter and Burdick, *ibid.*, **412**, 149 (1916).

(7) (a) Pregl, "Quantitative Organic Microanalysis" (Translated by Ernest Fyleman from 2d ed., 1924), pp. 15–72, 102–127; (b) *ibid.*, pp. 150–158.

the acid solution for two and one-half minutes. Crystals of the anthocyanidin chloride began to separate after the solution had boiled for one minute. At the end of two and one-half minutes the solution was immediately cooled and placed in the refrigerator for several hours. The non-glucoside salt separated from the solution as long red-brown needles with a metallic luster. These were collected in a weighed, fritted-glass bottom crucible, washed with a little cold 7% hydrochloric acid and dried over sulfuric acid. Recovery of the air-dried anthocyanidin chloride amounted to 64.09% of the original weight. $C_{21}H_{21}O_{11}Cl \cdot 2.5\ H_2O$ theoretically yields 64.24% of anthocyanidin chloride.

The sugar in the filtrate from the hydrolysis of the glucoside was identified in the following manner: the slightly red acid solution was neutralized with solid lead carbonate, the resulting lead chloride precipitate was filtered and the excess lead was removed from the filtrate by precipitation with hydrogen sulfide. The filtrate from the hydrogen sulfide precipitate was neutralized with solid sodium bicarbonate and the solution was concentrated to a small volume by evaporation at 40–45° before an electric fan. The yellow solution was decolorized with Norit and the colorless sugar solution in a test-tube was converted to the osazone by adding to it 0.160 g. of pure phenylhydrazine hydrochloride and 0.240 g. of sodium acetate and heating in a boiling water-bath. The osazone separated after several minutes as clusters of orange-yellow needles. After thirty minutes in the boiling water-bath the contents of the tube were allowed to cool. The osazone was then filtered, washed with cold water and twice recrystallized from hot 10% aqueous pyridine solution. The purified osazone melted at 195–196° with decomposition. The melting point corresponds to that of galactosazone. A mixture of galactosazone, prepared from pure galactose, and the unknown osazone mixed in about equal proportions also melted at 195–196° with decomposition. The identification of the sugar as galactose was further confirmed by saccharimetric readings and copper oxide reduction values on a solution of the sugar. The specific rotation of the unknown sugar calculated from the saccharimeter readings was +81.0° at 20°. The specific rotation of galactose is recorded as +80.2° at 20° when determined on a 1% solution.[8] Likewise, the copper oxide values for the unknown sugar averaged 4.3% higher than the corresponding values for an equivalent weight of pure galactose when the latter was subjected to the same acid treatment as that used to hydrolyze the glucoside.

The anthocyanidin chloride obtained by the hydrolysis of the glucoside was recrystallized by dissolving in ethyl alcohol, adding one-half its volume of 7% hydrochloric acid, and allowing the alcohol to evaporate slowly from a loosely covered beaker. After twenty-four hours the crystals were filtered and three times recrystallized by the same procedure. The final crystallization yielded a product free from amorphous material and apparently pure. The anthocyanidin chloride is soluble in methyl and ethyl alcohols giving beautiful violet-red solutions. It is much less soluble in water and only slightly soluble in dilute hydrochloric acid. The crystals failed to melt when heated to 350°. Dilute solutions of inorganic reagents gave the following results: ferric chloride changed the color of an aqueous solution of the pigment from red to violet; lead acetate gave a violet precipitate of the lead salt; sodium or potassium hydroxide gave a blue color which on standing turned green and then brown; sodium carbonate when added to an aqueous or alcoholic solution of the pigment gave first a violet then a blue color; ferric chloride when added to an alcoholic solution gave a pure blue color.

The non-glucoside salt loses its water of crystallization when heated to 108° for twenty-four hours at one to five mm. pressure.

Analyses of the air-dried sample of the anthocyanidin chloride gave C, 52.64; H, 3.95; Cl, 10.43; O, 32.98 (by difference); and H_2O, 5.55, respectively. Calculation of the empirical formula gave $C_{15}H_{11}O_6Cl \cdot H_2O$, which requires C, 52.85; H, 3.85; Cl, 10.41; O, 32.89; and H_2O, 5.29, respectively. Calculation of the percentage composition of the water-free salt gave C, 55.73; H, 3.53; Cl, 11.04; O, 29.70 (by difference). $C_{15}H_{11}O_6Cl$ requires C, 55.80; H, 3.44; Cl, 10.99; O, 29.77.

Here also the analyses, the physical and chemical properties and the color reactions of the unknown anthocyanidin chloride correspond very closely to cyanidin chloride. The identity with cyanidin chloride was further confirmed by the products formed when it was fused with alkali. The material was heated with potassium hydroxide and a small amount of water in a crucible at 210–220°. Decomposition took place in about one minute. After five minutes the temperature was raised rapidly to 250° for just a moment. After the melt had cooled it was dissolved in water, the solution was neutralized with hydrochloric acid and the slightly acid solution was shaken out with ether. After evaporation of the ethereal solution the residue was dissolved in warm water, made slightly alkaline with sodium bicarbonate and again shaken with ether. The sodium bicarbonate solution, from which the phenol was removed, was then acidified weakly and shaken with ether to remove the acid portion. The two ether solutions were evaporated to dryness and the residues dissolved in warm water. The aqueous solutions were decolorized with Norit, filtered and the filtrates were evaporated until crystals began to separate. Solid compounds separated on cooling. The phenolic constituent was shown to be phloroglucinol by the intense red color imparted to a pine shaving when immersed in concentrated hydrochloric acid. Also, the crystalline form appeared identical with that of pure phloroglucinol when both were crystallized under similar conditions. The acid constituent was probably protocatechuic acid as characterized by the greenish color produced with ferric chloride and by the sublimate it formed when heated. The sublimate gave the green color test for catechol when treated with ferric chloride. The identity of the acid portion could not be fully confirmed because of the small amount of material available. No other constituents were found. Since the alkali decomposition products of cyanidin chloride are phloroglucinol and protocatechuic acid, the identity of the anthocyanidin chloride obtained from the apple is further confirmed as cyanidin chloride.

Summary

The anthocyanin pigment in the skins of Winesap apples has been isolated in pure form and

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(8) "International Critical Tables," Vol. II, p. 351.

identified as idaein chloride, a pigment which Willstätter and Mallison[5] isolated from the cranberry. The glucoside was isolated as the lead salt. By the use of differential solvents it was partially purified and was then converted to the picrate. The pigment was eventually obtained in pure form as the chloride salt. The anthocyanin chloride on hydrolysis yields molecular proportions of cyanidin chloride and galactose.

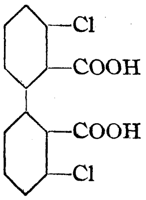
MORGANTOWN, W. VA. RECEIVED MARCH 16, 1936

[CONTRIBUTION NO. 139 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Constitution of the Isomeric Dichlorofluorenone Carboxylic Acids Formed by the Action of Sulfuric Acid on 3,3′-Dichlorodiphenic Acid

BY ERNEST H. HUNTRESS AND EDWARD R. ATKINSON

Earlier work in this Laboratory[1] has shown that when 3,3′-dichlorodiphenic acid (I) is heated with concentrated sulfuric acid at 170° there is formed a ketocarboxylic acid isomeric with, but different from, the 1,6-dichlorofluorenone-5-carboxylic acid (II) quantitatively obtained at 125°. This isomeric acid (designated in the cited reference as "Acid X") has now been identified as 1,6-dichlorofluorenone-4-carboxylic acid (VII) and is identical with the product obtained by the action of sulfuric acid upon 5,5′-dichlorodiphenic acid (VI). Experiments undertaken to elucidate such an unexpected result have now led to the further discovery that 1,6-dichlorofluorenone (XI) and 1,8-dichlorofluorenone (XII) are converted to 3,6-dichlorofluorenone (XIII) on heating in concentrated sulfuric acid. The rearrangement of fluorenones with other substituents is being examined further.



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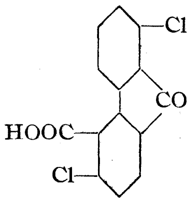

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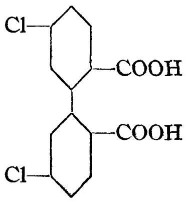

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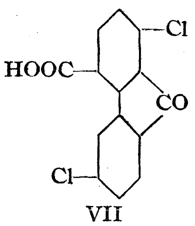

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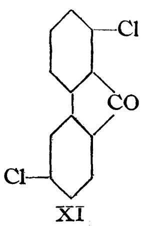
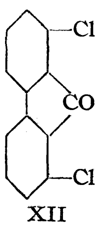


XI



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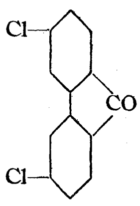

XIII

In carrying out the preparation of the isomeric ketocarboxylic acids from 3,3′-dichlorodiphenic acid (I), it is now evident that our previous isolation of 1,6-dichlorofluorenone-5-carboxylic acid (II) after heating the 3,3′-dichlorodiphenic acid in sulfuric acid at 125° for one hour was fortuitous, since if the treatment be continued longer (*e. g.*, for five hours) the product is 1,6-dichlorofluorenone-4-carboxylic acid (VII) ("Acid X"). A brief study of the temperature at which this isomerization occurs is given in the Experimental Part.

This change does not occur when phosphoric acid is used instead of sulfuric acid. With phosphoric acid at 215°, 3,3′-dichlorodiphenic acid yields only 1,6-dichlorofluorenone-5-carboxylic acid (II); 5,5′-dichlorodiphenic acid (VI) similarly treated gives only 1,6-dichlorofluorenone-4-carboxylic acid (VII). Thus, although phosphoric acid does not effect rearrangement, it does cause ring closure.

The Evidence for the Structure of 1,6-Dichlorofluorenone-5-carboxylic Acid (II)

The original data on this acid[2] have been confirmed and extended. The acid gives correct analysis for halogen and the expected neutralization equivalent. On treatment with thionyl chloride it yields the corresponding acid chloride (m. p. 180–181°, uncorr.) and this with ammonium hydroxide gives an amide (m. p. 281°, uncorr.). The latter yields[1] (p. 4268) an amine (m. p. 257°, uncorr.). These three derivatives are all distinctly different from the corresponding products of the "Acid X" series, and the depression of corresponding mixed melting points has been confirmed. Furthermore, this keto acid on heating gave 1,6-dichlorofluorenone (XI). In addition to the above results, we have also been able to effect the deamination of the aminodichloroflu-

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(1) Huntress, Cliff and Atkinson, THIS JOURNAL, **55**, 4262–4271 (1933).

(2) Huntress and Cliff, *ibid.*, **55**, 2559–2567 (1933).

renone obtained above from the keto acid chloride and have likewise obtained 1,6-dichlorofluorenone (XI). Finally the keto acid has been oximated and the resultant derivative hydrolyzed back to the original compound.

Characterization of "Acid X" as 1,6-Dichlorofluorenone-4-carboxylic Acid (VII)

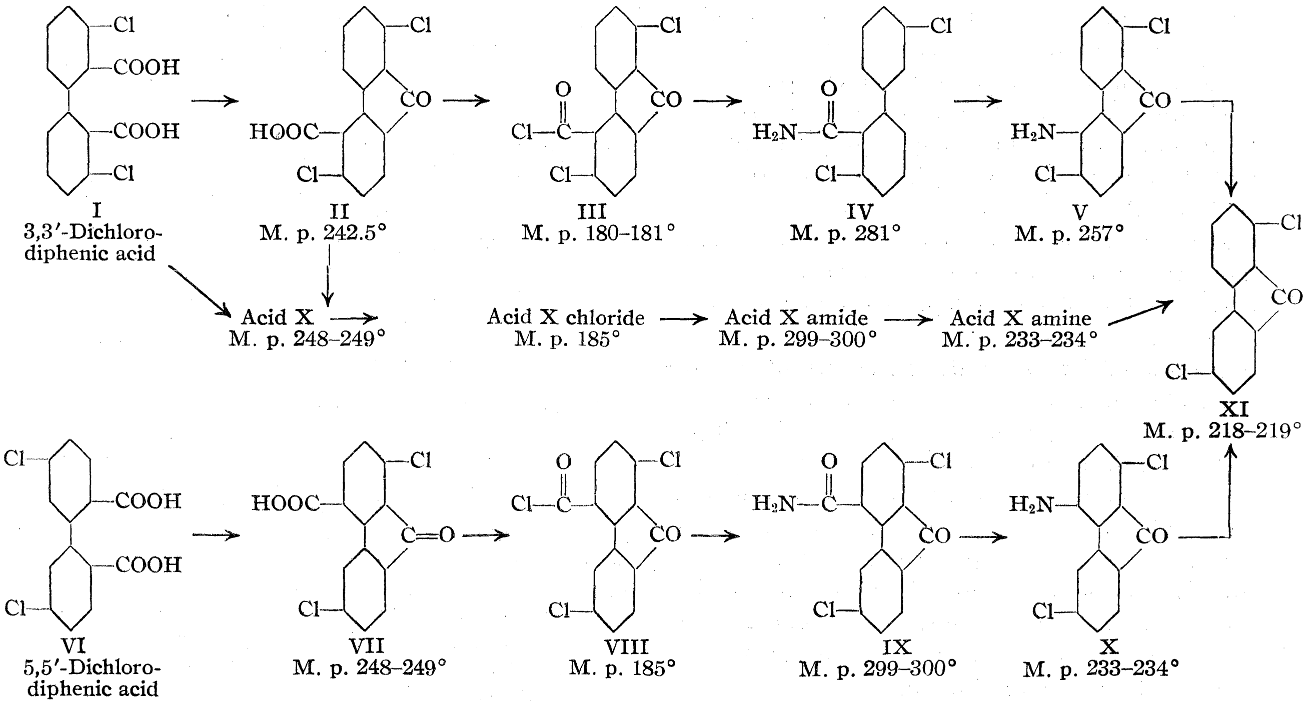
Improved Physical Constants of "Acid X" and its Derivatives.—As a result of much further experience in the preparation and purification of "Acid X" and its derivatives, products with higher melting points than those reported in the earlier paper[1] have been obtained. These are indicated in Chart I. The melting points of the acid, acid chloride, acid amide, amine, and corresponding deaminated ketone of the "Acid X" series, were found to be identical with those for the corresponding compounds of the 5,5′-dichlorodiphenic acid series. Furthermore, the melting points of mixtures of corresponding derivatives were *not depressed.* The structure of "Acid X," therefore, is that of 1,6-dichlorofluorenone-4-carboxylic acid and the relations of the various series of derivatives are portrayed in Chart I.

Our previous difficulty in obtaining satisfactory neutralization equivalents for "Acid X" was at first again experienced in the present work and, as might be expected, since the two are identical, a similar difficulty in obtaining satisfactory values for 1,6-dichlorofluorenone-4-carboxylic acid (VII) (in contrast to the satisfactory value for the latter obtained in our last paper where impure material was used).

Many determinations of the neutralization equivalent of this acid (either as "Acid X" or as 1,6-dichlorofluorenone-4-carboxylic acid) and also halogen analyses on various samples showed that it formed compounds with the solvents used for crystallization. The melting points of all samples, regardless of solvent present, was 248–249°. The samples were desolvated by methods described in the Experimental Part and then gave the theoretical values for the neutralization equivalent.

The Direct Decarboxylation of "Acid X."—Earlier attempts to decarboxylate "Acid X" by dry heating under reduced pressure had been unsuccessful, due to its sublimation in unchanged condition; 1,6-dichlorofluorenone-5-carboxylic acid, on the other hand, had readily lost carbon dioxide and given 1,6-dichlorofluorenone. Dur-

CHART 1.—RELATIONSHIPS OF 3,3′- AND 5,5′-DICHLORODIPHENIC ACIDS AND THEIR DERIVATIVES



The substances of the "Acid X" series are identical with the substances derived from VI and represented by VII to X, respectively.

ing this present work it was noticed that certain non-acidic substances were present in the crude product from the treatment of 3,3′-dichlorodiphenic acid (I) and 5,5′-dichlorodiphenic acid (VI) with sulfuric acid at the higher temperatures. This suggested that concentrated sulfuric acid might serve as an aid in the decarboxylation of "Acid X." Such proved to be the case and experiment showed that on heating in sulfuric acid at about 200° there was obtained 3,6-dichlorofluorenone (XIII) accompanied by small quantities of unidentified material. Identification of the 3,6-dichlorofluorenone was facilitated by the fact that it is the highest melting of the three dichlorofluorenones involved in this work. That the sulfuric acid was not merely serving as a medium for heat transfer is indicated by our observation that upon its replacement by phosphoric acid neither decarboxylation nor rearrangement occurred.

The Rearrangement of the Dichlorofluorenones

In the course of the work on the decarboxylation of "Acid X" (1,6-dichlorofluorenone-4-carboxylic acid) by heating in sulfuric acid, it was discovered that under the conditions employed 3,6-dichlorofluorenone (XIII) was obtained. Since the other evidence for the 1,6-position of the chlorine atoms in the acid seemed entirely reliable, the observation suggested that 1,6-dichlorofluorenone itself (and perhaps also other dichlorofluorenones) might suffer rearrangement on heating with sulfuric acid. It was then found that although 3,6-dichlorofluorenone is stable in concentrated sulfuric acid at 185–200° for forty-five minutes, both 1,6- and 1,8-dichlorofluorenone undergo rearrangement to 3,6-dichlorofluorenone. This was identified by the failure of it and of the corresponding oxime to depress the melting point of authentic samples.

Additional Proof for the Structure of the Dichlorofluorenones.—The previous evidence for the structure of the dichlorofluorenones was as follows.

1,6-Dichlorofluorenone.—Obtained by direct heat decarboxylation of 1,6-dichlorofluorenone-5-carboxylic acid. The oxime of this fluorenone described in an earlier paper[2] (p. 2565) (m. p. 230°) appears to be that individual of two possible stereoisomers which is formed in preponderant amount. On hydrolysis with dilute sulfuric acid it yielded 1,6-dichlorofluorenone.

1,8-Dichlorofluorenone.—The previous work showed that this product was obtained by the action of heat on 3,3′-dichlorodiphenic acid anhydride and that it formed an oxime with great difficulty. Its structure has now been further supported by its preparation from distillation of calcium 3,3′-dichlorodiphenate.

3,6-Dichlorofluorenone.—The structure of this product was assigned because of its previous formation by heating the anhydride of 5,5′-dichlorodiphenic acid. It has now been prepared by distillation of the calcium salt of that acid.

Experimental Part

All melting points reported in this paper were taken by the method described in Mulliken's "Identification of Pure Organic Compounds," Vol. I, page 218, on a 360° rod form melting point thermometer immersed in the sulfuric acid to the 0° point. All melting points are uncorrected.

Temperatures at which 1,6-Dichlorofluorenone-5-carboxylic Acid (II) Isomerizes to 1,6-Dichlorofluorenone-4-carboxylic Acid ("Acid X") (VII).—As indicated in the following table, the isomerization has been found to occur at a temperature considerably lower than that previously described. Since "Acid X" was much less soluble in solvents than its isomer, its detection in mixtures of the two compounds (even when present in small proportion) was readily effected. Such was not the case, however, with the isomeric acid.

The crude products were purified by the method previously described for the individual acids. Only those experiments are here cited in which the product consisted mainly of one isomer. In general 3 cc. of c. p. concd. sulfuric acid was used for every gram of original material. The identity of the purified substances was established by mixed melting points with authentic samples.

Table I

Original substance	Temp. of H_2SO_4, °C.	Time of heating, hr.	Product
3,3′-Dichlorodiphenic acid	150–160	1	"Acid X"
	135–145	4	"Acid X"
	125	1	1,6 - dichlorofluorenone-5-carboxylic acid
	125	5	"Acid X"
	95–104	1	1,6 - dichlorofluorenone-5-carboxylic acid
	80–90	24	1,6 - dichlorofluorenone-5-carboxylic acid
"Acid X"	95–99	10	"Acid X"

Phosphoric Acid as a Condensing Agent.—Sirupy phosphoric acid (85%) was heated at 160° for one hour until evolution of water ceased. One-tenth gram of 3,3′-dichlorodiphenic acid was heated in 2 cc. of this phosphoric acid at 200° but no solution occurred. At 215°, however, a brown solution formed after two hours and from this, by the purification used in the sulfuric acid condensations, there was obtained pure 1,6-dichlorofluorenone-5-carboxylic acid, with no detectable amounts of "Acid X." A similar experiment with 5,5′-dichlorodiphenic acid gave 1,6-dichlorofluorenone-4-carboxylic acid ("Acid X").

Oximation of 1,6-Dichlorofluorenone-5-carboxylic Acid (II).—Three-tenths of a gram of the acid in 15 cc. of alcohol was refluxed for forty-five minutes with 0.43 g. of hydroxylamine hydrochloride in 5 cc. of water. The oxime separated after further dilution. In some runs sodium bicarbonate solution was used and the oxime precipitated by acidification. The melting point of the resulting oxime varied irregularly on recrystallization from various solvents, but the product from dilute acetone generally melted at 263°, dec. No attempt was made to separate the possible stereoisomeric forms. The oxime was not hydrolyzed by boiling 6 *N* sodium hydroxide, nor by concentrated sulfuric acid, but when refluxed for two hours with 50% sulfuric acid, the original keto acid was regenerated.

1,6-Dichlorofluorenone (XI) from 1,6-Dichloro-5-aminofluorenone (V).—In a typical run, 0.1 g. of amine was suspended in a mixture of 10 cc. of alcohol with 0.8 cc. of concentrated sulfuric acid. To the suspension at 0° a concentrated aqueous solution of sodium nitrite was added slowly until excess was present, motor stirring being used. After a heavy precipitate of diazonium salt formed 20 cc. of alcohol was added and the mixture stirred ten minutes at 0°. One-half gram of copper bronze was added and the mixture warmed until evolution of acetaldehyde ceased. After standing for twelve hours the pale yellow product was filtered off and sublimed at 150–190° under 18 mm. pressure. The product weighed 0.05 g. and melted at 217–218°. It did not depress the melting point of an authentic sample of 1,6-dichlorofluorenone. It was converted to the oxime by the procedure previously described[2] (p. 2565); the product so obtained melted at 230° dec. and did not depress the melting point of an authentic sample of the oxime.

The Neutralization Equivalent of 1,6-Dichlorofluorenone-4-carboxylic Acid ("Acid X") (VII).—The titrations were carried out in neutral alcohol using 0.1 *N* sodium hydroxide with phenolphthalein as indicator. If a pure sample (m. p. 248–249°) was crystallized from glacial acetic acid and then titrated, values from 177.8 to 261.2 were obtained (calcd. 293). Either the material recovered from these determinations or fresh material again recrystallized from dilute alcohol, gave neutralization equivalents varying from 296.8 to 301.4. Similar results were obtained on products from aqueous dioxane.

Halogen analyses on the products from acetic acid or from dilute alcohol were always low: *e. g.*, from acetic acid, Cl found, 21.67, 22.41; from dilute alcohol: Cl found, 23.32, 22.75; calculated for $C_{14}H_{16}Cl_2O_3$: Cl, 24.23%. This suggested possibility of solvation.

The product from acetic acid was desolvated by drying in a vacuum oven for five hours at 110°, during which time the needle-like crystals effloresced completely. In some cases samples were desolvated by solution in anhydrous benzene, boiling with decolorizing carbon, and adding ligroin, the precipitated solid being dried at 110°. In one instance no ligroin was added and on cooling, brilliant yellow needles formed which apparently consisted of an addition compound with benzene since they effloresced rapidly at 110°.

All desolvated samples showed the same melting point as the solvates from which they were derived (248–249° in every case). Titration of the desolvated samples gave neutralization equivalents of 294.3, 291.6, 293.3, 291.6, calculated 293.

Direct Decarboxylation of 1,6-Dichlorofluorenone-4-carboxylic Acid ("Acid X") (VII).—In a typical experiment, 0.1 g. of the acid was heated in 1 cc. of C. P. concd. sulfuric acid at 200–215° for one hour. Gas evolution was noticed. The solution was poured on ice and the dark brown solid shaken with dilute sodium bicarbonate solution to remove acidic substances. The undissolved residue was then filtered off, dried and sublimed. At one atmosphere and 140–165° a light sublimate melting at 205–230° first formed which represented about 10% of the total product. The pressure was then reduced to 10 mm. and at 160–180° a bright yellow sublimate, melting at 299–300°, formed. There was also a non-sublimable sulfur-containing residue of high melting point. In other experiments the crude product was recrystallized from dilute acetone before sublimation. The low melting sublimate, obtained in all runs, was not identified.

The sublimate melting at 299–300° was shown to be 3,6-dichlorofluorenone. It did not depress the melting point of an authentic sample and it gave an oxime of m. p. 246–247° which also did not depress the melting point of authentic 3,6-dichlorofluorenone oxime. This portion usually represented about 90% of total sublimate.

The same results were obtained when 3,3'-dichlorodiphenic acid, 5,5'-dichlorodiphenic acid and 1,6-dichlorofluorenone-5-carboxylic acid, all of which are known to yield "Acid X" at the temperatures used, were heated in sulfuric acid at about 200°. The non-acidic material obtained during preparative runs on "Acid X" at 170° also consisted chiefly of 3,6-dichlorofluorenone.

The Rearrangement of the Dichlorofluorenones.—Fifty milligrams of pure 3,6-dichlorofluorenone (m. p. 300°) was heated in 1 cc. of C. P. concentrated sulfuric acid at 185–200° for forty-five minutes. The color of this solution was deep violet. After pouring on ice, the resulting solid was dried and sublimed. At 140–165° and 1 atm. a small amount of light yellow sublimate formed, but at 180° and 10 mm. pure 3,6-dichlorofluorenone was recovered. There was also a small sulfur-containing residue which did not sublime under these conditions.

Approximately 500 mg. of pure 1,8-dichlorofluorenone (m. p. 254°) was heated in 5 cc. of C. P. concd. sulfuric acid for forty-five minutes at 180–190°. The deep brown solution slowly changed to the violet color characteristic of 3,6-dichlorofluorenone. The product was separated in the usual way. At 140–160° and 1 atm., 20 mg. of a sublimate, m. p. 200–225°, was removed and at 180° and 10 mm. 70 mg. of pure 3,6-dichlorofluorenone sublimed. There was also a residue which did not sublime. The product of 3,6-dichlorofluorenone was converted into the oxime (m. p. 246–247°, dec.) and this oxime did not depress the melting point of an authentic sample.

Fifty milligrams of pure 1,6-dichlorofluorenone (m. p. 218°) was heated at 150° in 2 cc. of C. P. concd. sulfuric acid for thirty minutes. The color change from brown to violet was again noted. On subliming the product there was obtained at 150° and 1 atm. a small amount of sublimate, m. p. 195–215°, and at 180° and 10 mm., pure 3,6-dichlorofluorenone. This experiment was repeated using 70 mg. of 1,6-dichlorofluorenone and heating at 125° for forty minutes. The sublimate was separated into two fractions as before, which, however, were *equal* in amount.

the one having m. p. 199–230°, the other m. p. 299–300° (3,6-dichlorofluorenone). There was no residue from these sublimates. This experiment indicates that while the rearrangement occurred at 125° it was not complete in forty minutes. As before the product of 3,6-dichlorofluorenone gave an oxime identical with authentic 3,6-dichlorofluorenone oxime.

1,6-Dichloro-4-aminofluorenone (X) and its Deamination.—Both the preparation and deamination of this amine have been described previously[1] (p. 4268) when the substance was derived from "Acid X." In this work the substance has been derived from 1,6-dichlorofluorenone-4-carboxylic acid which had been prepared from 5,5′-dichlorodiphenic acid.

The preparation of the amine was carried out by a modified method which gave much better results. Potassium hydroxide was used; the ratio of excess alkali to hypobromite was 3/1; the amide–hypobromite ratio was 1/1.2; the concentration of the hypobromite was about 0.0002 mole per cc. of solution; motor stirring was used. Recrystallization from benzene and ligroin gave the amine of m. p. 233–234°, dec. The deamination of this amine was carried out by the procedure previously described for the amine derived from "Acid X."

Summary

1. "Acid X," formed by the rearrangement of 1,6-dichlorofluorenone-5-carboxylic acid in sulfuric acid, is identical with 1,6-dichlorofluorenone-4-carboxylic acid formed when 5,5′-dichlorodiphenic acid is heated with sulfuric acid.

2. The temperatures at which the two isomeric dichlorofluorenone carboxylic acids (formed from 3,3′-dichlorodiphenic acid) are stable have been examined.

3. Phosphoric acid has been found to condense both the 3,3′- and the 5,5′-dichlorodiphenic acids but not to effect the *rearrangement* by which "Acid X" is produced.

4. Certain anomalous observations in the determination of the neutralization equivalent of "Acid X" appear to have been due to formation of solvates with the recrystallizing solvents.

5. "Acid X" has been decarboxylated directly by heating in sulfuric acid to give 3,6-dichlorofluorenone.

6. 1,6-Dichlorofluorenone and 1,8-dichlorofluorenone rearrange in hot concentrated sulfuric acid to give 3,6-dichlorofluorenone.

7. The condensations of other substituted diphenic acids and the rearrangements of the fluorenones and fluorenone carboxylic acids derived from them are being examined.

CAMBRIDGE, MASS. RECEIVED APRIL 10, 1936

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Properties of Unsaturated Sulfur Compounds. III. Alpha Beta Unsaturated Ketosulfones

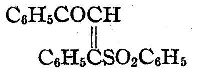
BY E. P. KOHLER AND R. G. LARSEN

In continuation of our investigation of unsaturated ketosulfones[1] we have prepared a representative in which one of the unsaturated carbon atoms holds both a phenyl and a phenylsulfonyl group, the relation between the present and the former sulfones being shown by the formulas

$C_6H_5COCH{=}C(C_6H_5)SO_2C_6H_5 \quad C_6H_5COCH{=}CHSO_2C_6H_5$

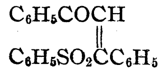
The preparation of this substance enabled us to compare a number of similarly constituted compounds with respect to their stereoisomerism, the facility with which they enter into addition reactions and the mode of addition of unsymmetrical addenda.

The new ketosulfone, like the one described in the earlier paper, occurs in two forms of which one is yellow and the other colorless. From the analogy with the most closely related compounds of which the configuration is known—dibenzoyl ethylene and phenyl-β-benzoylpropionic ester—one would expect the polar groups to be in the *trans* position in the more stable yellow form. We therefore represent this form with I and designate it the *trans* compound.



$$\begin{array}{c} C_6H_5COCH \\ \| \\ C_6H_5CSO_2C_6H_5 \end{array}$$

I *Trans*



$$\begin{array}{c} C_6H_5COCH \\ \| \\ C_6H_5SO_2CC_6H_5 \end{array}$$

II *Cis*

The relative melting points and solubilities of the two forms are the reverse of those of the unphenylated ketosulfones but the relative stabilities remain the same; a trace of base immediately produces a yellow color in solutions of the *cis* compound and in a short time converts it completely into the *trans* isomer. Owing to the reversal of the solubilities the effect of exposing concentrated solutions of the unphenylated and phenyl-

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[1] Kohler and Larsen, THIS JOURNAL, 57, 1448 (1935).

ated compounds to sunlight is quite different; in the case of the former the *trans* compound is converted practically completely into the *cis* while in the case of the latter both forms are converted into an equilibrium mixture containing but little of the *cis* compound.

Nearly all methods of preparation yield only the *trans* compound but when benzene sulfinic acid is added to benzoyl phenylacetylene the *cis* compound is formed exclusively. The two stereoisomers add other substances with practically the same ease. Both are easily oxidized and reduced and both also add halogen acids rapidly. As this easy addition of halogen acids was rather surprising it was important to establish the mode of addition with certainty. To this end we prepared one of the possible hydrogen bromide addition products by a method which was certain to give a compound of known structure, namely, by the addition of benzene sulfinic acid to α-bromo benzalacetophenone. The two diastereomeric bromo compounds obtained by this reaction were quite different in chemical and physical properties from the product obtained by adding hydrogen bromide to the unsaturated ketosulfone. The relations are shown by the following equations

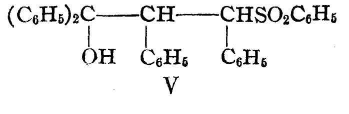
$$C_6H_5COCH{=}C(C_6H_5)SO_2C_6H_5 + HBr \longrightarrow C_6H_5COCH_2CBr(C_6H_5)SO_2C_6H_5 \quad \text{III}$$

$$C_6H_5COCBr{=}CHC_6H_5 + C_6H_5SO_2H \longrightarrow C_6H_5COCHBrCH(C_6H_5)SO_2C_6H_5$$

These results show that the additional phenyl group has but little effect on the ease and none at all on the mode of addition of hydrogen compounds. In contrast it greatly affects both the facility and mode of addition of Grignard reagents. As a consequence of the accumulation of groups in the β position the primary reaction between the phenylated ketosulfone and phenylmagnesium bromide is addition to carbonyl. By operating with excess of reagent and at a higher temperature it is possible to add a second molecule of the reagent but the mode of addition is the reverse of that which occurs with the unphenylated ketosulfone. The two compounds which can be obtained in this manner are represented by the formulas

$$(C_6H_5)_2C(OH)C{=}(C_6H_5)SO_2C_6H_5$$

IV



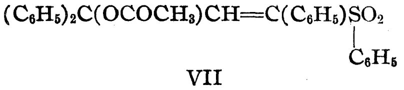
$$\begin{array}{ccccc}(C_6H_5)_2C & — & CH & — & CHSO_2C_6H_5\\ | & & | & & | \\ OH & & C_6H_5 & & C_6H_5\end{array}$$

V

The first of these substances is of special interest in connection with the peculiar behavior of the corresponding unphenylated compound $(C_6H_5)_2C(OH)CH{=}CHSO_2C_6H_5$.[2] The phenylated compound does not exhibit these peculiarities. All samples melt at the same temperature and decompose at the same rate regardless of origin and subsequent treatment. The substance not only does not itself undergo the allylic rearrangement but there also is no indication of rearrangement in metathetical reactions involving the hydroxyl group as, for example, when it is converted into its ethers, esters or chloride.

$$(C_6H_5)_2C(OCH_3)CH{=}C(C_6H_5)SO_2C_6H_5$$

VI



$$(C_6H_5)_2C(OCOCH_3)CH{=}C(C_6H_5)\underset{\underset{C_6H_5}{|}}{SO_2}$$

VII

$$(C_6H_5)_2CClCH{=}C(C_6H_5)SO_2C_6H_5$$

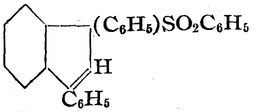
VIII

The structure of the products IV, VI and VII was established conclusively. Thus the carbinol IV on catalytic hydrogenation gives the same saturated compound that is formed when the ketosulfone is first reduced and then treated with phenylmagnesium bromide.

$$\begin{tikzcd}[column sep=small] \underset{\text{IV}}{(C_6H_5)_2C(OH)CH{=}C(C_6H_5)SO_2C_6H_5} \arrow[dr] & & \underset{\text{A}}{C_6H_5COCH_2CH(C_6H_5)SO_2C_6H_5} \arrow[dl] \\ & \underset{\text{IX}}{(C_6H_5)_2C(OH)CH_2CH(C_6H_5)SO_2C_6H_5} & \end{tikzcd}$$

The methyl ether VI can be oxidized to the corresponding ether of benzilic acid and the acetate VII reverts to the carbinol when it is hydrolyzed by weak acids—a process which is not accompanied by rearrangement. The structure of the chloro compound VIII was not established with the same certainty but its properties and its relations to other members of the series are in accord with the formula. Above its melting point it loses hydrogen chloride rapidly and passes into an indene derivative—presumably by way of an intermediate allene.

$$(C_6H_5)_2CClCH{=}C(C_6H_5)SO_2C_6H_5 \longrightarrow$$



X

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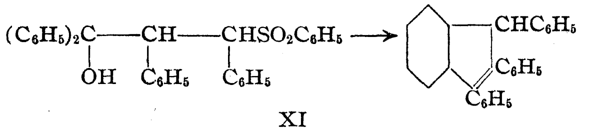
(2) In the earlier paper it was assumed that this compound spontaneously undergoes an allylic rearrangement into an isomer which decomposes at a lower temperature. As a result of a physical investigation of the two products—which is described in the following paper by H. E. Bent and his collaborators—this interpretation is no longer tenable.

While the mode of addition of the first molecule of the Grignard reagent is evidently due to the properties of the conjugated system C═C—C═O, that of the second depends on the character of the system C═C—SO$_2$. The structure of the di-addition product was established by converting it into a known triphenylindene



XI

The foregoing account shows that the introduction of a phenyl group in the β position of an α,β unsaturated ketosulfone does not greatly affect its chemical properties. Except in the case of Grignard reagents the mode of addition is dependent on the character of the conjugated system C═C—C═O and the properties of the addition products express the tendency to revert to this system.

Experimental

The unsaturated ketosulfone was made from benzalacetophenone in a series of steps which can be represented as follows

$$C_6H_5COCH{=}CHC_6H_5 \longrightarrow C_6H_5COCH_2CH(C_6H_5)SO_2C_6H_5 \longrightarrow$$

A

$$C_6H_5COCHBrCH(C_6H_5)SO_2C_6H_5 \longrightarrow$$

B

$$C_6H_5COCH{=}C(C_6H_5)SO_2C_6H_5$$

I

The saturated ketosulfone (A) had been made previously by Posner[3] by adding thiophenol to benzalacetophenone and oxidizing the addition product to the sulfone but we found it simpler as well as more economical to form the sulfone in a single step by adding benzene sulfinic acid. The structure of the bromo compound (B) was established definitely by a synthesis which gives a compound of known structure, namely

$$C_6H_5COCBr{=}CHC_6H_5 + HSO_2C_6H_5 \longrightarrow C_6H_5COCHBr{-}CH(C_6H_5)SO_2C_6H_5$$

α-Phenyl-β-benzoyl Ethyl Phenyl Sulfone (A).—Equimolar quantities of ketone and pure sulfinic acid were brought together in concentrated alcoholic solution. The mixture evolved heat and soon solidified. One recrystallization from alcohol gave a product which melted at 159°. The yield was 93%.

α-Phenyl-β-bromo-β-benzoyl Ethyl Phenyl Sulfone (B).—The bromination of the ketosulfone in chloroform presented no difficulty; once the reaction was started it proceeded smoothly at the ordinary temperature until one mole of bromine had disappeared. The crystalline product that remained after removing the chloroform was subjected to fractional crystallization from methyl alcohol, and was thus eventually separated into two diastereomeric bromo compounds. The principal product, obtained in a yield of 90%, crystallized in coarse needles and melted at 189°. The second product, the yield of which was less than 3%, crystallized in very fine needles and melted at 209°.

Anal. Calcd. for $C_{21}H_{17}O_3BrS$: C, 58.8; H, 3.9. Found: (189°) C, 58.5; H, 4.0. (209°) C, 58.9; H, 4.2.

For the purpose of establishing the structure of these compounds concentrated solutions of equimolar quantities of α-bromo benzalacetophenone and benzene sulfinic acid in ethyl alcohol were kept at the ordinary temperature. In the course of several days the bromo compound melting at 209° crystallized from the solution.

α-Phenyl-β-benzoyl Vinyl Phenyl Sulfone I.—Both of the β-bromo derivatives of the saturated sulfone lose hydrogen bromide slowly when boiled with excess of potassium acetate in methyl alcohol or in acetic acid. In methyl alcohol the reaction with the compound melting at 189° was complete after the solution had been boiled for eighteen hours while that of the higher melting bromo compound required three days. In both cases the product was the yellow *trans* compound. It separated in yellow prisms which after recrystallization from methyl alcohol melted at 151°. The yield was 72%.

Anal. Calcd. for $C_{21}H_{16}O_3S$: C, 72.4; H, 4.6. Found: C, 72.0; H, 4.7.

The Cis Unsaturated Sulfone II.—To a solution of 2.75 g. of benzoyl phenyl acetylene in hot methyl alcohol was added 2.6 g. of benzene sulfinic acid. The mixture was boiled for a short time, then set aside. It yielded 2.8 g. of a colorless product a part of which crystallized from the solution while the remainder was obtained on evaporation. The *cis* compound crystallizes from methyl alcohol in colorless prisms and it melts at 132°.

Anal. Calcd. for $C_{21}H_{16}O_3S$: C, 72.4; H, 4.6. Found: C, 72.0; H, 4.7.

Attempts to ozonize the unsaturated sulfones were unsuccessful. Both forms reduce permanganate in acetone rapidly, being oxidized to two molecules of benzoic acid and one of benzene sulfonic acid. Both forms can also be reduced catalytically and with zinc and acid. Catalytic reduction is extremely slow and incomplete, doubtless because there is some elimination of benzene sulfinic acid which poisons the catalyst. Zinc and acetic acid, however, rapidly reduce the unsaturated sulfones to the same saturated compound.

Interconversion of the Two Isomers by Light.—A solution of 6 g. of the *trans* compound, and a little iodine, in chloroform was exposed to sunlight for three days in a quartz apparatus. At the end of the first day one-third of the solution was evaporated to dryness. The residue, separated by extraction and crystallization from methyl alcohol, was found to contain 0.2 g. of the *cis* compound—indicating about 10% conversion. A similar procedure at the end of the second and third days, gave in each case nearly 0.3 g. of the *cis* compound. In the reverse operation, carried out in the same way but starting with one gram of the *cis* form, the residue after exposure for three days contained 0.85 g. of *trans* and 0.13 g. of *cis*.

Isomerization with Chemicals.—A small drop of sodium methylate was added to a warm solution of 0.5 g. of the

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[3] Posner, *Ber.*, **35**, 810 (1902).

cis compound. The mixture was left to itself for ten hours, then evaporated in a current of air. It left 0.48 g. of *trans* compound and a trace of oil. A similar solution when treated with a little methyl alcoholic solution of hydrogen chloride turned yellow and deposited some *trans* compound but most of the acid was removed by addition.

Addition of Hydrogen Bromide: α-Bromo-α-phenyl-β-benzoyl Ethyl Phenyl Sulfone, III.—A solution of the *trans* sulfone in glacial acetic acid was saturated with hydrogen bromide and left in an ice-box for thirty-six hours. As nothing separated from the solution it was diluted with ether, and freed from acid by washing with water and dilute bicarbonate. The dried ethereal solution, on concentration, deposited the bromide in large needles which, after recrystallization from methyl alcohol, melted with decomposition at 124°.

Anal. Calcd. for $C_{21}H_{17}O_3BrS$: C, 58.8; H, 3.9. Found: C, 59.0; H, 4.0.

The bromo compound is much less stable than the isomeric β-bromo derivative. At the melting point it rapidly loses hydrogen bromide and reverts to the *trans* unsaturated sulfone and when its alcoholic solutions are boiled they gradually turn yellow in color and become acidic.

The corresponding chloro compound—prepared in the same way—is more stable. It crystallizes in colorless needles and melts at 175°.

Anal. Calcd. for $C_{21}H_{17}O_3ClS$: C, 65.5; H, 4.4; Cl, 9.2. Found: C, 65.6; H, 4.6; Cl. 9.1.

Addition of Phenylmagnesium Bromide: the Mono-addition Product.—To an ethereal solution which contained four times the calculated quantity of reagent and which was cooled in ice, was added 7 g. of finely powdered yellow sulfone. The mixture was stirred vigorously for several hours, then decomposed with iced ammonium chloride solution. The product crystallized with two molecules of methyl alcohol in large colorless prisms melting at about 107°. Heated to 100° under diminished pressure, the crystals lost methyl alcohol and passed into a powder melting at 133°.

Anal. Calcd. for $C_{27}H_{22}O_3S \cdot 2CH_3OH$: C, 71.0; H, 6.1. Found: (Prisms) C, 71.2; H, 6.1. Calcd. for $C_{27}H_{22}O_3S$: C, 76.2; H, 5.4. Found: (Powder) C, 76.0; H, 5.1.

Reduction: α-Phenyl-γ-hydroxy-γ,γ-diphenyl Propyl Phenyl Sulfone, IX.—Catalytic hydrogenation with platinum oxide was almost impossible because of the rapidity with which the catalyst was poisoned. With palladium on calcium carbonate, however, the hydrogenation was accomplished without much difficulty, the sparingly soluble product separating from the ethyl acetate used as solvent as fast as it was formed. It crystallized in thin needles melting at 223°. The same compound was obtained, in a yield of 75%, when phenylmagnesium bromide was added to the saturated ketosulfone.

Anal. Calcd. for $C_{27}H_{24}O_3S$: C, 75.7; H, 5.6. Found: C, 75.5; H, 5.6.

The Methyl Ether, VI.—A drop of acetyl chloride was added to a solution of the unsaturated carbinol in boiling methyl alcohol and the solution was then allowed to evaporate in a current of air. It deposited the ether in hexagonal tables melting at 130°.

Anal. Calcd. for $C_{28}H_{24}O_3S$: C, 76.4; H, 5.5. Found: C, 76.6; H, 5.6.

Oxidation.—A dilute solution of the ether in acetone was acidified with a little acetic acid, then treated with the calculated quantity of permanganate in acetone and set aside until completely decolorized. Among the neutral products isolated by the usual manipulations was a substance which crystallized in needles melting at 100° and which was identified as the methyl ether of benzilic acid by comparison with a sample prepared directly from benzilic acid. The yield was 30%.

The Acetate, VII.—A solution of the mono-addition product in acetic anhydride was boiled for four hours, then cooled and poured into water. From the resulting suspension ether extracted a solid which recrystallized from absolute methyl alcohol in needles melting at 168°.

Anal. Calcd. for $C_{29}H_{24}O_4S$: C, 73.7; H, 5.3. Found: C, 73.7; H, 5.4.

The acetate was not affected by boiling water but when it was hydrolyzed with methyl alcoholic potassium hydroxide it reverted to the carbinol and when it was boiled with methyl alcohol that contained a trace of acetic acid it was slowly converted into the methyl ether.

α-Phenyl-γ-chloro-γ,γ-diphenyl Propyl Phenyl Sulfone, VIII.—Dry hydrogen chloride was passed through a solution of the carbinol in benzene until the turbidity, caused by the separation of water, was removed. The solution was then allowed to evaporate spontaneously and the residual green oil was diluted with dry ether. It deposited the chloride in long colorless needles which after recrystallization from dry ether melted with decomposition at about 142°. The yield was quantitative.

Anal. Calcd. for $C_{27}H_{21}OSCl$: C, 72.9; H, 4.8. Found: C, 72.4; H, 5.0.

The chloro compound is stable in the air. When it is boiled with methyl alcohol or with methyl alcoholic potassium acetate it is converted into the ether. Potassium acetate in glacial acetic acid converts it into the acetate.

1,3-Diphenyl-3-phenylsulfonyl Indene, X.—The chloro compound which has just been described loses hydrogen chloride rapidly at the melting point. The residue is an amber colored liquid that is readily soluble in ether. The ethereal solution gradually deposits colorless needles melting at 171°.

Anal. Calcd. for $C_{27}H_{20}O_2S$: C, 79.4; H, 4.9. Found: C, 79.2; H, 5.1.

In proof that the product is an indene derivative 1 g. was oxidized with 1.5 g. of sodium dichromate in glacial acetic acid. The product, isolated in the usual manner, was ortho dibenzoyl benzene—identified by comparison with an authentic sample. The yield was 70%.

$\alpha,\beta,\gamma,\gamma$-Tetraphenyl-$\gamma$-hydroxy Propyl Phenyl Sulfone, V.—To an ethereal solution of phenylmagnesium bromide prepared from 2.25 g. of magnesium was added 10 g. of finely powdered unsaturated ketosulfone. The mixture was boiled for two hours, then cooled and decomposed with iced acid. A part of the product was deposited during the acidification, the remainder being isolated by the usual manipulations of the solution. Three substances were obtained in this manner, namely: the mono-addition product (57%), a di-addition product melting at 178°

(15%), and a stereoisomeric di-addition product melting at 223° (12%). In a similar experiment in which the reacting mixture was boiled for six hours the yields were 22% of mono-addition product, 26% of product melting at 178° and 32% of product melting at 196°. Both of the di-addition products are sparingly soluble in common organic solvents. The lower melting—which is the less soluble—crystallizes from acetone in small prisms and the higher melting crystallizes in six-sided tables containing acetone of crystallization.

Anal. Calcd. for $C_{33}H_{28}O_3S$: C, 78.6; H, 5.6. Found: C, 78.6; H, 6.0. Calcd. for $C_{33}H_{28}O_3S \cdot C_3H_6O$: C, 77.1; H, 6.0; C_3H_6O, 10.3. Found: C, 77.1; H, 5.7; C_3H_6O, 10.1.

The structure of the di-addition products was established by converting them into triphenyl indene. To this end a solution of each in glacial acetic acid containing a small quantity of sulfuric acid was heated on a steam-bath for half an hour, then diluted first with methyl alcohol and finally with water. In each case the product was identified by comparison with a sample on hand.

Summary

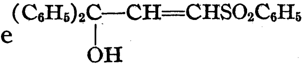
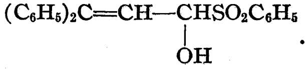
The paper contains a comparison of $C_6H_5COCH{=}C(C_6H_5)SO_2C_6H_5$ and $C_6H_5COCH{=}CHSO_2C_6H_5$ with respect to their stereoisomerism, the facility with which they enter into addition reactions, the mode of addition of hydrogen compounds and the mode of addition of Grignard reagents.

CAMBRIDGE, MASS. RECEIVED JUNE 3, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Physical Investigation of β-Hydroxy-β,β-diphenylvinyl Phenyl Sulfone

BY H. E. BENT, E. S. LARSEN AND H. BERMAN

In a recent paper Kohler and Larsen[1] described two compounds which "are interesting by reason of the very remarkable ease with which they undergo the allylic rearrangement.... Most solutions, on chilling, deposit a mixture of both isomers but by slow crystallization from properly selected solvents it is possible to secure both isomers in a pure condition—the tertiary alcohol VIII from benzene and the secondary alcohol X from methyl or ethyl alcohol." The tertiary alcohol, β-hydroxy-β,β-diphenylvinyl phenyl sulfone, has the structure  $\underset{\mathrm{OH}}{\underset{|}{(C_6H_5)_2C}}{-}CH{=}CHSO_2C_6H_5$ and the secondary alcohol, α-hydroxy-β,β-diphenylpropenyl phenyl sulfone, X, has the structure  $(C_6H_5)_2C{=}CH{-}\underset{\mathrm{OH}}{\underset{|}{CH}}SO_2C_6H_5$. The melting point of the tertiary alcohol is given as 193° and of the secondary alcohol as 164°. Both compounds crystallize readily but differ greatly in appearance. This apparent reversal of the direction of transformation by different solvents at the same temperature is, however, thermodynamically impossible, and we have therefore reëxamined more carefully the physical properties of these two substances.

Crystallographic measurements were made as follows:

OPTICAL CRYSTALLOGRAPHY

	Cpd. VIII	Cpd. X
α	1.608	1.607
β	1.656	1.657
γ	1.710	1.706
Opt. sign	(+) 2*V* med.	(+) 2*V* med.
Orientation	*Z* = *b*	*Z* = *b*
	*X*Λ*C* = 23°	*X*Λ*C* = 23°

CRYSTALLOGRAPHY

Measurements on X

Forms: (010)(100)(110)(011)(101) Monoclinic-holohedral

$a:b:c = 1.0597:1:0.3277$ $\beta = 99° \, 05'$

$p_0 = 0.30926$ $q_0 = 0.32362$ $e = 0.15784$

Form	Observed (averages) φ	ρ	Calculated φ	ρ	Number of observations
(010)	0°	90° 00′	0°	90° 00′	4
(100)	90° 00′	90° 00′	90° 00′	90° 00′	1
(110)	43° 42′	90° 00′	43° 42′	90° 00′	12
(011)	26° 00′	20° 02′	26° 00′	20° 02′	6
(101)	90° 00′	25° 17′	90° 00′	25° 19′	1

Ranges: for (110) 43° 32′ to 43° 55′
(011) 25° 40′ to 26° 41′ 19° 47′ to 20° 10′

Measurements on a single crystal of VIII

Form	φ	ρ
(010)	0°	90° 00′
(110)	39° 49′	90° 00′
(011)	25° 51′	20° 09′

Crystals X are much superior in quality and the angles of these are to be relied upon for a good axial ratio for the substance. Crystals VIII were difficult to measure since they were of the order of 0.1 mm. in maximum size. Several crystals

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[1] Kohler and R. G. Larsen, THIS JOURNAL, 57, 1448 (1935).

yielded rather poor measurements, the best being given above. The data given above indicate that substances VIII and X are crystallographically identical and that although they do have a different superficial appearance they are actually similar in habit as well as in the prevalence of particular forms.

The melting points were carefully re-determined, first by conventional methods and second by the use of the copper block. The results obtained with an ordinary melting point tube depend upon the rate of heating, rapid heating giving much higher results. The following table gives typical results obtained with a copper block.

T, °C.	Time required for melting, in sec. VIII	X
159	180	60
165	120	30
170	120	30
178	75	22
188	50	15
193	50	12
195	25	12
199.5	2-3	2-3

It is clear from these results that the melting points as determined in tubes are really decomposition or rearrangement points and as usual are greatly affected by variations in the rate of heating. Since decompositions are known to be very sensitive to the presence of impurities, the low apparent melting point of substance X may well be due to an impurity present in it when recrystallized from methyl alcohol, but absent or present in smaller amounts when recrystallized from benzene.

Finally, the solubilities of VIII and X were determined in benzene and methyl alcohol at several temperatures. The saturation was accomplished by shaking the solutions in a small container of about 10-cc. capacity surrounded by a jacket containing a boiling liquid. This vessel was conveniently made like a small Dewar flask with the boiling liquid in the space usually evacuated, to which a reflux condenser was sealed. To prevent evaporation of the solvent there was a ground glass stopper halfway down the neck of the flask. The whole apparatus was mounted on a shaker which not only served to agitate the solution but also to minimize superheating. The temperatures were read on a thermometer immersed in the solution itself and these remained constant to ±0.1°. One cubic centimeter samples were removed by means of a filter pipet and evaporated to constant weight on a steam-bath. Duplicate determinations usually agreed to about ±1 mg. depending on the concentration of the solution. The results are given in Table I.

Table I

Temp., °C.	Time of shaking	Vol. of soln. 1 cc. C_6H_6	Wt. of solute VIII, g.	Wt. of solute X, g.
34.4	10 min.	"	0.0054	0.0043
55.2	5	"	.0114	.0108
64.4	4	"	.0167	.0163
80.3	5	"	.0303	.0293
0	12 hr.	CH_3OH	.0030	.0027
0	12	C_6H_6	.0015	.0015
0	25 min.	satd. CH_3OH	.0030	.0032

These results are not as precise as perhaps one might wish, and if it seemed worth while a somewhat greater expenditure of time would doubtless improve them considerably. However, the values given for the solubilities of the two materials agree as well as values obtained on successive runs on the same material. The time was intentionally made as short as five minutes for the shaking in order to diminish the chance of a rearrangement taking place in solution. Perhaps the last row in the table is the most significant. In this case a saturated solution of one compound in methyl alcohol was shaken with the other solid. Unless there is a rapid equilibrium established at 0° one would have expected the total amount of solute to be about twice that observed. The only alternative is that both materials are the same.

Cambridge, Mass.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Accuracy of the Potentiometric Iodide–Silver Titration

BY I. M. KOLTHOFF AND J. J. LINGANE

This study of the potentiometric iodide–silver titration was undertaken with a three-fold purpose: (a) to determine the accuracy of the titration, (b) to locate the isoelectric point of freshly precipitated silver iodide, and (c) to study the adsorption of silver and iodide ions by flocculated silver iodide, at extremely low concentrations. A knowledge of the accuracy of the iodide–silver titration was necessary before the required data for topics b and c could be obtained. The present paper contains the results of the experiments made to determine the accuracy of the titration, and subjects b and c will be discussed in a subsequent communication.

Although the *precision* of the potentiometric iodide–silver titration has been studied exhaustively by Lange and Berger,[1] these authors did not establish the *accuracy* of the titration since they worked with solutions of potassium iodide and silver nitrate whose concentrations were not exactly known. In lieu of direct experimental evidence of the accuracy of the titration, they studied the adsorption of silver and iodide ions on silver iodide, and concluded from the data so obtained that the titration should give results accurate to at least ±0.01%, when performed under the most favorable conditions. They found that titration at room temperature was impractical because of the strong adsorption of silver and iodide ions by the precipitate with consequent slow attainment of steady e. m. f. They found that the deleterious effects of adsorption were practically eliminated when the titration was performed at 90°, and they showed that the results were highly precise under these conditions.

Unfortunately, Lange and Berger did not pay particular attention to the purity of the materials which they used. Since commercial samples of potassium iodide almost invariably are contaminated by traces of bromide and chloride, this neglect casts some doubt on their conclusions. In the present study we have taken special care to use materials of a high degree of purity. Instead of working in neutral solution, as Lange and Berger did, we performed all titrations in the presence of a small amount of nitric acid, since adsorption of silver ions on the glass wall of the container is eliminated under such conditions.

Materials Used

Potassium Iodide.—Since potassium iodide is not easily purified by usual recrystallization methods, because of its great solubility in water and because of the doubtful removal of possible traces of chloride and bromide, we prepared the salt from pure hydriodic acid and purified potassium bicarbonate. Hydrogen iodide was synthesized directly from purified iodine and hydrogen by the classical method in which platinized asbestos is used as catalyst, and the gas was dissolved in water to give a concentrated solution.[2] The solution of hydriodic acid was nearly neutralized with purified potassium bicarbonate, and evaporated in a hydrogen atmosphere until a considerable quantity of potassium iodide separated out, which was filtered off and dried.

Silver.—The preparation of the pure silver used in this study has been described in a previous paper from this Laboratory.[3]

Nitric Acid.—The nitric acid used in this work was obtained by distilling C. P. concentrated acid in an all-glass still, the middle fraction only being collected.

Water.—Conductivity water was used in all preparative work and in the preparation of all solutions.

Apparatus.—A silver iodide electrode was used as indicator electrode in the titrations, and a saturated calomel electrode was used as reference electrode. The silver iodide electrodes were prepared by plating platinum gauze electrodes (cylinders 1 cm. in diameter and 1 cm. long) with silver from a 10% potassium argentocyanide solution at low current density. The silver electrodes were then iodized by making them anodes in the electrolysis of a dilute potassium iodide solution for a few minutes at low current density, followed by thorough washing with water.

The titration vessel consisted of a one-liter beaker, painted black on the outside, and provided with a tightly fitting bakelite cover with suitable holes for the buret-tip, salt bridge, electrode, thermometer and stirrer. This arrangement provided efficient light protection. A saturated solution of potassium nitrate, free from chloride, was used in the salt bridge, which was filled with fresh solution for each titration. For the hot titrations, the titration beaker was placed in an electrically heated water-bath whose temperature could be held constant to ±0.5°.

Weights and volumetric apparatus were calibrated carefully by standard methods. Weighings were corrected to vacuum on the following density basis, weights (brass) 8.4, silver 10.5, potassium iodide 3.12 and air 0.0012 g. per cc.

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[1] E. Lange and R. Berger, *Z. Elektrochem.*, **36**, 171, 980 (1930).

[2] We are indebted to E. R. Caley and M. G. Burford (private communication) for suggesting the apparatus for this synthesis. Details of the methods of preparation are described by the authors in Volume I of "Inorganic Syntheses."

[3] I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **57**, 2126 (1935).

Preparation of Potassium Iodide for Weighing.—Potassium iodide decomposes slightly when fused in air or nitrogen,[4] and the fused salt is strongly alkaline. We have found, however, that the salt may be melted in pure dry hydrogen with no trace of decomposition. Solutions of the salt which had been fused in hydrogen were always perfectly colorless, and showed no trace of alkalinity. Portions of the salt were prepared for weighing by melting for ten minutes at 700–725° in pure dry hydrogen in a platinum boat. The fused sample was allowed to cool to below 200° in hydrogen, and was then removed to a desiccator containing fused potassium hydroxide, where it remained until weighed.

Technique of the Titrations

Separate samples of silver and potassium iodide were weighed out for each titration, the silver being in the form of buttons weighing from 1.0 to 1.5 g. each. A silver button was first carefully weighed and transferred to a small Kjeldahl flask in which it was dissolved in 3 cc. of concentrated nitric acid with gentle heating. The solution was then heated to remove oxides of nitrogen, the heating being continued for at least fifteen minutes after the disappearance of brown fumes. The solution was cooled, transferred to the titration beaker, and diluted to approximately 500 cc. The resulting solution was approximately 0.02 *N* in silver and 0.04 *N* in nitric acid.

The carefully weighed sample of potassium iodide was dissolved in approximately 100 cc. of water in a special dropping funnel previously described,[3] and the solution was mixed thoroughly. The potassium iodide solution was run dropwise into the silver solution with constant mechanical stirring, from ten to fifteen minutes being required for the addition. The funnel and platinum boat were rinsed out with eight to ten portions of water, which brought the total volume of solution to between 750 and 850 cc., after which the bakelite cover was placed on the beaker. The beaker was placed in the water-bath, the electrode, stirrer, thermometer and salt bridge were put in place, and after heating to the desired temperature, the titration was completed with 0.01 *N* potassium iodide solution added from a microburet. Efficient mechanical stirring was employed, and the titrations were carried out in very faint diffuse daylight in a room with closely drawn shades, although this latter precaution was probably unnecessary because the titration vessel itself served as an efficient protection against light.

Titrations were made at room temperature, at 70 and at 90°, and some experiments were also made in which the precipitate was digested for some time at 95 to 100° before finishing the titration. A reflux condenser was used in the long digestion experiments to prevent evaporation of the solution.

In the majority of the titrations the end-point was found in the classical way from the maximum in $\Delta E/\Delta V$. However in the titrations at room temperature (without digestion) the maximum in $\Delta E/\Delta V$ was not well defined, and in these titrations the end-point was found by titrating to the equivalence potential.[5,3] The equivalence potential was determined by titrating very small amounts of silver with the dilute potassium iodide solution under the same conditions of acidity, temperature, and volume as in the actual titrations. At room temperature the equivalence potential found in this way was +0.098 volt against the saturated calomel electrode, in a 0.035 *N* nitric acid solution. The average solubility product of silver iodide in 0.035 *N* nitric acid, calculated from the data of several such "dilute" titrations, was 2.18×10^{-16} at 25°. Titration at room temperature is not practical because of the long time required for the e. m. f. to reach steady values, and furthermore (Table II) the error of the titration is greatest at this temperature. As long as an hour is required to obtain steady e. m. f. readings between each addition of reagent at 25°. The drift is particularly bad in the immediate vicinity of the end-point, and the exact position of the maximum in $\Delta E/\Delta V$ is difficult to locate. Under the conditions described, the end-point determined by titrating to the equivalence potential agreed within the limits of the experimental error with that determined from the maximum in $\Delta E/\Delta V$. This was no longer true when the titration was performed in the more usual manner, by taking e. m. f. readings five minutes after each addition of reagent without waiting until the potential had attained constant values. By titrating to the equivalence potential, exactly the same result was obtained as in the slow titration; however, the values of $\Delta E/\Delta V$ changed in an irregular way in the neighborhood of the equivalence potential and two maxima were found. For this reason, fast titration at room temperature is not recommendable.

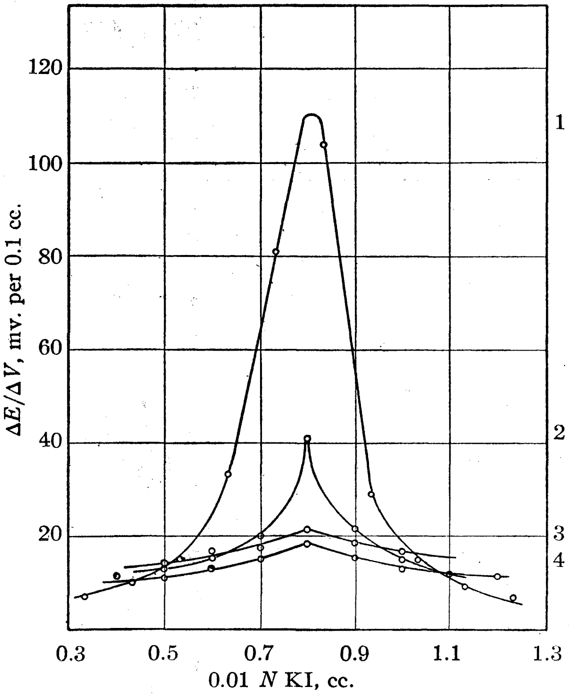

Fig. 1.—$\Delta E/\Delta V$ curves in region of equivalence point under various conditions: (1) digested 40 hours at 95°, titrated at room temp.; (2) direct titration at 70°; (3) direct titration at room temperature; (4) direct titration at 90°.

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[4] G. P. Baxter and F. N. Brink, THIS JOURNAL, **30**, 46 (1908).

[5] I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, 1932, p. 100.

Constant e. m. f. readings can be obtained in a relatively short time at 70 or 90°, except in the immediate vicinity of the end-point where fifteen to thirty minutes are required. The same is true when the precipitate is digested previous to titration at room temperature. Under the latter conditions the most pronounced break in the potential is found, since the adsorptive properties of the precipitate have become extremely small, and the solubility is much smaller than at higher temperatures (Curve 1, Fig. 1).

In Fig. 1 the change of $\Delta E/\Delta V$ in the region of the equivalence point is plotted against the volume of 0.01 N potassium iodide solution, under various conditions of titration. To simplify comparison the curves have been drawn so that the maximum value of $\Delta E/\Delta V$ came at the same point on the abscissa in each case. The numerical values of the volumes are thus without significance.

The final volume of the solutions varied between 750 and 850 cc., and the final concentration of nitric acid was 0.03 to 0.04 N.

Data of the Titrations

The data of a typical titration at 90° are given in Table I, which is self-explanatory. Table II contains a summary of all the various titrations. The values of the atomic weights given at the head of Table II were taken from the International Table of Atomic Weights for 1935.

Table I

Data of a Typical Titration at 90°

1.33153 g. of silver (vacuum) dissolved in 3 cc. of concd. nitric acid and diluted to 500 cc. 2.04659 g. potassium iodide (vacuum) dissolved in 100 cc. of water and added to silver solution at room temperature. Mixture heated to 90 ± 0.5°, and titrated at this temperature with 0.01036 N potassium iodide from microburet.

0.01036 N KI, cc.	E, volts	$\frac{\Delta E}{\Delta V}$	$\frac{\Delta^2 E}{\Delta V^2}$
0	+0.2218		
1.0	.1964		
1.4	.1657		
		109	
1.5	.1548		
		135	
1.6	.1413		+40
		175	
1.7	.1238		−52
		123	
1.8	.1115		
		100	
1.9	.1015		

$V = 1.6 + \frac{40}{92} \times 0.1 = 1.64$ cc. Correction to KI = 2.82 mg. Total KI = 2.04659 + 0.00282 = 2.04941 g. Ratio KI/Ag = 2.04941/1.33153 = 1.53913. Theory = 1.53889, Error = +0.016%.

Discussion of Results

A comparison of curves 2 and 4 in Fig. 1 shows that the magnitude of the break decreases with increasing temperature above about 70°, due to an increase in the solubility of silver iodide with increasing temperature. However, if the titration is made at a lower temperature, the magnitude of the break again decreases because of the increased adsorptive power of the precipitate. Curve 3 was obtained by performing the entire titration at room temperature, and it furnishes a striking illustration of the way in which the maximum is depressed by adsorption effects. Comparison of curves 1 and 3 illustrates the drastic decrease in the adsorptive power of silver iodide on aging. Although the solubility product of silver iodide at 70° is several hundred times greater than at room temperature, the adsorptive power of the precipitate as a result of aging is much less at the higher temperature, and hence the maximum is much more pronounced than that obtained in a titration carried out at room temperature in which the precipitate is not digested.

Although curves 3 and 4 of Fig. 1 indicate that the magnitude of the break is about the same at room temperature (without digestion) as at 90°, the e. m. f. readings obtained at the higher temperature are much more reliable, and hence the end-point can be accurately found from the location of the maximum in $\Delta E/\Delta V$ (Table I). In the titration at room temperature without digestion, the end-point can be found much more accurately by titrating to the equivalence potential than from the maximum in $\Delta E/\Delta V$.

An inspection of the data of Table II shows that the precision (reproducibility) of the titrations is very good; the average deviation from the mean of all the experiments at 70 and 90° is only ±0.005%. Titration at 90° gives the most accurate results, and the accuracy decreases in a very regular manner as the temperature of titration decreases. Digestion of the precipitate at 90°, and finally finishing the titration at room temperature, gives results almost as accurate as those at 90°. Furthermore, the e. m. f. in the final titration at room temperature after digestion, becomes steady more quickly than under any of the other conditions of titration.

A critical survey of the analytical data reported in Table II reveals that in the slow titration at room temperature the precipitate contains 0.1% of iodide in excess at the equivalence potential. In subsequent work it could be shown that this excess of iodide was present in the adsorbed state. On the basis of their study of electrodialyzed silver iodide sols, Verwey and Kruyt[6] predicted that the potentiometric iodide–silver titration should be in error by some tenths of a per cent. at

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[6] E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, **A167**, 149 (1933); see also Verwey, *Kolloid Z.*, **72**, 187 (1935).

TABLE II

RESULTS OF POTENTIOMETRIC COMPARISON OF POTASSIUM IODIDE AND SILVER

Ag = 107.880, I = 126.92, K = 39.096. Theoretical Ratio KI/Ag = 1.53889

No.	Ag (vacuum), g.	KI (vacuum), g.	Additional KI, g.	Total KI, g.	Ratio KI/Ag	Error, %	Conditions of titration, at
1	1.19100	1.82934	0.00370	1.83304	1.53907	+0.012	90°
2	1.33153	2.04659	.00282	2.04941	1.53913	+ .016	90°
3	1.15309	1.76976	.00498	1.77474	1.53911	+ .014	90°
4	1.14648	1.76258	.00215	1.76473	1.53925	+ .023	90°
5	1.16336	1.78937	.00106	1.79043	1.53902	+ .008[a]	90°
6	1.01570	1.56214	.00135	1.56349	1.53932	+ .028[a]	90°
7	1.19303	1.83414	.00213	1.83627	1.53916	+ .018[a]	90°
				Av.	1.53915	+ .017	
	Av. deviation from mean = ±0.005%.						
8	1.32755	2.03139	0.01260	2.04399	1.53967	+0.051	70°
9	1.41576	2.16939	.01040	2.17979	1.53966	+ .050	70°
10	1.23658	1.90227	.00144	1.90371	1.53950	+ .040	70°
11	1.13746	1.74996	.00139	1.75135	1.53970	+ .053	70°
				Av.	1.53963	+ .048	
	Av. deviation from mean = ±0.005%.						
12	1.18840	1.82652	0.00276	1.82928	1.53928	+0.025	Digested 30 hrs. at 95–100°. Final titration at room temp.
13	1.21629	1.86862	.00370	1.87232	1.53937	+ .031	
				Av.	1.53933	+ .028	
14	1.29978	1.99741	0.0046	2.0020	1.5402	+0.08	Slow titration at room temp.
15	1.05426	1.61901	.0051	1.6241	1.5404	+ .10	
16	1.08617	1.66334	.0100	1.6733	1.5405	+ .10[b]	Fast titration at room temp.

[a] Digested for twenty hours at 95 to 100° before finishing titration at 90°. [b] Waited only five minutes between each addition of dilute potassium iodide solution.

room temperature, since they deduced from their data that aged silver iodide at the equivalence potential ($C_{\mathrm{Ag}^+} = C_{\mathrm{I}^-}$) will contain adsorbed iodide. Under the experimental conditions described in this study it has been found that in the direct titration at room temperature the error due to the asymmetric location of the isoelectric point amounts to 0.10 ± 0.02%.

When the titration is carried out at 70° the precipitate is subjected to a fairly drastic aging process, consequently the error due to adsorption decreases to 0.05%. The error decreases to 0.017% when the titration is carried out at 90°. Under these conditions the aging is so drastic that the adsorptive power of the precipitate becomes virtually negligible. The error found at 90° is greater than the experimental error, and may be attributed to an extremely slight adsorption of iodide at the equivalence potential or to a slight error in the atomic weight of iodine, since the second decimal place in the latter is still somewhat uncertain.[7]

The fact that the error increases from 0.017 to 0.028% when the precipitate is titrated at room temperature after a drastic aging at 90°, lends support to the former assumption. Actually it could be shown that such a precipitate at room temperature exerted a slight adsorptive power toward silver and iodide ions.

Acknowledgment.—We wish to express our appreciation to the Graduate School of the University of Minnesota for a grant which enabled us to pursue this study.

Summary

1. Pure potassium iodide has been synthesized from hydriodic acid and potassium bicarbonate. The salt can be melted in a hydrogen atmosphere without decomposition.

2. The accuracy of the potentiometric iodide–silver titration has been investigated in a precise manner. The results show that in the slow titration of silver with iodide, the error at room temperature amounts to 0.1%, at 70 to 0.048% and at 90° to 0.017%. When the precipitate was digested at 90° near the equivalence point, and the titration finished at room temperature, the error was 0.028%. In all cases the precipitate contained an excess of iodide at the equivalence potential.

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(7) G. P. Baxter, O. Hönigschmid, P. LeBeau and R. J. Meyer, THIS JOURNAL, **57**, 787 (1935).

3. The errors found in the titration are caused by adsorption of iodide ions by the precipitate, and the error (adsorption) can be reduced to a very small value by titrating at 90°, or by digesting the precipitate at 90° in the presence of a slight excess of silver previous to finishing the titration at room temperature.

MINNEAPOLIS, MINN. RECEIVED MARCH 30, 1936

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Adsorption of Silver and Iodide Ions by Freshly Precipitated Silver Iodide. The Isoelectric Point of the Fresh Precipitate

BY I. M. KOLTHOFF AND J. J. LINGANE

In a previous communication,[1] we described the results of an investigation of the accuracy of the potentiometric iodide–silver titration. It was found that when the titration was performed at room temperature, to the equivalence potential, approximately 0.10% too much potassium iodide was required. In this paper we present experimental evidence which proves that the excess requirement of potassium iodide at room temperature is due to an adsorption of iodide ions by the fresh precipitate at the potentiometric end-point.

We have also directly determined the "isoelectric point" of freshly precipitated silver iodide. The isoelectric point, or "zero-point charge," is defined as the silver-ion concentration at which neither silver nor iodide ions are adsorbed by the precipitate.

In their study of the precision of the potentiometric iodide–silver titration, Lange and Berger[2] determined the adsorption of silver nitrate and potassium iodide on freshly precipitated silver iodide at various temperatures. They found that the adsorption of the "potential determining" silver and iodide ions agreed with the expression, $\Delta X = K \Delta \log C$; in which X is the amount adsorbed, K is a constant and C is the equilibrium concentration of the ion being adsorbed. They found that this relation was valid at temperatures between 30 and 90°. It is very doubtful, however, whether the values of X determined at the higher temperatures are really significant, because the fresh precipitate ages quite rapidly at higher temperatures, causing a continuous decrease in its adsorptive power with resultant continuous desorption of the ion initially adsorbed. We have found that this desorption process is very slow at room temperature in the presence of an excess of silver, but is greatly accelerated at the higher temperatures.

Lange and Berger concluded from their experiments that silver ions are adsorbed more strongly than iodide ions at equal equilibrium concentrations. Their conclusion was based on the erroneous assumption that neither adsorption of silver nor iodide ions occurs at the potentiometric end-point, or "equivalence potential," where $c\text{Ag}^+$ in solution is equal to $c\text{I}^-$. Actually, as will be shown in the present paper, the isoelectric point of freshly precipitated silver iodide at room temperature is found at a silver ion concentration of approximately 10^{-6} molar, the silver ion concentration thus being nearly 10,000 times as great as the iodide-ion concentration.

In agreement with Lange and Berger, Verwey and Kruyt[3] found in their work with well aged electrodialyzed silver iodide *sols* that the adsorption of iodide ions follows the expression $\Delta X = K \Delta \log C$. They could not determine the location of the isoelectric point directly without flocculating the sols, but with the aid of the foregoing expression they extrapolated to the point of zero adsorption (isoelectric point), and found that this point corresponded to a silver-ion concentration of 10^{-6} molar. This value agrees very well with the value we determined directly with a fresh *precipitate*.

Gorochovsky[4] found that the isoelectric point of silver iodide sols depended greatly on the silver iodide concentration of the sols. The results of his experimental work, however, are inconclusive since he did not correct for adsorbed silver or iodide ions on the surface of the silver iodide.

Lange and Berger mention the possibility of an

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[1] I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **58**, 1524 (1936).

[2] E. Lange and R. Berger, *Z. Elektrochem.*, **36**, 171, 980 (1930).

[3] E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, **A167**, 149 (1933).

[4] G. N. Gorochovsky, *J. Phys. Chem.*, **39**, 465 (1935); see also G. N. Gorochovsky and J. R. Protass, *Z. physik. Chem.*, **A174**, 122 (1935).

adsorption of silver ions from neutral solution on the glass walls of containing vessels, but they made no attempt to determine its extent. In order to exclude such possible adsorption we worked in dilute nitric acid medium.

Experimental

The materials and apparatus used in this work have already been described.[1] In all experiments the iodide solution was added at room temperature to a slight excess of silver solution, slightly acidified with nitric acid, and the same titration technique was followed as in the paper already referred to.[1]

In order to obtain quantitative information regarding the absorption of silver and iodide ions, it was necessary to know the relation between the measured e. m. f. of the titration cell and the silver-ion concentration of the solutions. As a result of many measurements of the e. m. f. obtained with solutions of known and widely varied silver-ion concentration, in which the total ionic strength and the concentration of nitric acid were the same as in the titrations, we found the following empirical relation: $E_{298} = 0.560 + 0.0591 \log (\mathrm{Ag^+})$. This equation holds at 25° for measurements in solutions 0.035 N in nitric acid, and 0.01 N in potassium nitrate, the potential of the silver iodide electrode being measured against the saturated calomel electrode with saturated potassium nitrate in the salt bridge.

The interpretation of the experimental data also required a knowledge of the solubility of silver iodide under the conditions of the titrations. We determined the solubility product by performing titrations with extremely dilute silver and iodide solutions, and calculated the desired quantity from the data so obtained.[5,6] The average value of the solubility product of silver iodide determined in this way was 2.18×10^{-16} at 25° in 0.035 N nitric acid ($\sqrt{S_{\mathrm{AgI}}} = 1.48 \times 10^{-8}$). Hence at the equivalence potential $p\mathrm{I} = p\mathrm{Ag} = 7.83$, and $E = +0.098$ v.

Adsorption of Iodide at the Equivalence Potential.—The amount of iodide adsorbed at the equivalence potential was first determined by measuring the amount of iodide desorbed when a fresh precipitate at the equivalence potential was aged by digestion at 90°.

It was found that such a fresh precipitate aged only very slowly at room temperature. For example, in a typical experiment the titration was stopped when the e. m. f. reached 0.113 v. and had remained steady at this value for an hour. The mixture was allowed to age overnight at room temperature with constant stirring, during which time the e. m. f. only decreased to 0.098 v.; in other words, the pAg only increased from 7.56 to 7.83. Therefore, only a very slight desorption of iodide takes place during the time required to reach steady e. m. f. at room temperature (*ca.* two hours), previous to digestion at 90°.

The amount of excess iodide retained by a fresh precipitate at room temperature at the equivalence potential was then determined in the following way. A titration was carried out according to the careful technique described in a previous paper,[1] using exactly known amounts of silver and potassium iodide. The titration was stopped when the e. m. f. reached +0.091 v. (practically the equivalence potential), and had remained steady at this value for an hour. A slight excess of pure solid potassium bicarbonate was added to neutralize free nitric acid, and thus eliminate the possibility of oxidation of desorbed iodide by the acid during the digestion. The mixture was then heated to 90–95°, and digested for twenty hours at this temperature under reflux. After cooling to room temperature, the mixture was again acidified to a concentration of 0.035 N in nitric acid, the e. m. f. was measured and found to be −0.075 v., corresponding to a change in pAg from 7.94 to 10.74, showing that much iodide was desorbed during the digestion. This desorbed iodide was titrated potentiometrically with 0.01 N silver nitrate, and found to correspond to 1.39 mg. of potassium iodide. 1.6241 g. of potassium iodide was used in the preparation of the silver iodide, hence the error due to adsorption of iodide amounts to 0.086%, whereas in the precise titrations[1] an error of 0.1 ± 0.02% was found. Within the experimental error, therefore, this deviation can be attributed to iodide adsorbed on the precipitate at the equivalence potential.

Although the precipitate was obtained by adding the iodide solution to the silver solution, the objection might be raised that the excess iodide in the precipitate at the equivalence potential is occluded within, and not adsorbed on, the precipitate. In the following manner it was shown that the excess iodide was actually absorbed. If iodide ions are primarily adsorbed by silver iodide, then either hydrogen or potassium ions (or both) must be adsorbed as counter ions, since these are the only cations present in the solution. The univalent counter ions may be replaced by a cation of higher valence. Thus, if a dilute solution of aluminum is added to the system, the following replacement reaction will take place

$$\mathrm{AgII^-}\,\Big|\,\underset{\text{Counter ion}}{\mathrm{K^+}} + \underset{\text{Solution}}{1/3\mathrm{Al^{+++}}} \longrightarrow \mathrm{AgII^-}\,\Big|\,\underset{\text{Counter ion}}{1/3\mathrm{Al^{+++}}} + \underset{\text{Solution}}{\mathrm{K^+}}$$

The aluminum exchange experiments were carried out in the following way. Two fresh silver iodide precipitates were prepared by precipitating 0.01 mole of silver with slightly less than the equivalent amount of potassium iodide at room temperature, in a final volume of about 140 cc. The first precipitate was adjusted to a pAg of 6.0 (isoelectric point) by adding 0.01 N potassium iodide solution, and after the e. m. f. had become steady at this point, the precipitate was washed eight to ten times by decantation with 1.0×10^{-6} N neutral silver nitrate solution. The precipitate was then suspended in 50 cc. of a solution that was 6.0×10^{-5} molar in aluminum nitrate and 1.0×10^{-6} N in silver nitrate (isoelectric solution), and the suspension was stirred mechanically at room temperature for thirty minutes. The amount of aluminum in the solution was just sufficient to displace the adsorbed potassium or hydrogen ions equivalent to 0.1% adsorbed iodide, if iodide was adsorbed on the precipitate. The supernatant solution was poured off and tests for aluminum ion were made on 10-cc. portions, using 1,2,5,8-hydroxyanthraquinone as reagent, according to the procedure given by Kolthoff.[7] A pure water blank, and the original aluminum

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[5] I. M. Kolthoff, *Rec. trav. chim.*, **47**, 397 (1928).

[6] I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **57**, 2126 (1935).

[7] I. M. Kolthoff, *Chem. Weekblad*, **24**, 544 (1927).

solution, were used for comparison. The supernatant solution gave virtually as strong a reaction for aluminum as the original solution, showing that no aluminum ions were adsorbed or exchanged by the fresh silver iodide at the isoelectric point. In other words, there was no iodide adsorbed on the isoelectric precipitate.

The second fresh precipitate was adjusted to a *p*Ag of 7.8 (equivalence point) by the addition of dilute potassium iodide solution, and after the e. m. f. had become steady, the precipitate was washed by decantation with eight to ten portions of pure water. The washed precipitate was stirred with 50 cc. of 6.0×10^{-5} molar (18×10^{-5} *N*) aluminum nitrate solution for thirty minutes as in the case of the first precipitate, and the supernatant solution was tested for aluminum ion as before. The tests showed that practically all the aluminum (more than 80%) had disappeared from the solution on shaking with the equivalence-point precipitate. The amount of exchange found at this point corresponds to the presence of 0.08–0.09% *adsorbed* iodide.

The desorption and the exchange adsorption experiments furnish conclusive confirmation of the fact that freshly precipitated silver iodide (at room temperature) contains between 0.08 and 0.10% excess iodide in the adsorbed state at the equivalence potential. Incidentally it may be mentioned that from the change of the hydrogen-ion concentration of the supernatant liquid in the exchange experiments, it was found that potassium and not hydrogen ions were the counter ions originally adsorbed with the iodide.

Isoelectric Point of Freshly Precipitated Silver Iodide.—The silver ion concentration corresponding to the isoelectric point of silver iodide was determined in the following way. A slight deficiency of a solution of potassium iodide was added at room temperature to a solution of silver nitrate slightly acidified with nitric acid. Dilute potassium iodide solution was added until the *p*Ag indicated in Table I was reached, after which the mixture was stirred at room temperature for two to three hours until the e. m. f. became practically constant. The mixture was digested overnight at 90 to 95° in a closed glass-stoppered flask, and then cooled to room temperature and the e. m. f. measured. The direction in which the e. m. f. (*p*Ag) changed on digestion indicated whether silver or iodide ions had been desorbed, and the magnitude of the change was a measure of the amount desorbed. By repeating the experiments at various silver-ion concentrations, it was possible to locate the point at which there was no change in the e. m. f. on digestion (no desorption) and this point was the isoelectric point of the precipitate.

In the experiments in which iodide was desorbed, the free nitric acid in the solution (0.035 *N*) was neutralized with a slight excess of pure potassium bicarbonate before digestion, in order to prevent oxidation of the iodide. The solution was again acidified, after it had been cooled to room temperature for the final e. m. f. measurement.

The amount of silver iodide was the same in all experiments (0.01 of a mole), and the final volume of solution was 135 to 145 cc.

The data of the desorption experiments are given in Table I. The last column of the table gives the amount of silver or iodide desorbed, expressed in micro-equivalents (10^{-6} equivalents) per 0.01 mole of silver iodide.

TABLE I

RESULTS OF DESORPTION EXPERIMENTS. ISOELECTRIC POINT OF SILVER IODIDE

0.01 mole of AgI in all experiments, in volume of 135 cc. to 145 cc.; 0.035 *N* in nitric acid.

	E, volts		*p*Ag		*X*
	Before digestion	After digestion	Before digestion	After digestion	Micro-equiv. desorbed per 0.01 mole of AgI
1	0.3285	0.3441	3.92	3.66	12.6 Ag$^+$
2	.2977	.3192	4.45	4.08	6.7 Ag$^+$
3	.2673	.3002	4.96	4.41	4.1 Ag$^+$
4	.2431	.2707	5.37	4.91	1.1 Ag$^+$
5	.2061	.2265	6.00	5.65	0.18 Ag$^+$
6	.1999	.171	6.12	6.60	.07 I$^-$
7	.1974	.172	6.15	6.58	.09 I$^-$
8	.1828	.077	6.40	8.19	(.05) I$^-$

The data of the experiments in which iodide was desorbed are less reliable quantitatively, than in the experiments in which silver was desorbed, because of difficulty in obtaining steady e. m. f. readings in the acid iodide solutions. For this reason we have not extended the experiments very far to the iodide side.

An inspection of the data shows that the isoelectric point lies at a *p*Ag of about 6.05. This result is in excellent agreement with the value found by Verwey and Kruyt, who worked with well aged electrodialyzed silver iodide *sols*.

Adsorption of Silver and Iodide Ions by Freshly Precipitated Silver Iodide.—Precision titrations of silver with iodide were carried out at room temperature as described in a previous paper,[1] and the amounts of silver and iodide ions adsorbed by the fresh precipitate were calculated by comparing the titration curve obtained in this way with the theoretical curve. The theoretical curve is based on the assumption that the precipitate has no adsorptive properties.

The data obtained in a typical titration are given in Table II, and plotted in Fig. 1. The differences between points on the abscissas of the theoretical and experimentally observed titration curves at equal values of the e. m. f. are a direct measure of the amount of silver or iodide ions adsorbed by the precipitate.

The following examples will illustrate the method used to calculate the theoretical curve, and the amounts of silver and iodide ions adsorbed at various points on the experimental curve.

The initial amounts of potassium iodide and silver taken for the experiment were 1.61901 and 1.05426 g., respectively. Since the theoretical KI:Ag ratio is 1.53889, the theoretical amount of silver required to precipitate 1.61901 g. of potassium iodide is 1.05206 g. Therefore, the total amount of excess silver distributed between the liquid and solid phases, at the zero point on the curve before any dilute potassium iodide solution was added, was 1.05426 − 1.05206 = 0.00220 g. in 750 cc. If we assume that this excess silver is entirely in the liquid phase (no adsorption), the silver-ion concentration of the solution should be $2.72 \times 10^{-5} N$. Hence $p\text{Ag}_{\text{calcd.}}$ is 4.57, and $E_{\text{calcd.}}$ is +0.290 volt (see Fig. 1). However, the observed e. m. f. at this point was 0.283 volt, corresponding to a silver-ion concentration of $2.04 \times 10^{-5} N$ ($p\text{Ag}_{\text{obsd.}} = 4.69$). The difference between the calculated and observed silver-ion concentrations is, therefore, 6.8×10^{-6} equiv. per liter, corresponding to 5.1×10^{-6} equiv. per 750 cc. (5.1 microequivalents) which is the amount of silver adsorbed (X_{Ag}).

The theoretical end-point of the titration, corresponding to the original excess of 0.00220 g. of silver, is 1.96 cc. of 0.0104 N potassium iodide. After the addition of 1.9 cc., the observed silver-ion concentration was greater than that calculated, the difference corresponding to an adsorption of 0.3 of a microequivalent of iodide. Upon addition of more than 1.96 cc. of dilute iodide solution, the calculated iodide-ion concentration is found from the difference between 1.96 cc. and the amount added. The difference between the calculated and observed iodide-ion concentrations (multiplied by 0.75) corresponds to the amount of iodide adsorbed, after allowance for the amount of silver in the solution ($p\text{Ag}_{\text{obsd.}}$). For example, after addition of 2.3 cc., the excess iodide in the system (actually in the precipitate) corresponded to 3.52 microequivalents per 750 cc. and the solution contained 0.25 microequivalents of silver. Therefore, $X_{\text{I}} = 3.52 + 0.25 = 3.77$ microequivalents.

TABLE II

DATA IN REGION OF EQUIVALENCE POINT IN TITRATION AT ROOM TEMPERATURE. ADSORPTION OF SILVER AND IODIDE

1.61901 g. of potassium iodide in 100 cc. of water added at room temperature to 500 cc. of solution containing 1.05426 g. of silver. Titration finished slowly at room temperature with 0.0104 N potassium iodide solution. Final volume 750 cc.; 0.035 N in nitric acid.

0.0104 N KI, cc.	Volts	pAg, obsd.	pAg, calcd.	X_{Ag} Micro-equiv. per 0.01 mole AgI	X_{I} Micro-equiv. per 0.01 mole AgI
0	0.283	4.69	4.57	5.1	
0.5	.274	4.84	4.69	4.3	
1.0	.260	5.08	4.88	3.8	
1.5	.238	5.45	5.19	2.1	
1.7	.225	5.66	5.44	1.1	
1.9	.211	5.92	6.08		0.3
2.1	.195	6.18	9.95		2.0
2.3	.177	6.48	10.33		3.8
2.5	.156	6.84	10.54		5.7
2.6	.145	7.03	10.61		6.7
2.7	.133	7.23	10.67		7.7
2.8	.121	7.43	10.73		8.7
2.9	.107	7.67	10.78		9.8
3.0	.090	7.96	10.83		10.8
3.1	.071	8.28	10.86		11.8
3.2	.049	8.64	10.90		12.8
3.3	+.029	8.98	10.93		13.8
3.5	−.007	9.61	10.99		15.4
3.7	.032	10.02	11.04		16.4
4.0	.055	10.42	11.11		16.9

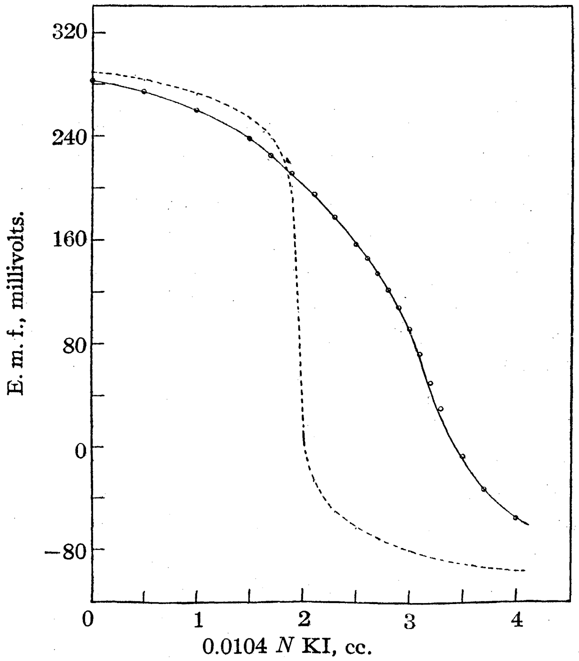


Fig. 1.—Titration curve at room temperature compared with theoretical (dotted) curve, data from Table II.

By reference to Fig. 1, it will be observed that the experimental and theoretical curves intersect at $E = +0.215$ v., corresponding to a pAg of 5.85, and hence there is no adsorption of silver or iodide ions at this point (isoelectric point). This value for the isoelectric point is in very good agreement with the value 6.05 determined in the desorption experiments. It must be clearly understood that the isoelectric point determined in this experiment and the method used to calculate the adsorption of silver and iodide ions by the precipitate, are entirely independent of any deductions or assumptions from the previous experiments. The calculations were based solely on the initial amounts of silver and potassium iodide taken and on the theoretical KI:Ag ratio.

Discussion

It is evident from Fig. 2, that the adsorption of silver ions by freshly precipitated silver iodide follows the expression $\Delta X = K \Delta \log C$. The same relation is found for the adsorption of iodide between *p*Ag = 5.85 and *p*Ag = 7.2, but at higher iodide-ion concentrations the values found for X_{I} are less than correspond to the foregoing equation.

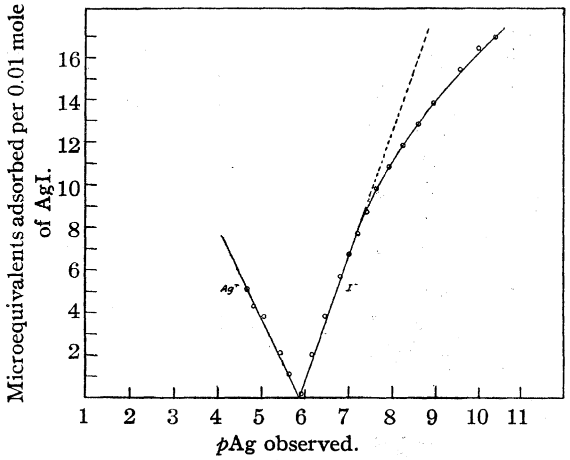


Fig. 2.—Adsorption of silver and iodide ions by freshly precipitated silver iodide, data from Table II.

It should be mentioned that this deviation is probably connected in some way with the fact that the e. m. f. measurements in the acid iodide solutions are somewhat unreliable. In addition, the precipitate ages more rapidly in the presence of excess iodide than when an excess of silver is present, and it is therefore to be expected that adsorption of iodide will become correspondingly less. It is possible, therefore, that the foregoing relation actually does hold over a wider range of iodide-ion concentrations, but it is very difficult to verify this possibility with a fresh precipitate. Working with an aged silver iodide *sol*, Verwey and Kruyt[3] found that the adsorption of iodide obeyed the foregoing relation over a much greater concentration range, than we have found with a fresh *precipitate*.

The K value found for iodide is greater than that of silver, indicating a greater adsorption of iodide than of silver ions. This result is contrary to that of Lange and Berger,[2] who failed to realize that over the region on their "silver adsorption" line between *p*Ag 6.0 and 7.8, there is actually an adsorption of iodide and not of silver ions.

If the foregoing deductions from the experimental data are correct, the precipitate should have the stoichiometric composition at the isoelectric point (*p*Ag = 6.0). As a matter of fact, we have found in the precise titrations that the theoretical KI:Ag ratio is found at the isoelectric point, when the proper correction is made for the excess silver in the solution. For example, in the titration whose data are given in Table II, if the end-point is assumed to be at the equivalence potential (+0.098 v.) the corresponding volume of 0.0104 N potassium iodide solution is 2.95 cc., the correction to the initial amount of potassium iodide taken is +5.1 mg., and hence the total amount of potassium iodide required to react with 1.05426 g. of silver is 1.6190 + 0.0051 = 1.6241 g. Therefore, the ratio KI:Ag calculated from these data is 1.5404, compared to the theoretical value 1.53889, and hence 0.10% too much potassium iodide was required. However, if the end-point of the titration is taken at the isoelectric point (E = 0.202 v., *p*Ag = 6.05), the corresponding volume of 0.0104 N potassium iodide solution is 2.01 cc., the correction to the initial amount of potassium iodide taken is 3.46 mg., and hence the total amount of potassium iodide is 1.61901 + 0.00346 = 1.62247 g. The amount of silver corresponding to *p*Ag = 6.05 in a volume of 750 cc. is 0.08 mg., and when this amount is subtracted from the initial weight of silver taken (1.05426 g.) the net amount of silver required is 1.05418 g. Therefore, the ratio KI:Ag is 1.62247 ÷ 1.05418 = 1.53908, which is only 0.006% larger than the theoretical ratio 1.53889. This result furnishes further striking confirmation of the deductions put forward in this paper.

Finally, this study shows that it is virtually impossible to obtain a true equivalent body of silver iodide by titration to the equivalence potential. Even if such a precipitate is washed repeatedly, it will be impossible to free it entirely of adsorbed iodide. A true equivalent body can be prepared by titration to the isolectric point (*p*Ag = 6.0), but such a precipitate will remain a true equivalent body only as long as it is kept in the isoelectric solution (*p*Ag = 6.0), because on washing with water it will again adsorb an excess of iodide.

Acknowledgment.—We wish to acknowledge our gratitude to the Graduate School of the University of Minnesota for the financial assistance which made this work possible.

Summary

1. The isoelectric point of freshly precipitated silver iodide has been found at a pAg of 6.0.

2. It has been shown that freshly precipitated silver iodide at the equivalence potential ($p\text{Ag} = p\text{I} = 7.83$) retains an excess of iodide adsorbed, corresponding to 0.09% of the total amount of iodide in the precipitate.

3. The adsorption of silver and iodide ions by the fresh precipitate follows the expression $\Delta X = K\Delta \log C$ in the pAg range between 4 and 7.2, iodide ions being more strongly adsorbed than silver ions.

4. The theoretical ratio KI:Ag is found in the potentiometric titration of silver with iodide at room temperature, if the end-point of the titration is taken at the isoelectric point ($p\text{Ag} = 6.0$), instead of at the equivalence potential, and if a correction is applied for the excess silver ions in the solution.

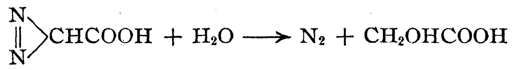
MINNEAPOLIS, MINN. RECEIVED MARCH 30, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Catalytic Decomposition of Diazoacetate Ion in Aqueous Solution[1]

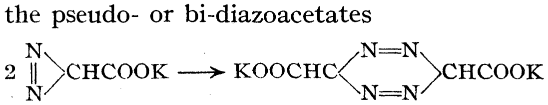
BY CECIL V. KING AND EDGAR DARE BOLINGER

Solutions containing salts of diazoacetic acid were first prepared by Curtius,[2] by alkaline hydrolysis of diazoacetic ethyl ester. The salts are, he found, stable in alkaline solution, but decompose with rapid evolution of nitrogen on neutralization with even carbonic acid, indicating that the acid is unstable



$$\begin{matrix}\mathrm{N}\\ \| \\ \mathrm{N}\end{matrix}\!>\!\mathrm{CHCOOH} + \mathrm{H_2O} \longrightarrow \mathrm{N_2} + \mathrm{CH_2OHCOOH}$$

Traube[3] made the sodium salt both by alkaline hydrolysis of the ester and by reduction of isonitroaminoacetic acid with sodium amalgam, and isolated the pure crystals from the solution. The preparation was further studied by Hantzsch and Lehmann[4] and by Müller,[5] who showed that the salts polymerize slowly in alkaline solution to the pseudo- or bi-diazoacetates



$$2\begin{matrix}\mathrm{N}\\ \| \\ \mathrm{N}\end{matrix}\!>\!\mathrm{CHCOOK} \longrightarrow \mathrm{KOOCHC}\!<\!\begin{matrix}\mathrm{N{=}N}\\ \\ \mathrm{N{=}N}\end{matrix}\!>\!\mathrm{CHCOOK}$$

(or isomers)

Pure solid potassium diazoacetate is stable if kept dry, cool and in the dark. It explodes on heating or on shock.

In this research it was found possible to study the rate of nitrogen evolution when the potassium salt is dissolved in dilute alkali or in buffers of very weak acids and their salts. The reaction is exceedingly sensitive to general acid catalysis, and is of particular interest because the reaction of a negative ion with the acid catalyst is involved. So far as the authors are aware, no other case of this type has been studied. If it is assumed that the rate-controlling step in such a catalysis involves the transfer of a proton from the acid to the reacting molecule, a negative ion should be much more sensitive to such catalysis than a neutral molecule. In accordance with this supposition it is found that the hydrogen-ion catalysis of this reaction is greater than the corresponding diazoacetic ester catalysis by some ten million-fold.

The reaction is of interest, too, because it shows abnormalities of a type first observed in the basic catalysis of nitramide decomposition in *m*-cresol solution.[6] In that case catalysis by anion bases was found to vary inversely with the concentration of the corresponding acid so that it was necessary to extrapolate the molar basic constants to $1/C_{\text{acid}} = 0$ to obtain comparable values. The catalysis by the anion of the solvent was variable and much lower than the value predicted from the catalysis by other bases. The latter abnormality was also found in the nitramide catalysis in water solution, *i. e.*, catalysis by the hydroxyl ion is lower than that predicted from the other

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[1] Condensed from Master's and Doctor's theses presented by Edgar Dare Bolinger in partial fulfilment of the requirements for these degrees at New York University, in 1934 and 1936.

[2] Curtius, *Ber.*, **18**, 1283 (1885).

[3] Traube, *ibid.*, **29**, 667 (1896).

[4] Hantzsch and Lehmann, *ibid.*, **34**, 2521 (1901).

[5] Müller, *ibid.*, **41**, 3136 (1908).

[6] Brönsted, Nicholson and Delbanco, *Z. physik. Chem.*, **A169**, 379 (1934).

bases.[7,8] In the diazoacetate decomposition it has been found possible to study these abnormalities in greater detail. The catalysis by an acid decreases with increasing acid concentration, with increasing base concentration, and on addition of other acids. While it is possible to systematize these irregularities, no explanation has been found; one similar to that offered by Brönsted, Nicholson and Delbanco[6] is obviously inadequate.

In buffers of *p*H 10 or higher, the diazoacetate decomposition is strictly unimolecular. In neutral or slightly acid solutions, however, side reactions take place which increase the *p*H. The most important of these is replacement of nitrogen by the glycolic acid formed instead of water. This is analogous to the acid catalysis of nitrogen replacement by acids in the diazoacetic ester decomposition, which takes place to some extent in aqueous, but especially in non-aqueous solutions.[9]

Materials, Apparatus and Procedure

Potassium Diazoacetate.—Diazoacetic ethyl ester was hydrolyzed as described by Müller[5] by shaking with an equal weight of potassium hydroxide in 2 *M* solution. When the ester phase had just disappeared (about four hours) the solution was evaporated, as rapidly as possible, almost to dryness (at 25° *in vacuo* with an oil pump and "dry-ice" trap). The desired salt is somewhat soluble in alcohol, practically insoluble in ether; the polymer (which is formed to some extent) is practically insoluble in alcohol. Consequently the residue was extracted with alcohol and the diazoacetate precipitated by adding about 5 volumes of ether; potassium hydroxide remains in solution. This differs from Müller's method in that he recovered the salt by evaporating the solution almost to dryness, sucking off the mother liquor and washing the crystals with alcohol. This procedure, we found, almost invariably leads to a product containing 10–20% of the polymer, which seems to be formed rather rapidly in the presence of alcohol. In one preparation 22 g. of crude salt was obtained from 57 g. of diazoacetic ester, and 12 g. of pure salt was obtained on recrystallization (solution in alcohol, precipitation by adding ether). The best salt gave off 96–99% of the theoretical nitrogen on addition of acid; other samples containing 10–20% polymer were used in some of the experiments with no appreciable effect on the rate.

All water used was redistilled from acid permanganate in a quartz still. All alkaline solutions were made up free from carbonate, protected from the air with soda lime tubes, and withdrawn through side-arm burets. *Phenol* solutions were standardized by the bromate–bromide method[10] and the buffers made by mixing portions with the necessary amount of sodium hydroxide. Redistilled *piperidine* of the correct boiling point was dissolved and the solution standardized against hydrochloric acid (methyl red). All other solutions were made from C. P. or "Reagent" quality chemicals and standardized when necessary.

Apparatus.—Nitrogen evolution was followed with an apparatus similar to that used previously by Brönsted and Duus.[11] The reaction flasks were of 200-cc. capacity, and 100 cc. of solution was used in each run. The potassium diazoacetate was usually made 0.005 *M* (0.062-g. sample), although this was varied from 0.0025 to 0.01 *M* with not over 3% variation in rate constants. In very slow experiments the diazoacetate sample was dissolved, and a glass capsule containing solid oxalic acid was suspended in the flask neck; after sufficient pressure readings were obtained this was dropped in to hasten attainment of the final pressure. Since in this type of measurement the final reading is of greater importance than any other single reading, care was taken to check the final pressure over a period of several hours.

The reaction flasks were immersed in a thermostat maintained at 25 ± 0.01°. Since the manometers were not thermostated, care was taken to keep the room temperature constant to ±0.5° while readings were being made.

In a number of experiments it was necessary, as noted later, to measure the *p*H of the solutions after the decomposition. This was done with hydrogen electrodes of the Hildebrand type, the potential against a calomel half-cell being measured with a Leeds and Northrup type K potentiometer. Duplicate electrodes checked to 0.1 millivolt or less.

Velocity constants were obtained by plotting log $(a - x)$, or log (final pressure minus pressure at time t) against the time in minutes; the slope of the straight line obtained is $-1/2.303$. This method avoids errors due to lack of pressure equilibrium at the beginning of the run and was especially useful when the acidity decreased at the start and the reaction became unimolecular only after the first few minutes of the run.

Preliminary Experiments

Several experiments were made to determine whether the diazo salt contained any potassium hydroxide (especially the less pure samples), or was appreciably hydrolyzed. A solution containing 0.01 *M* phenol, 0.01 *M* phenate and a few drops of thymolphthalein solution was divided into two portions. To one, enough potassium diazoacetate to make the solution 0.005 *M* was added. No difference in color could be detected either immediately or after decomposition of some or all of the salt. Similar results were obtained when the *p*H of phosphate buffers was found to change little on addition and decomposition of the salt. When a sample of the salt was dissolved in water the *p*H rose to about ten; the *p*H, as measured with a glass electrode, did not change during the remainder of the decomposition. This could not indicate simple hydrolysis of the salt since in that case the *p*H should go back during the decomposition to that of potassium glycolate. It was caused by the initial formation of glycoylglycolate, to be described below. It can be concluded that the diazoacetic acid is at least as strong as glycolic acid, as would be ex-

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[7] Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

[8] Marlies and La Mer, THIS JOURNAL, **57**, 1812 (1935).

[9] Brönsted and Bell, *ibid.*, **53**, 2478 (1931).

[10] Treadwell and Hall, "Analytical Chemistry," 7th ed., Vol. II, John Wiley and Sons, Inc., N. Y., 1930, p. 591.

[11] Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

pected from its molecular structure. The experiments with buffers also showed that potassium hydroxide was negligible as an impurity in the samples of diazoacetate prepared.

Experimental Results

1. Hydrogen (Oxonium) Ion and Water Catalysis.—The rate in dilute sodium hydroxide was found to give a constant molar value for the hydrogen-ion catalysis between concentrations of 0.4×10^{-12} and 2.0×10^{-12} *M*. The solutions were made up as indicated in Table I, the ionic strength being kept constant at 0.105 by additions of sodium chloride. The half-time of the reaction varied from seven to fifty hours. The hydrogen-ion concentrations were calculated from the sodium hydroxide concentrations, using 1.71×10^{-14} for the ion product constant of water in sodium chloride at 0.1 μ.[12]

TABLE I

CATALYSIS BY HYDROGEN ION: 25°, 0.105 μ

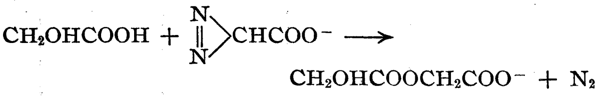
Expt.	C_{NaOH}, *M*	$C_{H_3O^+} \times 10^{12}$	$k \times 10^4$
31	0.008	2.14	7.76
27	.010	1.71	6.67
30	.0133	1.29	5.26
28	.020	0.85	3.45
29	.040	.43	2.08
32	.01	μ = .055	6.46
33	.01	μ = .015	6.22

The results are plotted in Fig. 1(A). The slope of the straight line, 3.57×10^8, is the molar catalytic constant for the hydrogen ion. The intercept, 5.5×10^{-5}, is the water constant, and when divided by the water concentration gives the molar water constant, 9.92×10^{-7}.

As shown by expts. 27, 32 and 33, catalysis in these solutions has a small, probably linear, positive salt effect amounting to 7% between μ = 0.015 and 0.105.

To obtain rates at higher hydrogen-ion concentrations, pure sodium chloride solutions were used, with or without the addition of very small amounts of hydrochloric acid. In these solutions a portion of the nitrogen was evolved very rapidly; the reaction then became slower and followed the unimolecular law for the remainder of the nitrogen evolution. The *p*H rose rapidly in this first period to the neighborhood of 10. A rate curve is shown in Fig. 2, compared with a normal rate curve in a phosphate buffer whose *p*H remains constant.

This abnormality was thought at first to be due to the formation of chloroacetic acid instead of glycolic acid, since a similar side reaction occurs with diazoacetic ester.[13] However, titration of the resulting solution with silver nitrate (dichlorofluorescein as indicator) showed no loss of chloride ion. The side reaction was finally shown to be formation of glycoylglycolate ion according to the reaction



$$CH_2OHCOOH + \overset{N}{\underset{N}{\|}}\!\!>CHCOO^- \longrightarrow CH_2OHCOOCH_2COO^- + N_2$$

Glycoylglycolic acid has been prepared and studied by Wolff and Lüttringhaus.[14] It is sufficiently stable, in cold solution, to titrate quantitatively with strong bases: heating on a water-bath with excess base hydrolyzes it completely to glycolate.

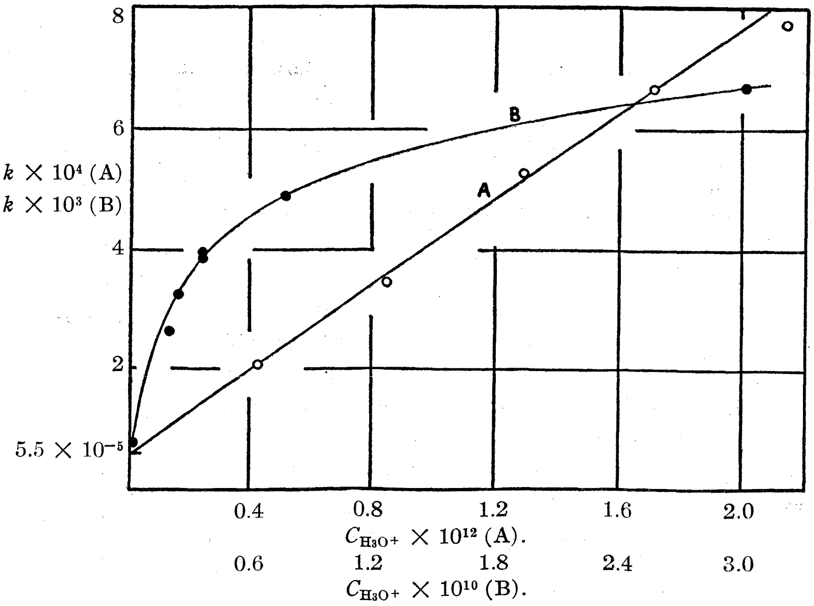


Fig. 1.—Catalysis by hydrogen ion.

The suspected formation of this ester was confirmed by experiments of the following type: 0.0005 mole of potassium diazoacetate was dissolved in 50 cc. of 0.2 *M* sodium chloride containing 0.000463 mole of hydrochloric acid. After

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(12) Harned, THIS JOURNAL, **47**, 930 (1925).

(13) Bredig and Ripley, *Ber.*, **40**, 4015 (1907).

(14) Wolff and Lüttringhaus, *Ann.*, **312**, 146 (1900).

one hour titration with sodium hydroxide showed that 0.000142 mole of acid had disappeared. A slight excess of alkali was added and the solution was heated to 90° for forty-eight hours. Titration with acid showed that 0.000142 mole of base (within experimental error) had disappeared.

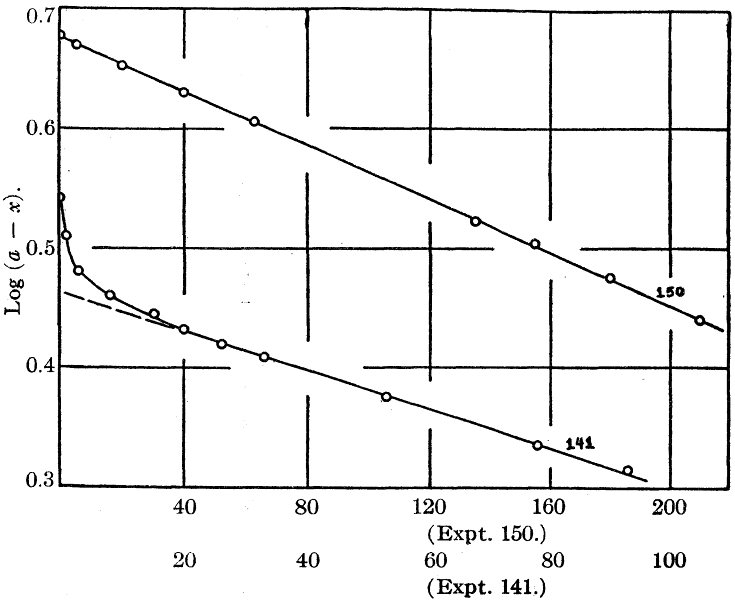

Fig. 2.—Typical time–rate curves: Expt. 150, phosphate buffer; Expt. 141, NaCl + a little HCl.

Heating for shorter periods (with these relatively low concentrations of reagents) showed partial return of the hydrogen ion which had disappeared initially.

In other solutions it was found by titration that the acid disappearing corresponded roughly with the amount of nitrogen evolved in the initial rapid reaction. Consequently it seemed safe to assume that the unimolecular rate after this initial rapid reaction was a measure of the catalysis by the hydrogen ion in the final solution, as measured a few hours later with the hydrogen electrode.

These rate constants are given in Table II with the corresponding hydrogen-ion concentrations, and are plotted in Fig. 1(B), the lowest point being the highest one of Fig. 1(A), expt. 29 (Table I). Most of these experiments were carried out at an ionic strength of 0.205; the results are comparable because of the low salt effect. The molar catalysis is constant only at very low values of the hydrogen ion concentration; however, it is still of the order of 10^7 at the highest concentration used.

TABLE II

CATALYSIS BY HYDROGEN ION AT HIGHER CONCENTRATIONS

Expt.	C_{NaCl}, M	C_{HCl} added $\times 10^4$	$C_{H_3O^+}$ at end $\times 10^{12}$	$k \times 10^4$
138	0.20	1.0	20.0	26.4
140	.20	2.0	25.1	32.6
141	.20	5.0	37.4	38.4
139	.20	5.0	37.4	39.6
137	.10	0	77.6	48.9
142	.20	10.0	302	67.0

2. Phenol Catalysis.—The experiments in phenol–sodium phenate buffers are summarized in Table III; the phenol concentration is designated by C_{HP} and the sodium phenate by C_{P^-}. The ionic strength was made 0.105 in every case by suitable additions of sodium chloride. The values of k are plotted in Fig. 3; the solid lines represent the effect of keeping the buffer ratio and consequently the pH constant. The phenol has a decided catalytic effect; but since the curves are not straight lines, are not parallel, and do not extrapolate satisfactorily to values to be ascribed to the hydrogen ion, it is evident that the catalysis is not of a simple type. The molar phenol catalysis decreases with increasing phenate concentration. Since the hydrogen ion catalytic constant in a one-to-one phenol–phenate buffer should be only about 0.005, this effect cannot be explained entirely by repression of the hydrogen-ion catalysis by the phenate.

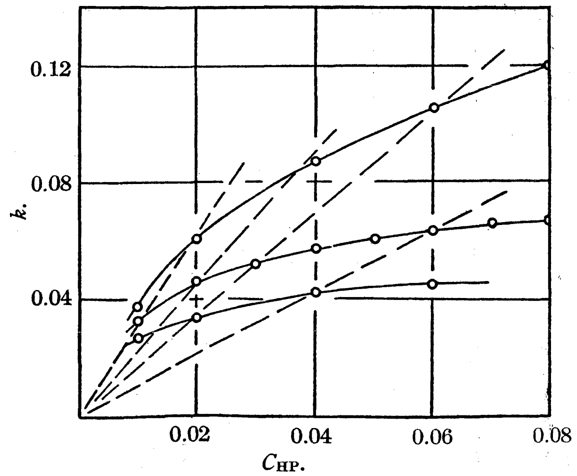

Fig. 3.—Catalysis by phenol: solid lines—constant phenol–phenate ratio; broken lines—constant phenate concentration.

The broken lines of Fig. 3 show that the molar catalysis by phenol at constant phenate concentration is approximately constant. Consequently, following the procedure of Brönsted, Nicholson and Delbanco,[6] the slopes of these lines were taken as molar constants, and plotted against $1/C_{P^-}$. The first three values (Fig. 5) lie on a straight line

$$k_m = 0.45 + 0.0344/C_{P^-}$$

The value 0.45 can be taken as the molar phenol constant at high base concentration.

TABLE III

CATALYSIS BY PHENOL: 25°, 0.105 μ

Expt.	C_{HP}, M	C_{P^-}, M	k
3	0.01	0.01	0.0325
4	.02	.02	.0456
5	.03	.03	.0515
6	.04	.04	.0570
7	.05	.05	.0604
8	.06	.06	.0631
9	.07	.07	.0660
10	.08	.08	.0664
11	.09	.09	.0675
2	.10	.10	.0690
13	.01	.015	.0264
14	.02	.030	.0332
15	.04	.060	.0420
16	.06	.090	.0451
17	.01	.005	.0371
18	.02	.010	.0600
19	.04	.020	.0872
20	.06	.030	.1055
21	.08	.040	.1202
25	.10	.050	.130
22	.01	.01	.0290 (μ = 0.015)
24	.01	.01	.0306 (μ = 0.055)

Salt effect in the phenol buffers was found to be small and probably of the linear type. It is about 12% between μ = 0.015 and 0.105, as shown by expts. 22, 24 and 3.

3. Ammonium-Ion Catalysis.—Concentrations were planned for this system to define better the effect of varying the ammonium-ion concentration at constant ammonia concentration. The details are given in Table IV and the values of k are plotted in Fig. 4. The molar catalysis constants may be represented by

$$k_m = 0.57 + 0.0274/C_{NH_3}$$

which is the equation for the straight line of Fig. 5.

There is a pronounced negative salt effect on the rate in ammonia–ammonium chloride solutions at low ionic strengths, and a number of experiments were run to investigate this. Table V gives the results, and in Fig. 6 the values of log k are plotted against $\sqrt{\mu}$. It was necessary, of course, to use a constant ammonia concentration throughout; since the secondary salt effect is small this is approximated in the solutions of Table V. At low ionic strengths the rates conform to the Brönsted requirement of a slope of −1.

TABLE IV

CATALYSIS BY AMMONIUM ION: 25°, 0.105 μ

Expt.	$C_{NH_4^+}$, M	C_{NH_3}, M	k
41	0.01	0.01	0.0163
57	.02	.02	.0260
50	.04	.04	.0420
51	.06	.06	.0593
53	.08	.08	.0766
52	.10	.10	.0833
55	.10	.10	.0813
36	.01	.02	.0154
37	.02	.04	.0243
38	.03	.06	.0297
39	.04	.08	.0363
34	.05	.10	.0422
56	.08	.16	.0597
35	.10	.20	.0658
54	.01	.03	.0137
58	.02	.06	.0214
59	.04	.12	.0314
68	.04	.12	.0348
60	.06	.18	.0438
61	.08	.24	.0523
63	.01	.04	.0127
64	.02	.08	.0201
65	.04	.16	.0303
66	.06	.24	.0411

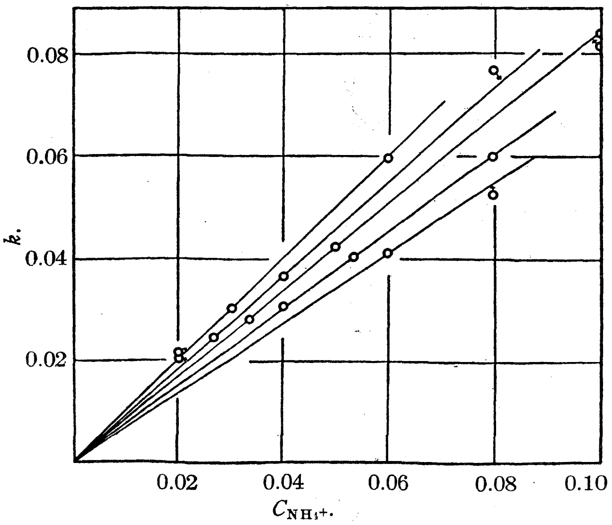

Fig. 4.—Catalysis by ammonium ion: straight lines for constant ammonia concentration.

TABLE V

SALT EFFECT IN AMMONIUM ION–AMMONIA BUFFERS

$C_{NH_4^+} = 0.005$ *M*, $C_{NH_3} = 0.005$ *M*, $C_{CHN_2COOK} = 0.005$ *M*

Expt.	C_{NaCl}, *M*	μ	*k*
69	0	0.010	0.0131
70	0	.010	.0134
85	0	.010	.0139
71	0.005	.015	.0126
86	.005	.015	.0131
73	.010	.020	.0122
75	.015	.025	.0118
87	.020	.030	.0117
77	.025	.035	.0110
78	.025	.035	.0114
79	.045	.055	.0110
80	.045	.055	.0111
81	.065	.075	.0107
82	.065	.075	.0106
159	.120	.130	.00965
157	.150	.160	.00934
160	.290	.300	.00953
158	.490	.500	.00940
155	.490	.500	.00920

TABLE VI

CATALYSIS BY PIPERIDINIUM ION: 25°, 0.105 μ

Expt.	C_{PH^+}, *M*	C_P, *M*	$k \times 10^3$
96	0.030	0.010	2.64
95	.020	.010	2.10
114	.010	.010	1.56
116	.005	.010	1.41
108	.0125	.050	0.92
103	.025	.050	1.20
104	.050	.050	1.79
106	.100	.050	2.73
110	.025	.100	0.88
112	.050	.100	1.25
115	.100	.100	1.91
98	.050	.200	0.825
113	.075	.200	1.06
111	.100	.200	1.25

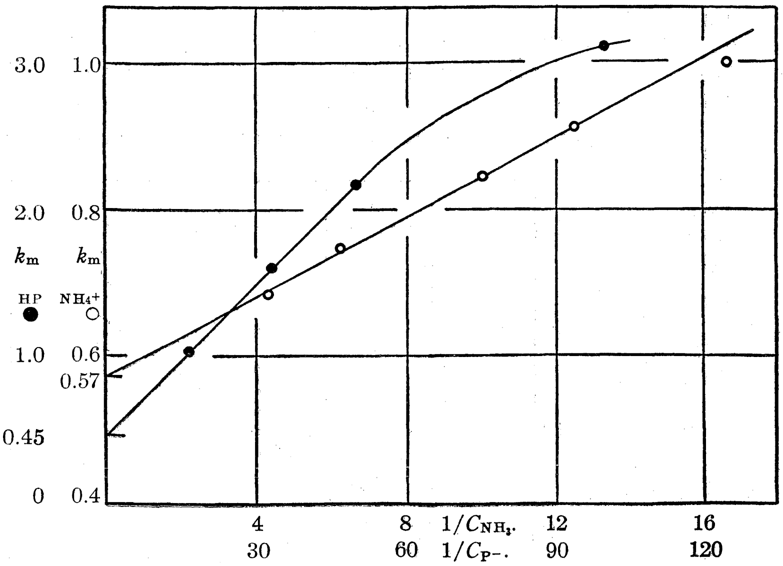

Fig. 5.—Plot of k_m *vs.* reciprocal of ammonia and phenate concentration.

4. Piperidinium-Ion Catalysis.—The piperidinium ion is an acid of the same charge type as the ammonium ion, but is much weaker. The experiments of this series are summarized in Table VI, where the piperidine and piperidinium-ion concentrations are represented by C_P and C_{PH^+}, respectively. The rate constants are plotted in Fig. 7 where the solid and broken lines have the same significance as before. The lines for constant buffer ratios are apparently straight and extrapolate to approximately the values expected for the hydrogen-ion catalysis (see Fig. 1); but the piperidinium-ion catalysis again decreases with increasing piperidine concentration. The slopes of the broken lines are taken as molar catalysis constants for the corresponding values of the piperidine concentration, and plotted in Fig. 9 against the reciprocal of the latter. The three lowest points lie approximately on the straight line

$$k_m = 0.0060 + 0.00086/C_P$$

5. Secondary Phosphate-Ion Catalysis.—Buffers of secondary and tertiary phosphate ions were made by adding sodium hydroxide to solutions of pure disodium hydrogen phosphate. All the experiments were carried out with the ionic strength 0.205 to make it possible to vary the ion concentrations sufficiently. Sodium sulfate was used as the inert salt to make up the ionic strength, in order to keep the valence types as nearly comparable as possible. The data are shown in Table VII and the values of *k* are plotted in Fig. 8. The solid curves are for constant ratios of $HPO_4^=$ and $PO_4^\equiv$ introduced into the solution rather than for the equilibrium mixtures, and this partly accounts for their slopes and lack of extrapolation to reasonable values for the hydrogen-ion catalysis. The points on the broken lines also do not represent quite the same base ($PO_4^\equiv$) concentrations, but this is not of great importance in analyzing the results. The slopes of the broken lines are plotted against $1/C_{PO_4^\equiv}$ in Fig. 9; the straight line is represented by the equation

$$k_m = 0.0050 + 0.00079/C_{PO_4^{=}}$$

TABLE VII

CATALYSIS BY SECONDARY PHOSPHATE ION: 25°, 0.205 μ

Expt.	$C_{HPO_4^-}$, M	$C_{PO_4^{=}}$, M	$k \times 10^3$
143	0.010	0.020	1.16
144	.020	.020	1.66
145	.030	.020	2.11
148	.005	.010	1.50
147	.010	.010	1.83
146	.015	.010	2.30
149	.005	.005	2.15
150	.0075	.005	2.56
151	.010	.010	1.58 (μ = 0.105)
152	.010	.010	2.15 (μ = 0.305)

This system shows a decided positive salt effect, which is to be expected theoretically. No attempt was made to study this at low ionic strengths, but expts. 151, 147 and 152 of Table VII indicate its magnitude.

6. Acetic Acid Catalysis.—The catalytic effect of acetic acid is far too great to be measured in ordinary buffers; the reaction proceeds at a measurable speed in pure sodium acetate solutions. Consequently this series was made in 0.2 M sodium acetate to which small amounts of acetic acid or sodium hydroxide were added; the pH of each solution was measured with the hydrogen electrode after the run. The acetic acid concentration was then calculated, using K_c for acetic acid = 2.18×10^{-5} in such solutions.[15] There was an initial rapid evolution of nitrogen as in the dilute hydrochloric acid solutions (Table II), though not as great; and this was accompanied by an initial rise in pH. The rates again were unimolecular during the remainder of the reaction. Data are given in Table VIII. The rate constants are corrected by subtracting values for the hydrogen-ion catalysis, estimated from the curve of Fig. 1. The validity of this procedure is rather doubtful since addition of acetic acid probably represses the hydrogen-ion catalysis somewhat; however, the correction is only about 10% of the total rate. The values of k fall reasonably well on the straight line of Fig. 10, considering the difficulties of obtaining accurate results in such solutions. The slope of this line, 1.20×10^4, is taken as the molar catalytic constant of acetic acid. The value is probably somewhat higher, however, than would be obtained for infinite acetate-ion concentration.

TABLE VIII

CATALYSIS BY ACETIC ACID: 25°, 0.205 μ

Expt.	C_{HAc}(a) or C_{NaOH}(b) added $\times 10^4$	$C_{H_3O^+}$ $\times 10^{10}$	C_{HAc} $\times 10^6$	k	k(corr.)
131	2.0a	6.17	5.66	0.0730	0.0650
130	1.0a	4.57	4.20	.0569	.0494
128	0.1a	3.47	3.18	.0428	.0358
132	1.0b	3.31	3.04	.0451	.0383
129	..	2.72	2.50	.0368	.0302
133	4b	1.92	1.75	.0266	.0205
134	10b	1.03	0.946	.0114	.0061
136	20b	0.776	.712	.0065	.0017
135	10b	.234	.215	.00575	.0028

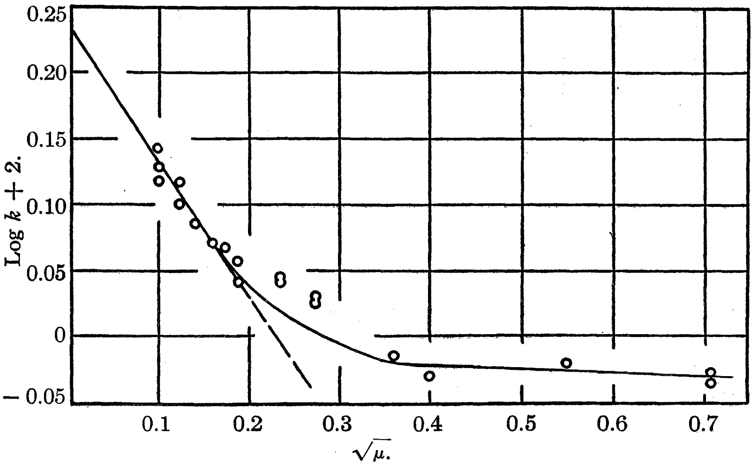

Fig. 6.—Salt effect on catalysis by ammonium ion.

Correlation and Discussion of Results

The molar catalytic constants conform well with the Brönsted expression for such catalysis.[16]

$$k_m = GK_A^x q^x p^{1-x}$$

The necessary data for applying this relation are given in Table IX. The values of k_m are those extrapolated to infinite base concentration except for hydrogen ion and acetic acid. The values of p and q are taken as the number of atoms in the acid molecule from which a proton can be detached and the number of atoms in the base molecule to which a proton can attach itself, as suggested by Pedersen.[17] Acid dissociation constants at infinite dilution are used in accordance

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(15) Cohn, Heyroth and Menkin, THIS JOURNAL, **50**, 696 (1928).

(16) Brönsted, *Chem. Rev.*, **5**, 231 (1928).

(17) Pedersen, *J. Phys. Chem.*, **38**, 581 (1934).

with the suggestion of Pedersen that these are a better measure of the "inner acid strength" than values at finite ionic strength. Conformity to the equation is somewhat improved by these modifications.

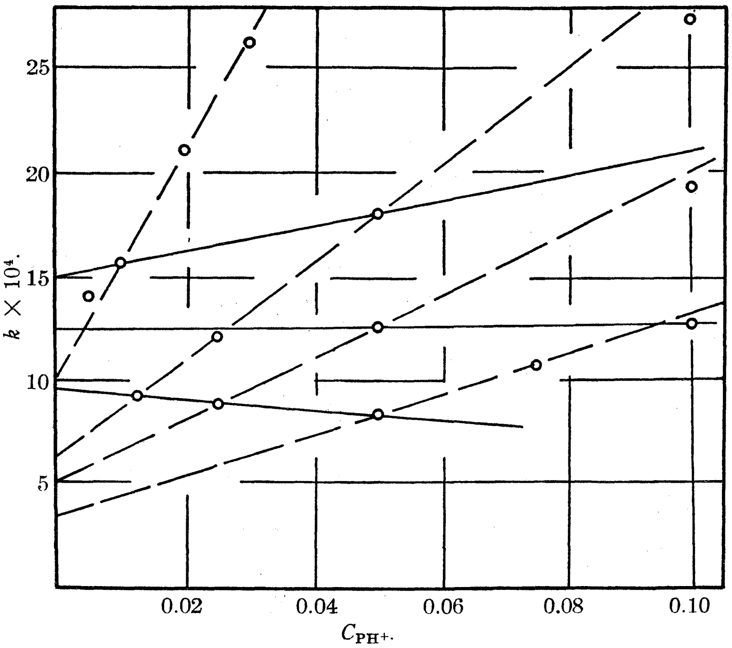

Fig. 7.—Catalysis by piperidinium ion: solid lines—constant buffer ratio; broken lines—constant piperidine concentration.

TABLE IX

THE RELATION BETWEEN VELOCITY CONSTANTS AND ACID STRENGTH

Acid	p	q	k_m	K^0_A
H_2O	1	1	9.92×10^{-7}	1.80×10^{-16}
$HPO_4^=$	1	4	0.0050	4.90×10^{-13}
$C_5H_{10}NH_2^+$	1	1	.0060	8.00×10^{-12}
C_6H_5OH	1	1	.45	1.06×10^{-10}
NH_4^+	1	1	.57	5.52×10^{-10}
$HC_2H_3O_2$	1	2	1.32×10^4	1.75×10^{-5}
H_3O^+	1	1	3.57×10^8	55.5

The values of K^0_A in Table IX for water, phenol and acetic acid were taken directly from the literature.[12,18,19] Those for piperidinium ion and ammonium ion were calculated from values for the basic constants[18] (pp. 273, 260) and Harned's value for water.[12] The value for the phosphate ion was determined from the data of Brönsted and King for the hydrolysis of the tertiary phosphate ion at 15°.[20] Their values of K_c were plotted against $\sqrt{\mu}$ and extrapolated to zero μ by drawing a straight line with the theoretical slope (−2) through the point of lowest concentration. The value obtained is probably not accurate, but seems more satisfactory than any value found in the literature. The value for the piperidinium ion was checked satisfactorily from the data of Brönsted and King.

In Fig. 11 values of log k_m/p are plotted against log (q/pK^0_A). The straight line corresponds to the equation

$$k_m/p = 1.90 \times 10^7 (q/pK^0_A)^{0.833}$$

The excellent conformity to this relation over a range of velocity constants from 10^{-6} to 10^{+8} and of dissociation constants from 10^{-16} to 10^{+2}, with such a variety of acid types, is rather remarkable. A detailed study would probably show some variation of both G and x with acid type, as in the nitramide decomposition. However, the effect of the charge type of the proton donor is small compared to that of the proton acceptor; the molar constant for hydrogen ion, 3.57×10^8, may be compared with that for hydrogen ion catalysis of diazoacetic ethyl ester decomposition, 13.6 at zero ionic strength at 15°.[21] This seems to indicate that formation of the true "critical complex" is intimately connected with the proton transfer.

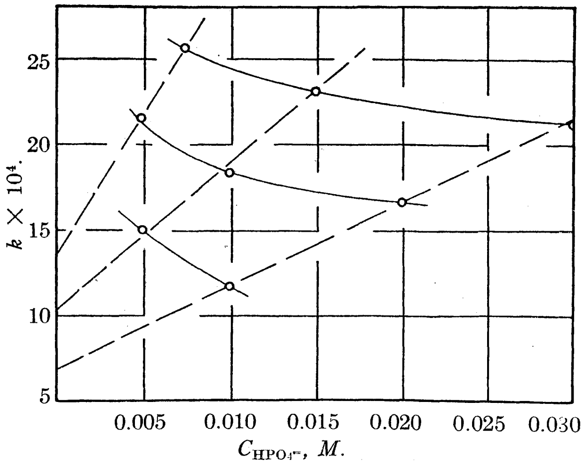

Fig. 8.—Catalysis by secondary phosphate ion.

Salt Effects and Mechanism.—It has been assumed in the preceding sections that the rate-controlling step is

$$N_2CHCOO^- + HA^z \longrightarrow \underset{\text{Intermediate Complex}}{(N_2CHCOO,HA)^{z-1}}$$

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(18) "International Critical Tables," Vol. VI, p. 271.

(19) Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932); MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

(20) Brönsted and King, *ibid.*, **47**, 2523 (1925).

(21) Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

This is in agreement with the salt effects found. With hydrogen ion as the catalyst there should be a negative primary salt effect of the exponential type. In ordinary concentrations of a strong acid secondary salt effect would be negligible; but in the solutions used here (Tables I and II) the concentration of hydrogen ion is controlled through the equilibrium

$$2H_2O \rightleftarrows H_3O^+ + OH^-$$

Since this has an exponential positive salt effect of the same magnitude as the primary salt effect, the net result is the small linear effect found.

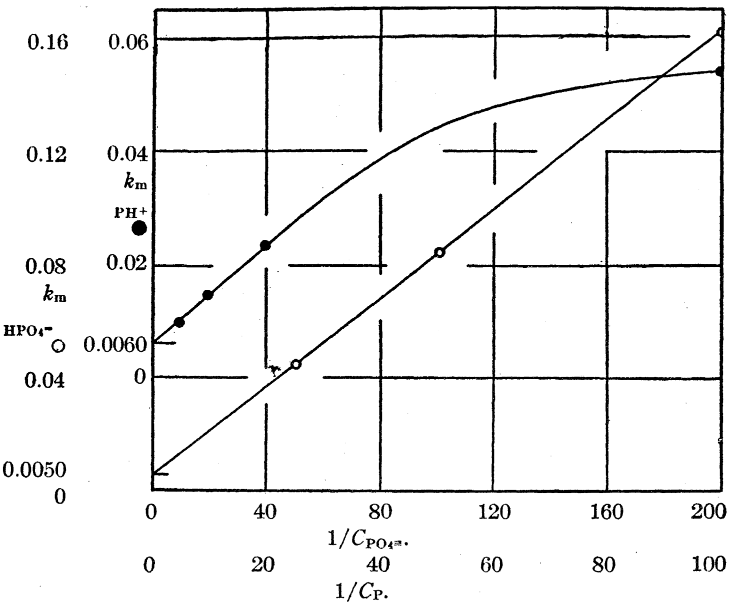

Fig. 9.—Plot of k_m *vs.* reciprocal of tertiary phosphate and piperidine concentration.

In the phenol–phenate buffers both primary and secondary salt effects are small, the largest effect being an increase in the hydrogen-ion concentration on addition of salt. In the ammonium ion buffers, however, the primary effect is of the negative, exponential type, while the secondary effect is small. The net effect at low ionic strengths is represented by the equation

$$\log k_c = \log k_a - \sqrt{\mu} \text{ (at 25°)}$$

as shown in Fig. 6. This relation is valid over only a very limited range, however, because of the several salt effects involved.

In the secondary phosphate solutions, the primary effect is of the negative exponential type, the secondary of the positive exponential type. The secondary phosphate ion increases in concentration on addition of salt sufficiently to make the net effect positive, although the hydrogen ion decreases in concentration simultaneously.

Other possible mechanisms for the reaction would be: (1) spontaneous reaction of the undissociated acid; (2) acid catalysis of the undissociated acid reaction; and (3) base catalysis of the undissociated acid reaction. The first is excluded by the general acid catalysis. The second would be compatible with the salt effect in some of the buffer systems, but not in the sodium hydroxide solutions. For if the rate equation were

$$dx/dt = kC_{N_2CHCOOH}C_{H_3O^+} f_0 f_1/f_1$$

the primary salt effect would be small; but since

$$C_{N_2CHCOOH} = K\frac{C_{N_2CHCOO^-} f_1}{C_{OH^-} f_0 f_1} \text{ and } C_{H_3O^+} = \frac{K^0_w}{C_{OH^-}} \frac{1}{f_1^2}$$

the rate would be proportional to the square of the hydrogen-ion concentration and have a large exponential salt effect. The third possibility would lead, in sodium hydroxide solutions, to a rate independent of the hydroxyl-ion concentration.

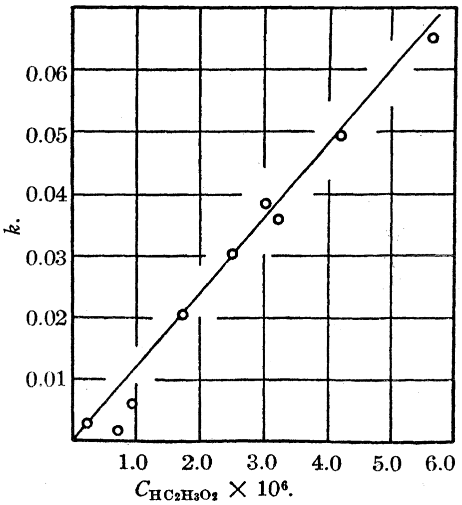

Fig. 10.—Catalysis by acetic acid.

Abnormalities.—The repressive effect of base on the acid catalysis was found in every system where the base concentration could conveniently be varied. The decreasing molar catalysis at higher acid concentration was most evident with the hydrogen ion, but sometimes appeared in the other systems. In Fig. 7 especially, all the points for the highest piperidinium-ion concentration fall below the straight lines for rates at constant base concentration. The acetic acid catalysis seems to fall off at higher concentrations, though the experimental accuracy is not great enough to warrant definite conclusions.

These abnormalities are probably generally characteristic of extremely high acid or base catalysis. In the nitramide decomposition in *m*-cresol[6] where similar effects were first found, the value of *G* in the Brönsted expression ($10^4 - 10^6$) is far higher than in any other case studied except the diazoacetate reaction described here. Even in the hydroxyl-ion catalysis of the nitramide decomposition in water, molar constants calculated from the data of Brönsted, Pedersen and Duus[7,11] are variable and lower than predicted from catalysis by other bases; and Marlies and La Mer[8] found, at an hydroxyl-ion concentration of 10^{-11} in hydrochloric acid solution, a molar catalytic constant 0.8×10^6 while the Brönsted relation predicts a value close to 10^9. If it were possible to measure the hydroxyl ion effect at lower concentrations, higher values would probably be found.

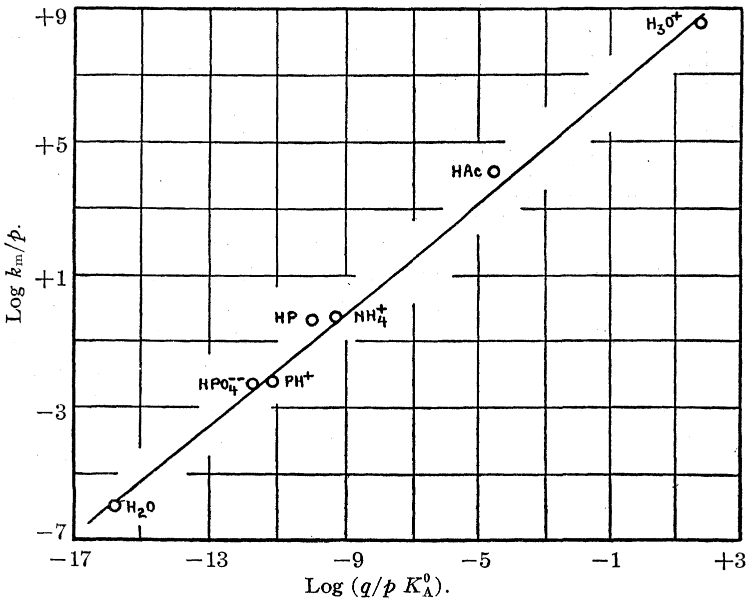

Fig. 11.—The relation between rate constants and acid dissociation constants: PH^+, piperidinium ion; HP, phenol; HAc acetic acid.

It is of interest to note that the value of *x* for the diazoacetate reaction, 0.833, is practically the same as that for the nitramide decomposition with some base types, both in aqueous and non-aqueous solution. This may be coincidence or may indicate a similar rate-controlling mechanism. According to the Brönsted picture the exponents for K_A and K_B should be the same for conjugate acids and bases when the rate-controlling mechanisms are similar, but this has not been found to hold for any systems studied previously.

Summary

The preparation of potassium diazoacetate, obtained by hydrolyzing diazoacetic ethyl ester, has been improved; the salt can easily be prepared free from alkali or polymerization products.

The reaction of the diazoacetate ion with water, giving nitrogen and glycolate ion, has been found to be phenomenally sensitive to general acid catalysis. The molar catalytic constant for the hydrion, 3.57×10^8 at 25°, is the highest recorded for any reaction. It may be compared with the corresponding molar constant for the decomposition of the neutral diazoacetic ethyl ester molecule, which is 13.6 at zero ionic strength at 15°. The exceptionally high rate indicates that in such catalysis the electric charge of the proton acceptor is far more important than the charge of the proton donor.

The catalysis shows abnormalities of a type found previously for the decomposition of nitramide in *m*-cresol solution. The molar catalysis constants decrease with increasing base concentration, and also with increasing acid concentration. A linear relation is found between the molar constants and the reciprocal of the base concentration except at low values of the latter.

The molar acid constants at high base concentration show excellent conformity with the equation

$$\frac{k_m}{p} = 1.90 \times 10^7 \left(\frac{q}{p} K_A^0\right)^{0.833}$$

and thus with the Brönsted theory. The value of *G*, 1.90×10^7 is the highest yet recorded; the value of *x*, 0.833, is practically the same as that found for basic catalysis of nitramide decomposition.

Salt effects in several buffer systems have been found to be in agreement with the general theory and with the mechanism postulated for this reaction.

NEW YORK, N. Y. RECEIVED MAY 28, 1936

[Contribution from the School of Chemistry of the University of Minnesota]

The Adsorption of Barium Salts on Barium Sulfate from Solutions in 50% Ethanol

By I. M. Kolthoff and Wm. M. MacNevin

In work previously reported in this Journal,[1] it was mentioned that a considerable adsorption of barium nitrate on barium sulfate was found from a medium containing approximately 50 volume per cent. ethanol, whereas the adsorption from aqueous medium was negligibly small. This medium effect upon the adsorption of electrolytes on ionic lattices has not been studied in the literature. The results of the investigation described in this paper constitute a first approach to the problem. Moreover, they allow us to test the quantitative relation between the adsorption of potential determining ions and the concentration of the latter under equilibrium conditions, and the relation between adsorbability and solubility (Paneth–Fajans rule).

Materials Used

Barium Sulfate.—The preliminary experiments were carried out with a fine product of barium sulfate used in previous work,[1a] the average particle size of which was about 0.14 micron. A large amount of a product prepared in a similar way was used in the determination of the adsorption isotherm of various barium salts.

Solvent.—A mixture of equal volumes of 95% undenatured ethanol and conductivity water was used as a solvent, and designated as 50% ethanol, although the alcohol content is slightly less.

Barium Nitrate.—A c. p. product was twice recrystallized from water, dried at 110° and stored over anhydrous calcium chloride.

Barium Chloride and Barium Bromate.—C. p. products were twice recrystallized from water, dehydrated and rehydrated over deliquescent sodium bromide. They were weighed as dihydrate and monohydrate, respectively, and dehydrated at 150° before dissolving in 50% ethanol. In the solubility experiments the anhydrous salts were used.

Barium Perchlorate.—This salt was prepared by neutralizing barium hydroxide with perchloric acid, and recrystallizing the salt from water. The monohydrate was dried at 150° before dissolving in 50% ethanol. In the solubility experiments Baker's "Dessicchlora" was used.

Barium Iodide.—A c.p. product was used without further purification.

Barium Bromide and Barium Thiocyanate.—C. p. products were recrystallized three times from water and dried over fused sodium hydroxide.

Barium Formate.—This salt was prepared by neutralizing formic acid with barium hydroxide. The product was recrystallized three times and dehydrated over fused sodium hydroxide.

Calcium Bromate.—To a suspension of barium bromate in water an equivalent amount of sulfuric acid was added and the mixture shaken until the transformation was complete (seventy-two hours). After shaking for five more days the barium sulfate was filtered off and the bromic acid in the filtrate neutralized with a calcium hydroxide suspension. The crystals separating out upon evaporation showed pronounced triboluminescence, either when dry or suspended in the mother liquor. The salt was recrystallized three times from water and dried at 120°.

Potassium Bromate.—A c. p. product was used.

Analytical.—The *barium* concentration was determined before and after adsorption by evaporating measured portions to a small volume and adding an excess of 0.1 molar potassium chromate to the hot solutions. The mixture was made alkaline with ammonia, digested for an hour and cooled. The barium chromate was filtered, washed, dissolved in 6 *N* hydrochloric acid and the chromate determined iodometrically after diluting with water.

Bromate was determined iodometrically. In order to get accurate results it was necessary to remove the alcohol by evaporation. The solution was made slightly alkaline with sodium hydroxide to prevent reduction of bromate by the alcohol and evaporated to dryness. The residue was taken up in water and the bromate determined iodometrically by the standard procedure.

Nitrate was determined by reduction to ammonia with Devarda's alloy.[2] The ammonia was distilled into an excess of dilute hydrochloric acid and determined iodometrically by the hypochlorite–bromide method.[3] Calcium was determined after removal of the alcohol by precipitation as calcium oxalate and titrating the precipitate with permanganate.

Experimental Results

Solubility Determinations in 50% Ethanol

An excess of the anhydrous salt was shaken at room temperature (25 ± 1°) in the 50% ethanol for forty-eight hours. The solution was filtered and 25 ml. of the filtrate evaporated in a weighed platinum dish. The residue was weighed after drying to constant weight at 150°. The results are given in Table I.

Table I

Solubility of Barium Salts in 50% Ethanol

Barium salt	Bromate	Nitrate	Formate	Chloride
Solubility in mols per liter	1.72×10^{-3}	5.71×10^{-2}	0.14	0.384
	Bromide	Iodide	Perchlorate	Thiocyanate
Solubility in mols per liter	1.46	2.53	2.77	2.89

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[1] I. M. Kolthoff and Wm. M. MacNevin (a) This Journal, **58**, 499 (1936); (b) **58**, 725 (1936).

[2] *Cf.* W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., 1929, p. 639.

[3] I. M. Kolthoff and V. A. Stenger, *Ind. Eng. Chem., Anal. Ed.*, **7**, 79 (1935).

The solubility of potassium bromate was found to be 0.051 molar and that of calcium bromate 1.05 molar.

Adsorption Experiments

Experiments were made in which samples of barium sulfate were shaken for half an hour, one hour and twenty-four hours with solutions of the barium salts in 50% ethanol. It was found that after a period of one hour of shaking the amount of salt adsorbed remained constant. A shaking period of one hour was adopted in the final experiments. Working with the fine product of barium sulfate used in previous work[1] it was ascertained first that an equivalent adsorption of barium ions and anions occurred. Experiments were carried out with barium nitrate and bromate at various concentrations and the amounts of barium and anion adsorbed determined separately (for details see doctor's thesis of junior author). Within the experimental error an equivalent adsorption of barium and anion was found. Thus, after shaking 0.6 g. of barium sulfate with 50 ml. of 0.0002 molar barium bromate in 50% ethanol, 24.8% of barium and 24.0% of bromate were found to be adsorbed. In the case of barium nitrate 28.0 (±1)% of nitrate and 26.6(±1)% of barium were found to be adsorbed from the 0.0002 molar solution. From the 0.001 molar solution 13.0% of nitrate and 12.4% of barium had disappeared.

The determination of the amount of salt adsorbed was attempted in a direct way by making use of the washing process described and applied by Miss de Brouckère.[4] This method did not yield useful results in our hands. After shaking, the suspensions were centrifuged, the supernatant liquid decanted and the precipitate shaken for one minute with 10 ml. of a saturated solution of barium sulfate in 50% ethanol. The mixture was centrifuged and the process repeated. After three such washings, 88% of the total amount of barium bromate originally adsorbed in a certain case was removed from the surface.

After the above results were obtained, it was decided to determine the amounts adsorbed in the following way. A given amount of the new sample of finely divided barium sulfate was shaken with 50 ml. of the barium salt solution in 50% ethanol for one hour, the suspension centrifuged and the barium or anion concentration determined in 25 ml. of the clear centrifugate.

The results are given in the following tables. It was found that within the range of concentrations studied, the adsorption was given quantitatively by the expression

$$x/m = ac^{1/n} \qquad (1)$$

in which x is the amount adsorbed expressed in moles, m the amount of adsorbent used in grams, c the final concentration in the solution, and a and $1/n$ constants.[5] The values of the latter, computed from the experimental results, and the values of x/m calculated with the aid of the above equation are reported in the tables.

TABLE II

ADSORPTION OF BARIUM BROMATE

1 g. of $BaSO_4$; 50 ml. of solution; BrO_3^- determined; $a = 1.80 \times 10^{-4}$; $1/n = 0.40$

Init. concen., molar × 10^3	Final concen., molar × 10^3	Absorbed in, %	$x \times 10^5$ Found	$x \times 10^5$ Calcd.
1.527	1.287	15.7	1.20	1.26
1.000	0.795	20.5	1.02	1.04
0.500	.348	30.4	0.76	0.76
.250	.146	41.7	.52	.52
.100	.039	61.2	.31	.32

TABLE III

ADSORPTION OF BARIUM NITRATE

5 g. of $BaSO_4$; 50 ml. of solution; Ba determined; $a = 0.69 \times 10^{-4}$; $1/n = 0.32$

Init. concn., molar × 10^3	9.48	3.79	1.90	0.948[a]
Final concn., molar × 10^3	8.01	2.74	1.14	.68
Adsorbed in %	15.4	27.8	40.0	28.3
$x/m \times 10^5$ found	1.46	1.05	0.76	0.67
$x/m \times 10^5$ calcd.	1.50	1.12	.79	.68

[a] Barium sulfate used, 2 g.

The adsorption of barium nitrate increases upon addition of alkali nitrate to the solution. The first experiment in Table III was repeated, the solution also containing 0.1 mole of sodium nitrate per liter. In the latter case 21.6% of the barium nitrate was adsorbed, as compared with 15.4% in the absence of sodium nitrate.

TABLE IV

ADSORPTION OF BARIUM PERCHLORATE

10 g. of $BaSO_4$; 50 ml. of solution; Ba determined; $a = 0.59 \times 10^{-4}$; $1/n = 0.40$

Init. concn., molar × 10^3	9.77	4.89	0.98[a]
Final concn., molar × 10^3	8.04	3.67	.65
Adsorbed in %	17.7	25.0	33.6
$x/m \times 10^5$ found	0.86	0.61	0.33
$x/m \times 10^5$ calcd.	.85	.63	.31

[a] Barium sulfate used, 2 g.

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(4) L. de Brouckère, *Ann. chim.*, [X] **19**, 92 (1933).

(5) In some preliminary work, P. P. von Weimarn, *Repts. Imp. Ind. Research Institute*, Osaka, Japan, **12**, 153 (1931), arrived at a similar conclusion.

TABLE V

ADSORPTION OF BARIUM CHLORIDE

5 g. of $BaSO_4$; 50 ml. of solution; Ba determined; $a = 0.54 \times 10^{-4}$; $1/n = 0.38$

Init. concn., molar $\times 10^3$	10.1	5.05	1.01	0.505
Final concn., molar $\times 10^3$	9.25	4.39	0.678	.260
Adsorbed in %	8.4	13.0	33.4	48.5
$x/m \times 10^5$ found	0.85	0.66	0.34	0.24
$x/m \times 10^5$ calcd.	.91	.68	.34	.23

The adsorption of the other salts was determined at one concentration only. The results are found in Table VI.

TABLE VI

ADSORPTION OF VARIOUS BARIUM SALTS

50 ml. of solution

$BaSO_4$, g.	10	10	10	2
Ba salt adsorbed	Bromide	Iodide	Thiocyanate	Formate
Init. concn., molar $\times 10^3$	1	1	1	1
Final concn., molar $\times 10^3$	0.52	0.54	0.63	0.73
Adsorbed in %	48.0	45.9	36.8	27.0
$x/m \times 10^5$	0.24	0.23	0.18	0.67

Discussion

1. One of the most interesting results of this study is that the Freundlich adsorption isotherm was found to hold for the adsorption of barium salts on barium sulfate from a medium of 50% ethanol. One certainly would expect to be dealing here with the adsorption of a "potential determining ion,"[6] in which case it is claimed[7] that the relation between the amount adsorbed x and the concentration c is given by an expression

$$\Delta x = k\Delta\log c \qquad (2)$$

and not by the expression

$$\log x = k\Delta\log c \qquad (3)$$

The only experimental proof of the validity of expression (2) has been found in the case of silver iodide[8] where the adsorption of silver and of iodide apparently occurs on the active surface. In our study we worked with well-aged barium sulfate. Although in none of the cases investigated (Tables II–VI) a saturated surface corresponding to a monomolecular layer of adsorbed barium salt was obtained, it is quite evident that in the present study we are mainly dealing with an adsorption on the normal surface and not on active surface. In the derivation of expression (2) assumptions have been made which, theoretically, are not entirely justified. On the basis of the present study it becomes doubtful whether equation (2) holds generally for the adsorption of potential determining ions. That the barium ions actually behave as potential determining ions is evidenced by their peptizing effect upon the barium sulfate. When the solid (average diameter about 0.14 micron) is shaken with aqueous solutions of barium nitrate or other barium salts a clear centrifugate is obtained readily. In 50% ethanol solutions of barium salts, it is difficult to obtain a clear centrifugate after shaking with barium sulfate. As much as two hours of centrifuging at 3000 r. p. m. was required to obtain a clear supernatant liquid. A maximum peptizing effect was found at a certain concentration of the barium salt, in the case of barium bromate in 0.002 molar solutions.

There is a possibility that only a small fraction of the adsorbed barium acts as potential determining ion and that we are dealing mainly with a "true adsorption" on the entire surface comparable to the adsorption of salts having no ion in common with the lattice, for which expression (3) holds within wide limits of concentration.[7b] Actually it was found that salts such as potassium bromate and calcium bromate from solutions in 50% ethanol gave a pronounced adsorption on barium sulfate. Upon shaking 10 g. of barium sulfate with 50 ml. of 0.002 molar potassium bromate, 15.7% of the salt was found to be adsorbed, corresponding to 1.6×10^{-6} mol per g. of barium sulfate. Equivalent amounts of cation and anion were adsorbed. The adsorption of calcium bromate was measured at different concentrations by determining the bromate content before and after adsorption. The results are given in Table VII; it is seen that the percentage of bromate adsorbed changes in an irregular way with the concentration. In order to decide whether an equivalent adsorption of calcium and bromate occurred, it was decided to determine the amount of calcium adsorbed from the 0.001 molar solution (first solution in Table VII). It was found that 45.7% of the calcium was adsorbed, which is just double the amount of bromate adsorbed (23.6%). This result indicates that a hydrolytic adsorption has taken place and that the salt is adsorbed in the form of $Ca(OH)(BrO_3)$. In agreement with this conclusion it was found that the supernatant liquid after the adsorption

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[6] E. Lange and R. Berger, *Z. Elektrochem.*, **36**, 171 (1930).

[7] (a) M. Andauer and E. Lange, *Z. physik. Chem.*, **A156**, 241 (1931); (b) E. J. W. Verwey, *Chem. Rev.*, **16**, 363 (1935).

[8] E. Lange and R. Berger, *Z. Elektrochem.*, **36**, 171, 980 (1930); E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, **A167**, 149 (1933); I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **58**, 1528 (1936).

showed a strongly acid reaction. The hydrolytic adsorption accounts for the irregular change of the bromate adsorption at different salt concentrations as it will be a function of the *p*H of the solution in equilibrium with the solid.

TABLE VII

ADSORPTION OF BROMATE FROM CALCIUM BROMATE

10 g. of $BaSO_4$; 50 ml. of solution

Init. concn., molar × 10^3	1	0.5	0.4	0.2
Final concn., molar × 10^3	0.764	0.358	0.303	0.169
Adsorbed BrO_3^- in %	23.6	28.4	24.3	15.5
$x/m \times 10^5$	0.12	0.071	0.049	0.015

2. In Table VIII the relation is given between adsorbability from and solubility of the barium salts in 50% ethanol. The value of the constant *a* in the expression for the adsorption isotherm (equation 1) is taken as a measure of the adsorbability. From the experimental data, *a* and $1/n$ were calculated for four barium salts, an average value of 0.38 for $1/n$ being found. For the other barium salts, the adsorption of which was determined at one concentration only, the value of $1/n$ equal to 0.38 was used in the calculation of the "*a*" values.

It is seen that there is no close parallelism between adsorbability and solubility.[9] Barium formate is adsorbed more strongly than the nitrate, although the latter is much less soluble. Particularly the perchlorate is out of place. Its adsorbability is of the same order as that of the chloride and much greater than that of the bromide or iodide, although its solubility in 50% ethanol is greater than that of the halides.

TABLE VIII

SOLUBILITY AND ADSORBABILITY

	Barium salt	Order of absorbability expressed in $a \times 10^4$	Relative solubility in 50% ethanol	Order of increasing solubility
1	Bromate	1.80	1	1
2	Formate	0.91	81	3
3	Nitrate	.69	33	2
4	Perchlorate	.59	1610	7
5	Chloride	.54	223	4
6	Bromide	.37	848	5
7	Iodide	.35	1477	6
8	Thiocyanate	.26	1663	8

Summary

1. The adsorption of barium salts on barium sulfate and of salts not having an ion in common with the lattice is much greater from 50% ethanol than from water.

2. Contrary to the expectation, the adsorption of barium salts from 50% ethanol on barium sulfate follows the Freundlich adsorption isotherm.

3. No close parallelism has been found between adsorbability and solubility.

4. Potassium bromate gives an equivalent adsorption of cations and anions. Calcium bromate yields a hydrolytic adsorption and was found to be adsorbed in the form of $Ca(OH)(BrO_3)$.

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(9) For a similar conclusion on the adsorption of silver salts on silver iodide compare the study of J. S. Beekley and H. S. Taylor, *J. Phys. Chem.*, **29**, 942 (1925).

MINNEAPOLIS, MINN. RECEIVED MAY 25, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WOOLWICH POLYTECHNIC]

The Primary and Secondary Dissociation Constants of Malonic, Succinic and Glutaric Acids by Potentiometric Titration

BY WILLIAM L. GERMAN AND ARTHUR I. VOGEL

The primary thermodynamic dissociation constants at 25° of malonic, succinic and glutaric acids have been determined by conductivity methods by Jeffery and one of us[1] but it has not yet been found possible to calculate the true secondary dissociation constants satisfactorily from conductivity data alone. Attention was therefore directed to the potentiometric method for the simultaneous evaluation of both constants. Previous electrometric titrations for these three acids have been carried out by Britton[2] at 18°, Gane and Ingold[3] at 25° for malonic acid; by Bjerrum[4] at 18°, Auerbach and Smolczyk[5] at 20°, Britton[2] at 18°, Kolthoff and Bosch[6] at 18°, Gane and Ingold[3] at 25°, Ashton and Partington[7] at 25° for succinic acid; and by Gane and Ingold[3] at 25°

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(1) Jeffery and Vogel, *J. Chem. Soc.*, 21 (1935).

(2) Britton, *ibid.*, **127**, 1906 (1925).

(3) Gane and Ingold, (a) *ibid.*, 1594 (1928); (b) 2158 (1931).

(4) Bjerrum, *Z. physik. Chem.*, **106**, 227 (1923); *cf.* Larsson, *Z. anorg. allgem. Chem.*, **125**, 291 (1925).

(5) Auerbach and Smolczyk, *Z. physik. Chem.*, **110**, 65 (1924).

(6) Kolthoff and Bosch, *Rec. trav. chim.*, **47**, 861 (1928).

(7) Ashton and Partington, *Trans. Faraday Soc.*, **30**, 598 (1934).

for glutaric acid. The large differences between the results of the various investigators for succinic acid cannot be attributed solely to the varying concentration and temperatures at which the titrations were performed; a particularly large discrepancy is that for succinic acid obtained by Gane and Ingold with the hydrogen electrode and by Ashton and Partington with the quinhydrone electrode. Gane and Ingold[3b] (p. 2153) remark in connection with the correction of their data for interionic effects that "the application of the Debye and Hückel equation for activities of electrolytes . . . involves practical difficulties" and they have accordingly employed an empirical method involving the determination of "K" at a series of concentrations and extrapolating to zero concentration. We have carried out new potentiometric titrations of malonic, succinic and glutaric acids against sodium hydroxide with the quinhydrone electrode at 25° and have calculated the thermodynamic dissociation constants by the method described recently by German, Jeffery and Vogel.[8] Table I summarizes our results: the conductivity values of Jeffery and Vogel[1] and Gane and Ingold's figures calculated by their empirical method, are included for purposes of comparison.

TABLE I

Acid	K_1 therm. $\times 10^5$ (Cond.)	Authors K_1 therm. $\times 10^5$	 K_2 therm. $\times 10^6$	Gane and Ingold K_1 therm. $\times 10^5$	 K_2 therm $\times 10^6$
Malonic	139.7	143	2.20	149	2.03
Succinic	6.626	6.37	2.54	6.41	3.33
Glutaric	4.535	4.46	3.77	4.53	3.80

It will be noted that the agreement of our potentiometric with the conductivity values for K_1 is within 2.5, 4 and 2% for malonic, succinic and glutaric acids, respectively.

Calculation shows that an error of one millivolt will cause a variation of *ca.* 5% in both K_1 and K_2. Our measurements were in general reproducible to 0.2–0.3 millivolt so that no greater accuracy than 1–2% could be expected in the final figures for K_1 and K_2. The somewhat greater difference for K_1 actually found must be attributed to the inherent disadvantages of the method of calculation. It would appear therefore that no greater accuracy than 2–4% can be realized in the determination of K_1 and K_2 by potentiometric titration with the quinhydrone electrode under the experimental conditions that we have employed.

The mean values of the true dissociation constants together with the intercarboxylic distances, expressed in Å., calculated after Bjerrum[4] (A) and Gane and Ingold[3b] (p. 2161) (B) are collected in Table II. Gane and Ingold's values[3b] (p. 2153) (G. and I.) for these acids are added for comparison.

TABLE II

Acid	K_1 therm. $\times 10^5$	K_2 therm. $\times 10^6$	r (A)	r (B)	r (G. and I.)
Malonic	143	2.20	1.39	3.47	3.43
Succinic	6.37	2.54	3.89	5.13	5.58
Glutaric	4.46	3.77	6.60	7.15	7.11

Experimental

Preparation of Materials. Acids.—The details have been described by Vogel[9] and by Jeffery and Vogel[1] (p. 23). Kahlbaum pure malonic acid was recrystallized twice from benzene–ether–light petroleum (b. p. 60–80°) and melted at 136° (dec.). Kahlbaum pure succinic acid was recrystallized from acetone and melted at 185–185.5°. Glutaric acid was prepared from the nitrile, b. p. 149–150° (14 mm.), and after crystallization from chloroform melted at 97.5–98°.

Sodium Hydroxide Solutions.—These were prepared by the electrolysis of chemically pure sodium chloride solution with a mercury cathode as described by Jeffery and Vogel[10] and were standardized immediately before use with constant b. p. hydrochloric acid.[11] All dilutions were carried out with equilibrium water prepared in a "Vogel" still.[12] The quinhydrone and calomel were prepared as detailed by German and Vogel.[13]

Apparatus.—Full details have been given by German and Vogel[13] and by German, Jeffery and Vogel.[8] An electrically-controlled oil thermostat maintained at 25 ± 0.01° was used. Stirring was effected with purified nitrogen. All titrations are accurate to 0.01 cc. The cell employed was

$$\mathrm{Hg} \mid \mathrm{Hg_2Cl_2},\ \mathrm{KCl}\ (\text{satd.}) \parallel \text{Solution, quinhydrone} \mid \mathrm{Pt}$$

The liquid junction potential was assumed to be negligible. Standardization was effected before and after each titration against at least two independent 0.1 N calomel cells[14] for which a value of 0.3376 volt was assumed,[15,16] and also against 0.05 M potassium hydrogen phthalate (chemically

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(8) German, Jeffery and Vogel, *J. Chem. Soc.*, 1624 (1935).

(9) Vogel, *ibid.*, 336 (1934).

(10) Jeffery and Vogel, *Phil. Mag.*, **15**, 400 (1932).

(11) Jeffery and Vogel, *J. Chem. Soc.*, 409 (1932).

(12) Vogel, *ibid.*, 1201 (1931).

(13) German and Vogel, *ibid.*, 913 (1935).

(14) Clark and Lubs, *J. Biol. Chem.*, **25**, 479 (1916).

(15) Clark, "The Determination of Hydrogen Ions," 1928, p. 487.

(16) MacInnes and Belcher, THIS JOURNAL, **53**, 3325 (1931).

pure).[16,17] The value of 0.3337 volt recently suggested by Guggenheim and Schindler[18] was not adopted in the present work as this figure was not in agreement with the value yielded by the standard buffer and, further, this would have led to values for the primary dissociation constants differing considerably from the strictly thermodynamic constants deduced from conductivity by Jeffery and Vogel[1] and would also have led to a similar deviation for phenylacetic acid.[13,19] The agreement, within 2–3%, of our values for K_1 with those deduced from conductivity provides the strongest evidence in support of our procedure and the neglect of diffusion potentials. Should, however, a new value for E_0 be *universally* accepted at some future date, our results can be recalculated readily.

The values of $K_{1\text{incomp.}}$ and $K_{2\text{incomp.}}$ (the "incomplete" or "unvollstandige" constants of Bjerrum and Unmack[20]) were computed by Britton's method[2] and are incorporated in Table IV for comparison with published data. The "ther-

TABLE III

POTENTIOMETRIC TITRATION OF 100 CC. OF 0.01 N ACID WITH 0.00997 N SODIUM HYDROXIDE SOLUTION

NaOH, cc.	Malonic acid *p*H	Succinic acid *p*H	Glutaric acid *p*H
0	2.679	3.271	3.342
10	2.834	3.687	3.778
15	2.929	3.849	3.958
17.5	2.980	3.924	4.042
20	3.027	4.001	4.113
22.5	3.081	4.076	4.181
25	3.135	4.147	4.252
27.5	3.203	4.215	4.313
30	3.267	4.282	4.374
32.5	3.335	4.350	4.431
35	3.411	4.421	4.492
40	3.585	4.557	4.600
50	4.232	4.837	4.820
60	4.952	5.115	5.037
65	5.189	5.250	5.155
67.5	5.287	5.321	5.216
70	5.376	5.392	5.277
72.5	5.463	5.467	5.338
75	5.545	5.533	5.406
77.5	5.629	5.606	5.470
80	5.714	5.683	5.545
82.5	5.802	5.761	5.622
85	5.890	5.846	5.707
90	6.096	6.035	5.910
100	6.831	6.190	6.861

TABLE IV

CLASSICAL AND THERMODYNAMIC DISSOCIATION CONSTANTS OF NORMAL DIBASIC ACIDS AT 25° BY POTENTIOMETRIC TITRATION

Pairs of points used	K_1 class × 10^3	K_2 class × 10^6	$\mu \times 10^3$	K_1 therm. × 10^3	K_2 therm. × 10^6
Malonic Acid					
17.5	1.53		2.49	1.44	
67.5		2.79	4.75		2.19
20	1.55		2.55	1.46	
70		2.81	4.94		2.20
22.5	1.53		2.61	1.45	
72.5		2.80	5.14		2.18
25	1.55		2.67	1.46	
75		2.82	5.31		2.19
27.5	1.49		2.74	1.40	
77.5		2.84	5.53		2.19
30	1.49		2.81	1.41	
80		2.86	5.67		2.20
32.5	1.50		2.87	1.42	
82.5		2.89	5.92		2.21
35	1.51		2.92	1.42	
85		2.93	6.10		2.24
			Mean	1.43	2.20
Succinic Acid					
17.5	6.74		1.55	6.44	
67.5		3.24	4.90		2.54
20	6.70		1.70	6.39	
70		3.24	5.09		2.53
22.5	6.68		1.84	6.36	
72.5		3.22	5.28		2.50
25	6.67		1.97	6.34	
75		3.27	5.47		2.53
27.5	6.69		2.09	6.35	
77.5		3.30	5.63		2.54
30	6.71		2.24	6.35	
80		3.31	5.78		2.54
32.5	6.67		2.33	6.31	
82.5		3.38	6.02		2.57
			Mean	6.37	2.54
Glutaric Acid					
17.5	4.69		1.42	4.49	
67.5		4.88	5.02		3.81
20	4.71		1.63	4.49	
70		4.87	5.20		3.79
22.5	4.72		1.76	4.50	
72.5		4.88	5.39		3.78
25	4.65		1.89	4.43	
75		4.87	5.58		3.75
27.5	4.67		1.98	4.43	
77.5		4.91	5.77		3.77
30	4.67		2.12	4.43	
80		4.91	5.93		3.75
35	4.62		2.31	4.37	
85		4.95	6.30		3.75
			Mean	4.46	3.77

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[17] Clark, ref. 15, p. 486.

[18] Guggenheim and Schindler, *J. Phys. Chem.*, **38**, 536 (1934).

[19] Jeffery and Vogel, *J. Chem. Soc.*, 166 (1934).

[20] Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab.*, **9**, 11 (1929).

modynamic" dissociation constants[21] were calculated from $pK_{1\text{therm.}} = pK_{1\text{incomp.}} + 0.505\ \mu^{0.5}$ (i) and $pK_{2\text{therm.}} = pK_{2\text{incomp.}} + 1.515\ \mu^{0.5}$ (ii), where $pK_{1\text{therm.}} = -\log K_{1\text{therm.}}$ etc., and the total ionic strength, which was deduced from the expression[8]

$$\mu = 0.5\left(a + h + c\left\{\frac{1}{(h/K_1 + 1 + K_2/h)} + \frac{4}{(h/K_2 + 1 + h^2/K_1K_2)}\right\}\right)$$

where c is total acid concentration, a is concentration of sodium hydroxide added, h is hydrion concentration, and K_1 and K_2 are the "incomplete" (previously termed "classical") values.

The use of the approximate expressions (i) and (ii) over the concentration range ($\mu = 0.0015$ to 0.006) that we have employed is justified by the following considerations. Morton[22] has deduced the equation

$$p_k = p\text{H} + \log\,[\text{Acid}]/[\text{Salt}] + \log f_a/f_s$$

in which f_a and f_s are the activity coefficients of the undissociated acid and of the salt anions or of the acid anions of lower and higher valency, respectively. This may be written in the form

$$\begin{aligned} pK_{\text{therm.}} &= pK_{\text{incomp.}} + \log f_a/f_s \\ &= pK_{\text{incomp.}} + (n - 0.5)\mu^{0.5} - B\mu \end{aligned}$$

since $\log f_a/f_s = (n - 0.5)\mu^{0.5} - B\mu$; n is the basicity of the acid. For phthalic acid, which is the acid most closely allied to those that we have studied, the highest value of B found by Morton was approximately 1 and this was in the presence of $M/3$ potassium sulfate. It can be readily shown that with $B = 1$ in the most concentrated solutions that we have employed, the maximum error introduced by the neglect of this term is *ca.* 1%. Actually the error will be much less than this.

Summary

The thermodynamic dissociation constants of malonic, succinic and glutaric acids have been determined by potentiometric titration with the quinhydrone electrode. The values for the primary dissociation constants agree within 2–4% with those determined by conductivity.

LONDON, S. E. 18, ENGLAND RECEIVED DECEMBER 20, 1935

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[21] It is appreciated that this term should be strictly confined to values obtained by experimental technique which does not involve uncertainties in liquid junction potentials and by strict thermodynamic methods, as in the precise work of Harned and co-workers. It is believed, however, that the approximations introduced are sufficiently precise for the ultimate accuracy of 2–3% which is claimed to justify the use of the term.

[22] Morton, *J. Chem. Soc.*, 1406 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

β-Amoxyethyl Esters of *p*-Aminobenzoic Acid

BY H. V. ASHBURN, A. R. COLLETT AND C. L. LAZZELL

In continuation of our work on the β-alkoxyethyl esters of *p*-aminobenzoic acid,[1] we have prepared a series of six amoxyethanols, three of which are new, together with the corresponding *p*-nitro and *p*-aminobenzoates. The alcohols used were purified by fractional distillation, until a sample having a boiling point range of 0.5° or less was obtained.

β-Amoxyethanols

The β-amoxyethanols were prepared by heating the desired alcohol with ethylene oxide in the presence of a small amount of sulfuric acid as a catalyst[2] except in the case of the tertiary amoxyethanol, for which acid aluminum fluosilicate was used as a catalyst.[3]

The method was as follows: 20 to 30 moles of the alcohol, 7 moles of ethylene oxide, and 1 cc. of concentrated sulfuric acid were placed in an autoclave and heated at 130–150° for eight to ten hours. The autoclave was then emptied and the contents fractionally distilled. The tertiary amyl compound was prepared by using acid aluminum fluosilicate as the catalyst and heating at 130–150° for twenty-five hours.

These compounds are all colorless, sweet smelling liquids, very soluble in alcohol and ether. The iso primary amyl, active primary amyl and tertiary amyl compounds are all appreciably soluble in water at 25° while the *n*-primary amyl, secondary amyl and active secondary amyl compounds are only slightly soluble.

Table I lists the yields and physical constants of all the amoxyethanols prepared, together with the analyses of the new compounds. The tertiary butoxyethanol has been prepared since the only physical property recorded in the literature is the boiling point, 150–153°. Its density is 0.8935

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[1] Ashburn, Collett and Lazzell, THIS JOURNAL, **57**, 1862 (1935).

[2] German Patent 580,075, July 5, 1933; *C. A.*, **27**, 4814 (1933).

[3] French Patent 39,773, Feb. 17, 1931; *C. A.*, **26**, 4826 (1932).

TABLE I

β-AMOXYETHANOLS, ($ROCH_2CH_2OH$)

Amyl group	Yield, %	B. p., °C.	Mm.	$d^{25}_{abs.}$	$n^{25}D$	C, % calcd. 63.6	H, % calcd. 12.2
$CH_3(CH_2)_4$-[a]	34	188.3	751.1	0.8893	1.42266	..	...
$(CH_3)_2CH(CH_2)_2$-	32	179.8	750.1	.8884	1.42092	..	...
$(CH_3)(C_2H_5)CHCH_2$-	43	176.8	748.0	.8978	1.42197	63.1	12.00
$(C_2H_5)_2CH$-	38	172.6	746.4	.9151	1.42200	63.3	12.02
$(CH_3)(n\text{-}C_3H_7)CH$-	34	173.8	746.0	.9144	1.42125	63.3	11.70
$(C_2H_5)(CH_3)_2C$-[b]	18	168.4	745.4	.9145	1.42322	63.5	11.90

[a] Recorded in the literature as 181° at 745 mm. [Cretcher and Pittenger, THIS JOURNAL, **46**, 1503 (1924)] and as 85.5–86.5° at 23 mm. [Tallman, THIS JOURNAL, **56**, 126–129 (1934)]. [b] This compound was analyzed since the only property listed in the literature was the boiling point given as 50–55° at 3 mm. [U. S. Patent 1,968,033 (1934); *C. A.*, **28**, 5832 (1934)].

TABLE II

p-NITROBENZOATES ($ROCH_2CH_2OOCC_6H_4NO_2(p)$)

Amyl group	% yield	B. p., °C., 4 mm.	$d^{25}_{abs.}$	$n^{25}D$	γ^{25}	N, % (Calcd. 4.98) Found	
$CH_3(CH_2)_4$-	87	191.5–192.5	1.1301	1.5141	36.1	4.95	4.90
$(CH_3)_2CH(CH_2)_2$-	80	184.1–185.1	1.1287	1.5136	34.9	4.87	4.88
$(CH_3)(C_2H_5)CHCH_2$-	89	188.1–189.0	1.1276	1.5129	35.1	4.85	4.87
$(C_2H_5)_2CH$-	87	183.0–184.0	1.1539	1.5138	36.2	4.93	5.01
$(CH_3)(n\text{-}C_3H_7)CH$-[a]	87	186.6–187.6	1.1633	1.5164	36.0	5.18	4.96
$(C_2H_5)(CH_3)_2C$-	89	164.0–166.0[b]	....	....	..	4.90	4.88

[a] Crystallized after setting for several weeks; recrystallized from ligroin gave a melting point of 74.5°. [b] Pressure 0.42 mm.

($d^{25}_{abs.}$), refractive index is 1.41322 $n^{25}D$, and it boils at 151.3 under 750 mm. pressure.[3]

All boiling points were taken with a certified thermometer completely immersed in the vapor. Refractive indices were taken with a dipping refractometer at 25°. The yields are based upon the amount of ethylene oxide used.

***p*-Nitrobenzoates.**—The *p*-nitrobenzoates of these β-amoxyethanols were prepared according to the method of Conn, Collett and Lazzell.[4] These esters are viscous, practically odorless liquids having a pale yellow color. They are insoluble in water but soluble in all the common organic solvents. Table II lists the analyses, physical constants and yields of all the new *p*-nitrobenzoates prepared.

The analyses were made by titration with titanous chloride. Refractive indices were determined by means of an Abbé refractometer at 25°. Surface tensions were obtained by means of a du Noüy tensiometer at 25° and Harkins' correction for the ring method was applied. The yields are based upon the amount of glycol ether used.

***p*-Aminobenzoates.**—The *p*-aminobenzoates were prepared from the corresponding nitro compounds as described in the previous article,[1] except for the distillation. After the removal of the alcohol, a small amount of zinc dust was introduced into the distilling flask and the distillation carried out at pressures of 1 mm. or less. This removed the red by-product which was formed upon exposure of the reduced solution to the air.

Table III lists the analyses and yields of the *p*-aminobenzoates, and the melting points of the picramides.

TABLE III

p-AMINOBENZOATES ($ROCH_2CH_2OOCC_6H_4NH_2$-*p*)

Amyl group	Yield, %	N analyses, % (Calcd. 5.58) Found		M. p., °C., picramide
$CH_3(CH_2)_4$-[a]	85	5.61	5.70	115.5
$(CH_3)_2CH(CH_2)_2$-	81	5.49	5.55	140.9
$(CH_3)(C_2H_5)CHCH_2$-	83	5.46	5.43	129.1
$(C_2H_5)_2CH$-	80	5.51	5.68	136.0
$(CH_3)(n\text{-}C_3H_7)CH$-	80	5.50	5.52	120.8
$(C_2H_5)(CH_3)_2C$-	76	6.07	5.48	134.9

[a] Fine white needles from ligroin, melting point 56.8°.

The picramides were prepared by the method given by Mulliken.[5] The *p*-aminobenzoates are all viscous oils at room temperature with the exception of the *n*-amyl compound. The yields are based upon the amount of nitro compound used. The picramides are all fine yellow needles, having a sharp melting point.

The physiological properties of the *p*-aminobenzoates are now being investigated.

The authors wish to express their appreciation to the Carbide and Carbon Chemicals Corpora-

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(4) Conn, Collett and Lazzell, THIS JOURNAL, **54**, 4370 (1932).

(5) Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1916, Vol. II, p. 32.

tion for the generous supply of ethylene oxide furnished for this investigation.

Summary

Three new β-amoxyethanols, six new β-amoxyethyl esters of *p*-nitrobenzoic acid and six new β-amoxyethyl esters of *p*-aminobenzoic acid have been prepared and some of their physical constants determined.

MORGANTOWN, WEST VIRGINIA RECEIVED JUNE 13, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Succinic-α-*d*,α'-*d* Acid and its Derivatives. II. Stereochemistry of the Type RR'CHD

BY MARLIN T. LEFFLER[1] AND ROGER ADAMS

The effect of deuterium upon the optical activity of organic molecules and the possibility of obtaining an answer to the question as to whether RR'CHD may be optically active has engaged the attention of investigators in several laboratories.[2]

Schoenheimer and Rittenberg[3] compared the optical activity of coprostanone-d_2 and coprostanone and noted that the difference in optical activity was very small, if at all appreciable. Erlenmeyer and Gärtner[4] were unable to resolve phenylpropionic-α-*d*,β-*d* acid of which they obtained an impure sample by reduction of cinnamic acid with deuterium iodide and phosphorus.

In the research now reported the reduction of diethyl fumarate and diethyl maleate was carried out using practically 100% deuterium in the presence of platinum catalyst. The resulting diethyl succinate-α-*d*,α'-*d* corresponds to the stereochemical R'CHD-CHDR' type, separable into a *meso* and a *racemic* modification. It is well known that the action of permanganate on maleic acid produces *meso*-tartaric acid while the *racemic* modification results from fumaric acid. Although the deuterium reduction of an ethylenic linkage probably does not follow the above "*cis*" addition, the reduction of diethyl maleate should still be capable of yielding a different form from that given by diethyl fumarate. As shown by the constants (Table I), the diethyl succinic-α-*d*,α'-*d* specimens from both sources appeared to be identical, nor was the presence of isomers in either sample noticed during the distillation of the ester.

The densities of diethyl succinate-α-*d*,α'-*d* (Table I) from different reductions of the same material show some variance, possibly due to varying amounts of hydrogen "impurity." In a previous paper[1b] it was pointed out that the observed densities of dimethyl succinate-α-d_2,α'-d_2 and succinic-α-d_2,α'-d_2 anhydride were lower than and did not agree with the calculated values. The calculation of these values was based primarily upon the assumption of identical molecular volumes for deuterium and hydrogen. Since that time it has been observed[5] that the molecular volumes of the two isotopes are not identical and may differ sufficiently to affect the densities of deuterium compounds. However, it is evident that this effect must vary with the substances in question, as the densities[6] of several deuterium compounds, of established purity, agree very well with the calculated values; others show less agreement. In any case, it is worth mentioning that the densities (Tables I, II) observed for diethyl succinic-α-*d*,α'-*d* and its derivatives show fair agreement with the theoretical values. It is entirely probable that the discrepancy which does exist may be due both to a difference in molecular volumes and to hydrogen "impurities."

Succinic-α-*d*,α'-*d* acid was prepared by the hydrolysis of the ester from both of the abovementioned sources. These specimens of dideu-

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[1] (a) This is a portion of a thesis submitted in fulfilment of partial requirements for the degree of Doctor of Philosophy in Chemistry; (b) for previous paper in this field see McLean and Adams, THIS JOURNAL, **58**, 804 (1936).

A description of the investigation herewith reported was included in an address in connection with the Willard Gibbs Medal award to the senior author, May 23, 1936.

[2] After the preparation of this manuscript, an article by Biilmann, Jensen and Knuth, *Ber.*, **69**, 1031 (1936), reports the preparation of a deuterio camphane derivative which must be optically active due to the —CHD group. This paper will be discussed in a subsequent communication.

[3] Schoenheimer and Rittenberg, *J. Biol. Chem.*, **111**, 183 (1935).

[4] Erlenmeyer and Gärtner, *Helv. Chim. Acta*, **19**, 145, 331 (1936).

[5] Brickwedde and Teal, *Rev. Mod. Phys.*, **7**, 34 (1935).

[6] Erlenmeyer, Lobeck, Gärtner and Epprecht, *Helv. Chim. Acta*, **19**, 336 (1936); Bowman, Benedict and Taylor, THIS JOURNAL, **57**, 960 (1935); Breuer, *ibid.*, **57**, 2236 (1935).

TABLE I

CONSTANTS OF DIETHYL SUCCINATE AND ITS DERIVATIVES

Compound		B. p., °C., at 40 mm. bath 155°	B. p. °C., at 16 mm., bath 125°	n^{20}_D	Density, d^{20}_4 Found	Calcd.[c]
Diethyl succinate-*α-d,α'-d* (from fumarate)	(I)	126.0–126.5	106.0–106.5	1.4193	1.0533	1.0542
	(II)	....	106.0–106.4	1.4194	1.0527	1.0542
Diethyl succinate-*α-d,α'-d* (from maleate)	(I)	126.2–126.5	106.5–106.8	1.4198	1.0543	1.0542
	(II)	126.0–126.5	....	1.4196	1.0527	1.0542
Diethyl succinate (from fumarate)		126.0–126.4	....	1.4200[a]	1.0420[b]	....
Diethyl succinate (from maleate)		126.0–126.4	....	1.4199[a]	1.0421[b]	....

[a] The value reported in the literature is: n^{20}_D 1.42007 (Karvonen, *Ann. acad. sci. Fennicae*, **10A**, 13 (1912)). [b] This density agrees with the previously reported value, d^{20}_4 1.042 ("Int. Crit. Tables," Vol. 1, 1926, p. 222). [c] The method of calculation was that employed previously.[1b]

TABLE II

PHYSICAL CONSTANTS AND ANALYSES OF HYDROGEN AND DEUTERIUM ANALOGS[a]

Compound (formula and name)	M. p., °C. (corr.)	Density, d^{13}_4 Found	Calcd.[c]		Subst., mg.	CO_2, mg.	Water, mg.	% C	% hydrogen[b] isotopes		% H
Diethyl succinate-*α-d,α'-d*;[b]	....	(See Table I)		Found	3.890	7.79	2.77	54.61	8.95	$\frac{2.30}{18.30}$	..
$C_8H_{12}D_2O_4$ (from fumarate)				Calcd.	...	..	..	54.51	9.15		..
Diethyl succinate-*α-d,α'-d*;	....	(See Table I)		Found	3.911	7.81	2.76	54.46	8.87		..
$C_8H_{12}D_2O_4$ (from maleate)				Calcd.	...	..	..	54.51	9.15		..
Diethyl succinate;	....	(See Table I)		Found	3.988	8.05	2.84	55.05	..		7.97
$C_8H_{14}O_4$				Calcd.	...	..	..	55.08	..		8.10
Succinic-*α-d,α'-d* acid;	184.0–184.5	....		Found	3.720	5.48	1.73	40.17	6.69	$\frac{2.69}{18.69}$	..
$C_4H_4D_2O_4$ (from fumarate)				Calcd.	...	..	..	39.98	6.71		..
Succinic-*α-d,α'-d* acid;	184.0–184.5	....		Found	3.743	5.52	1.73	40.22	6.65		..
$C_4H_4D_2O_4$ (from maleate)				Calcd.	...	..	..	39.98	6.71		..
Succinic acid; $C_4H_6O_4$	184.5–185	....		Found	3.708	5.55	1.67	40.82	..		5.04
				Calcd.	...	..	..	40.66	..		5.13
Succinic-*α-d,α'-d* anhydride;	119.3–119.6	1.2560	1.2588	Found	3.604	6.25	1.33	47.29	5.86	$\frac{3.02}{19.02}$	..
$C_4H_2D_2O_3$ (from fumarate)				Calcd.	...	..	..	47.04	5.92		..
Succinic-*α-d,α'-d* anhydride;	119.3–119.6	1.2563	1.2588	Found	3.800	6.56	1.41	47.08	5.89		..
$C_4H_2D_2O_3$ (from maleate)				Calcd.	...	..	..	47.04	5.92		..
Succinic anhydride;[d]	119.3–119.6	1.2340	....	Found	3.817	6.71	1.36	47.94	..		3.99
$C_4H_4O_3$				Calcd.	...	..	..	47.99	..		4.03

[a] In order to obtain satisfactory analyses on the acids and the anhydrides, only copper oxide was used in a combustion tube of twice the ordinary length. [b] A mixed melting point of the d_2-acid from fumarate and maleate showed no depression. A mixture containing approximately 50% of either the d_2-acid from fumarate or from maleate and succinic acid melted at 184–185°. [c] The method of calculation was that used previously.[1b] [d] Mixtures containing varying amounts of succinic anhydride and either of the d_2-anhydrides melted at 119.3–119.6°.

terio acid were identical in melting point, and fractional crystallization (Table II) failed to indicate the presence of more than one form. The two samples of dideuterio acid, on treatment with acetyl chloride, gave two identical specimens of succinic-*α-d,α'-d* anhydride (Table II).

As previously pointed out,[1b] carbon analyses of deuterium compounds may indicate semi-quantitatively the presence of deuterium, while hydrogen isotope analyses are generally of little value. The carbon analyses (Table II) are sufficiently different from the anhydride analogs to show clearly that deuterium was not entirely replaced during any of the previous treatments, and the density determinations (Table II) indicate that if any replacement at all occurred it was not appreciable in amount.

All of the evidence derived from the above-mentioned experimental results points, in a negative sense, to the symmetry of the carbon RR'CHD. It was thought to be of additional and equal interest to compare the degree of optical activity of several deuterium and hydrogen analogs. This was made possible by studying the rotations of the brucine, quinine, strychnine and cinchonine salts of both succinic-*α-d,α'-d* acid and succinic acid. The rotations of the hydrogen and deuterium salts (Table III) were observed under as nearly identical conditions as possible. Within the limits of experimental accuracy, these rotations were identical.

Granted that the one form of succinic-*α-d,α'-d* acid obtained from the above-mentioned reductions might have been the *meso* modification, it

TABLE III

ROTATIONS[a] OF ALKALOIDAL SALTS OF DEUTERIO-SUCCINIC AND SUCCINIC ACIDS

Alkaloidal salt	Weight[b]	Solvent	$\alpha^{20}_{\rm D}$[c]	$[\alpha]^{20}_{\rm D}$
Succinic acid (brucine)	0.1971	Water	−0.50	− 25.4 ± 0.5
Succinic-α-d,α'-d acid (brucine)	.1964	Water	− .50	− 25.5 ± .5
Succinic acid (quinine)	.1003	95% Alcohol	−1.66	−165.5 ± .5
Succinic-α-d,α'-d acid (quinine)	.1007	95% Alcohol	−1.66	−164.9 ± .5
Succinic-α-d_2,α'-d_2 acid[1b] (quinine)	.1004	95% Alcohol	−1.66	−165.3 ± .5
Succinic acid (strychnine)	.2033	Water	−0.52	− 25.6 ± .3
Succinic-α-d,α'-d acid	.2033	Water	− .51	− 25.3 ± .3

[a] All readings were taken at 20 ± 0.1° to prevent variations in ionization. [b] This weight was made up to 10.00 cc. [c] l = 1 dec.

was nevertheless desirable to attempt the resolution of this acid. The cinchonine salt was selected for this purpose as cinchonine has been used successfully to resolve tartaric acid.[7] The fractionation gave four crops of dideuterio salt, identical in crystalline form, melting point, and rotation. None of these fractions gave any evidence of mutarotation.

Experimental

Diethyl Fumarate.—This ester was prepared according to the method described in "Organic Syntheses,"[8] and was purified by two distillations at atmospheric pressure followed by a final distillation *in vacuo*. The fraction used in the reduction experiments below had the following physical constants: b. p. 218–218.5° (corr.) at 740 mm. or 109–110° at 16 mm.; $n^{20}_{\rm D}$ 1.4410.

Diethyl Maleate.—The product from esterification of maleic acid with absolute alcohol by the same procedure had, after careful fractionation, the following physical constants: b. p. 225° (corr.) at 740 mm. or 115–116° at 16 mm.; $n^{20}_{\rm D}$ 1.4415. These constants check those described in the literature.

Diethyl Succinate-α-d,α'-d (from Diethyl Fumarate).—The apparatus employed for the reduction was identical to that previously described.[1b] Two separate reduction experiments were carried out, the same conditions prevailing in each. Each reduction tube was charged with 4.00 g. of diethyl fumarate, 0.05 g. of platinum catalyst, and 7 cc. of dry ethyl acetate (acetic acid free). An excess of practically 100% deuterium was available. The reduction was complete at the end of eight hours and no additional absorption took place in an additional three hours. At the end of this time the reaction mixture was filtered from the catalyst and the ethyl acetate solvent distilled off below 60° at slightly reduced pressure. The residue was distilled *in vacuo* at two different pressures, the latter being carefully controlled by a constant pressure regulator. The boiling point (Table I) was constant and gave no indication of the presence of isomers. The yield of purified diethyl succinate-α-d,α'-d from 4.00 g. of diethyl fumarate was 3.4–3.7 g. (83–91%). This product was free from any unsaturated material as shown by an alkaline permanganate test.

Diethyl Succinate-α-d,α'-d (from Diethyl Maleate).—Complete reduction of diethyl maleate carried out in a similar manner was attained in six hours, and no additional absorption of deuterium took place in two more hours. The boiling point of the product was constant, gave no indication of the presence of isomers, and was identical with the boiling point of the product obtained from diethyl fumarate (Table I) (yield 88%). This product gave no indication of unsaturation as shown by alkaline permanganate.

Diethyl Succinate.—This ester was prepared by the reduction of either diethyl fumarate or diethyl maleate with hydrogen. The same conditions were used as in the reduction experiments with deuterium. The constants check those recorded in the literature (Table I).

Succinic-α-d,α'-d Acid (Origin: Diethyl Fumarate).—The hydrolysis of diethyl succinate-α-d,α'-d (origin: fumarate; d^{20}_4 1.0533) was accomplished by boiling 10 g. of the ester for five to six hours with 100 cc. of water containing three drops of concentrated nitric acid. After the hydrolysis was complete, the clear solution was cooled and the nitric acid was neutralized by adding the calculated quantity of sodium carbonate. The solution was then evaporated to dryness *in vacuo* at 40–50° to give 6.6 g. of crude acid. The latter was fractionally crystallized in the following manner. The entire amount of crude succinic-α-d,α'-d acid was dissolved in 90 cc. of hot water, filtered, and the resultant solution allowed to evaporate slowly. The evaporation was carried out in stages; a crop of crystals was separated after each 20% decrease in volume. These crops were purified by further crystallization.

In no case was the presence of isomers indicated during the fractionation of the acid, as the solubilities and melting points were essentially identical in all fractions. Succinic-α-d,α'-d acid crystallized in colorless needles which appeared to be identical to those obtained from the reduction of diethyl maleate and identical to succinic acid itself. The melting point of the deuterio acid was about 0.5° lower than that of succinic acid (Table II).

Succinic-α-d,α'-d Acid (Origin: Diethyl Maleate).—Diethyl succinate-α-d,α'-d (d^{20}_4 1.0543) obtained by the reduction of diethyl maleate was hydrolyzed in exactly the same manner as used in the hydrolysis above. The latter was fractionally crystallized by the procedure outlined for the dideuterio acid from diethyl fumarate. The melting points and solubilities were identical for the various fractions and also identical with the values of the acid from diethyl maleate reduced with deuterium (Table II).

Succinic Acid.—A pure specimen of succinic acid was prepared in the same way as the above by the saponifica-

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(7) Pasteur, *Ann. chim. phys.*, **38**, 469 (1853).

(8) "Organic Syntheses," Vol. X, 1930, p. 48.

tion of diethyl succinate. Both the diethyl succinate resulting from the reduction of diethyl fumarate and diethyl maleate were used in preparing succinic acid. The acid so obtained was recrystallized from water, which method gave a product with the same melting point as that obtained by sublimation. It was found that at low pressure (1 mm. at 145°) sublimation could be conveniently used to recover deuteriosuccinic acid (or succinic acid) from otherwise unworkable residues. Samples purified in this way had the same melting point as crystallized material.

Succinic-*α-d,α′-d* Anhydride.—The purified deuterio acid (2.36 g.; origin, diethyl fumarate) was refluxed for three hours with acetyl chloride (4.7 g.). At the end of this time, the clear solution was allowed to cool spontaneously whereby colorless prisms of succinic-*α-d,α′-d* anhydride were deposited. After further cooling in ice-water, the product was separated by filtration, washed with cold, absolute ether, and vacuum dried over soda-lime to remove traces of acid chloride. The crude succinic-*α-d,α′-d* anhydride (yield 91%) was fractionally crystallized from freshly distilled acetic anhydride. Only a single form was indicated, m. p. 119.3–119.6°.

Succinic-*α-d, α′-d* acid (origin: diethyl maleate) was converted in the same way as the above into the anhydride. The succinic-*α-d,α′-d* anhydride was identical with the product from diethyl fumarate, m. p. 119.3–119.6°. The density of both this and the sample above was determined by the procedure previously described.[1b] The values from these density determinations (Table II) indicate that under the conditions used in the previous hydrolyses there was no appreciable amount of deuterium lost by exchange with hydrogen.

Succinic Anhydride.—This anhydride was prepared in the same way as the dideuterio compound.

ALKALOIDAL SALTS OF SUCCINIC-*α-d,α′-d* ACID

A Comparison of the Rotations of Deuterium and Hydrogen Analogs

Brucine Salt of Succinic-*α-d,α′-d* Acid.—To a solution of 0.1800 g. of succinic-*α-d,α′-d* acid in 20 cc. of hot absolute alcohol was added 0.6994 g. of *l*-brucine (hydrate). The solution was boiled for several minutes after all of the alkaloid had dissolved, was filtered while hot, and set aside to crystallize. The first crop of colorless clusters amounted to 0.55 g. and the second, 0.12 g. Both crops melted at 216–218° (dec.) and the melting point was not changed by further recrystallization from absolute alcohol. Rotations of various fractions were identical.

Anal. (micro-Dumas). Calcd. for $C_4H_4D_2O_4 \cdot 2C_{23}H_{26}O_4N_2$: N, 6.16. Found: N, 6.04.

Brucine Salt of Succinic Acid.—This salt was prepared in the same manner as above for the deuterium analog. On recrystallization from absolute alcohol it formed colorless prism clusters melting at 216–218° (dec.).

Anal. (micro-Dumas). Calcd. for $C_4H_6O_4 \cdot 2C_{23}H_{26}O_4N_2$: N, 6.17. Found: N, 6.06.

Quinine Salt of Succinic-*α-d,α′-d* Acid.—To a solution of 0.150 g. of succinic-*α-d,α′-d* acid in 30 cc. of hot water was added 0.405 g. of *l*-quinine. The alkaloid went into solution immediately, and on allowing the solution to cool, colorless, soft needles of the salt separated. The first crop amounted to 0.32 g. and the second, 0.1 g. Both crops melted with shrinking at 175°, becoming entirely liquid at 201°. As indicated by the melting point, the salt was evidently hydrated.[9] The melting point was not altered by further recrystallization from water, but when the sample was dried *in vacuo* at 100° for twenty-four hours it melted without shrinking at 198–201°. All fractions were identical in properties.

Anal. (micro-Dumas). Calcd. for $C_4H_4D_2O_4 \cdot C_{26}H_{24}O_2N_2 \cdot H_2O$: N, 6.06. Found: N, 6.21.

Quinine Salt of Succinic-*α-d₂,α′-d₂* Acid.—This salt was prepared from the tetradeuterio acid[1b] by the same method used for the dideuterio compound. It crystallized from water in the same form and was dried in the same way as the analogs; m. p. 198–201°.

Anal. (micro-Dumas). Calcd. for $C_4H_2D_4O_4 \cdot C_{20}H_{24}O_2N_2 \cdot H_2O$: N, 6.03. Found: N, 6.06.

Quinine Salt of Succinic Acid.—This salt was prepared in the manner used above for the analogs. It crystallized from water in colorless, fluffy needles which, after drying *in vacuo* at 100°, melted at 198–201° (dec.).

Anal. (micro-Dumas). Calcd. for $C_4H_6O_4 \cdot C_{20}H_{24}O_2N_2 \cdot H_2O$: N, 6.08. Found: N, 6.11.

Strychnine Salt of Succinic-*α-d,α′-d* Acid.—An amount of 0.2400 g. of succinic-*α-d,α′-d* acid was dissolved in 20 cc. of hot absolute alcohol, followed by the addition of 0.668 g. of *l*-strychnine. The mixture was allowed to evaporate above 35° and two fractions separated. These were identical. After drying *in vacuo* at 100°, the crystals softened at 190° and melted at 210°. By the usual procedure of crystallization, strychnine crystallized and had to be separated mechanically from the salt.

Anal. (micro-Dumas). Calcd. for $C_4H_4D_2O_4 \cdot 2C_{21}H_{22}O_2N_2$: N, 7.11. Found: N, 7.29.

Strychnine Salt of Succinic Acid.—This was prepared as described for the deuterium analog. The colorless spurs[10] which crystallized from absolute alcohol were dried *in vacuo* at 100°. They softened at 190° and melted at 210°.

Anal. (micro-Dumas). Calcd. for $C_4H_6O_4 \cdot 2C_{21}H_{22}O_2N_2$: N, 7.13. Found: N, 7.19.

Attempted Resolution of Succinic-*α-d,α′-d* Acid

Cinchonine Salt of Succinic-*α-d,α′-d* Acid.—To a solution of 0.3600 g. of succinic-*α-d,α′-d* acid in 10 cc. of hot water was added 0.883 g. of *d*-cinchonine. The mixture was refluxed for several minutes to give a clear solution. As the salt crystallized only with great difficulty from an unseeded aqueous solution, crystalline salt was prepared from dioxane as a solvent, allowing the dioxane to evaporate very slowly. These crystals were later used to seed the water solution which was preferred to dioxane as a fractionating solvent. After two days of standing, large colorless prisms had separated. Several fractions were obtained as follows: (1) 0.26 g.; (2) 0.19 g.; (3) 0.27 g. and (4) 0.13 g., totalling 0.85 g. (68.5%). All of these fractions were obviously hydrated[11] as they effloresced on exposure to the air. The above weights of the various

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[9] Lindet, *Bull. soc. chim.*, [3] **15**, 1160 (1896).

[10] Crespi, *Gazz. chim. ital.*, **13**, 176 (1883).

[11] Hesse, *Ann.*, **176**, 232 (1874).

fractions were taken after drying the samples for a day in a vacuum desiccator over sulfuric acid. After this treatment, all of the crops melted over the range, 130–160°. The rotations were first read at 0°, then at 20°, and finally again at 0° in order to observe any possible mutarotation. All fractions exhibited, within the limits of experimental error, the following identical rotations: $[\alpha]^{0}\text{D}$ +158 ± 1 (c = 1.000, l = 1 dec., $\alpha^{0}\text{D}$ +1.58); $[\alpha]^{20}\text{D}$ + 152 ± 1 (c = 1.000, l = 1 dec., $\alpha^{20}\text{D}$ +1.52). There was no indication of mutarotation in any of the fractions.

Anal. (micro-Dumas). Calcd. for $C_4H_4D_2O_4 \cdot 2C_{19}H_{22}ON_2$: N, 7.90. Found: N, 7.80.

Cinchonine Salt of Succinic Acid.—This salt, used as a comparison standard, was prepared in the manner described above for the deuterium analog. The dried sample melted over a range of 130–160°. As in the above instance all rotations were taken on solutions of the same concentration and at temperatures controlled to within 0.1°. The latter precautions were taken to prevent ionization. The following rotations were observed for this hydrogen analog: $[\alpha]^{0}\text{D}$ +159 ± 1 (c = 1.008, l = 1 dec., $\alpha^{0}\text{D}$ + 1.60); $[\alpha]^{20}\text{D}$ + 153 ± 1 (c = 1.008, l = 1 dec., $\alpha^{0}\text{D}$ +1.54).

Summary

1. Diethyl succinate-α-d,α'-d was prepared from both diethyl maleate and diethyl fumarate by reduction with deuterium. The presence of more than one compound was not indicated.

2. Succinic-α-d,α'-d acid from diethyl succinate-α-d,α'-d from either diethyl maleate or fumarate appeared to be a homogeneous substance. It melted 0.5° lower than succinic acid. Its alkaloidal salts exhibited the same rotation as the corresponding salts of succinic acid. No separation of diastereoisomeric salts was possible.

3. Succinic-α-d,α'-d anhydride melted at the same point as succinic anhydride.

4. The densities of diethyl succinate-α-d,α'-d and of succinic-α-d,α'-d anhydride indicated no appreciable replacement of deuterium by hydrogen during the various reactions. The values were slightly lower than those calculated from the densities of the hydrogen analogs on the basis of the assumption that the molecular volume of hydrogen and deuterium is identical.

URBANA, ILLINOIS RECEIVED JUNE 4, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Stereochemistry of Deuterium Compounds of the Type RR'CHD: Camphane-2,3-d_2

BY MARLIN T. LEFFLER[1] AND ROGER ADAMS

A recent article by Biilmann, Jensen and Knuth[2] described the preparation and subsequent study of the optical properties of camphane-2-d. Although camphane, due to its symmetry, is optically inactive, camphane-2-d was found to have an observed rotation of αD + 0.08° (c = 10.00 of ether, l = 2 dec.). This was presented as direct evidence in favor of the asymmetry of the molecule RR'CHD. As pointed out by the above authors, the preparation of the hydrogen and deuterium analogs of camphane by the hydrolysis of bornylmagnesium chloride with water and deuterium oxide, respectively, is accompanied by the formation of several other optically active products. The latter must necessarily be removed completely by repeated crystallizations before any comparison can be drawn between the optical properties of camphane and camphane-2-d. The difficulty with which camphane derivatives are purified renders any process of purification questionable as to its thoroughness. No attempt was made by Biilmann to characterize the camphane or camphane-d used for comparative rotation studies either by analysis, density or other physical constants with the exception of melting points, which are not significant. Since the results of these investigators are not in complete accord with the present and previous[1,3] researches concerning this problem of asymmetry, it seems advisable to make the herein described report at this time before the investigation is satisfactorily finished. In addition, it is worth mentioning that the first mentioned authors found that the sample of active camphane-2-d was converted into an inactive product, presumably camphane, by treatment with hydrogen in the presence of platinum and carbon at room temperature. It is rather odd that cleavage by hydrogen of an ordinary carbon–deuterium bond would occur with

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(1) For the previous article in this field see Leffler and Adams, THIS JOURNAL, **58**, 1551 (1936).

A description of this investigation herewith reported was included in an address in connection with the Willard Gibbs Medal award to the senior author, May 23, 1936.

(2) Biilmann, Jensen and Knuth, *Ber.*, **69**, 1031 (1936).

(3) Erlenmeyer and Gärtner, *Helv. Chim. Acta*, **19**, 145, 331 (1936).

such ease and completeness. At least this does not seem in accord with our present knowledge of the hydrogen–deuterium interchange reactions.

The desirability of using a structure of the camphane type in studying this problem is worth emphasizing and may be most clearly brought out by mentioning briefly the difficulties involved in other modes of attack. A stereochemical study of a molecule of the type I, as described in the previous paper by the present authors,[1,4] is complicated by at least two factors: namely, the production of this type by the reduction of either the

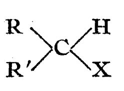
$R'CHD—CHDR'$ I

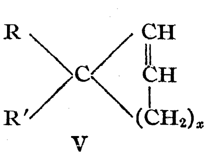
$RCHD—COOH$ II

$RCHD—(CH_2)_xCOOH$ III

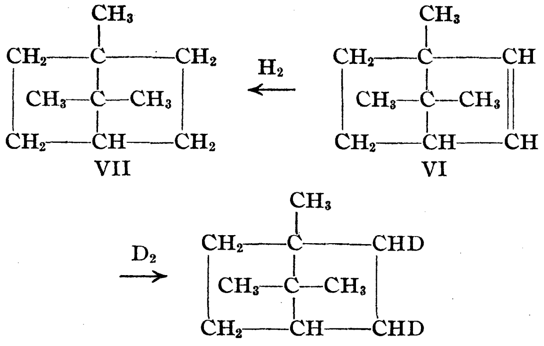
cis or *trans* unsaturated compound might lead to the formation of one and the same stereo form, thus making the search for a *meso* and a *racemic* modification of no consequence; in addition, if the *meso* modification was the one form so produced, obviously any attempts at resolution would be meaningless. The use of acids of the structure II in investigating the problem adds to the complication due to the possibility of racemization through the enolization of the alpha hydrogen or deuterium. The latter difficulty would be materially avoided by the use of the molecule shown in III. It is to be noted, however, that all of these three types involve either the isolation of diastereoisomers or the resolution into optically active forms. This evidence when obtained in the form of negative results is, at best, only indirect proof of the symmetry of the RR'CHD molecule.

A more direct and definite proof is possible through the utilization of an optically active substance which loses its activity on reaction with hydrogen, such as the structures illustrated in IV and V. Since the substitution of X in IV by


IV


V

deuterium involves the replacement of a group directly attached to the asymmetric center and thus the possibility of inversion and racemization, the structure V is the more desirable of the two. In addition, cyclic structures commonly have a higher rotation than open chain molecules. The latter is of distinct advantage in comparing the rotation of the products resulting from the action of hydrogen and deuterium on the original molecule. The terpene bornylene, VI, corresponds to the structure V and thus lends itself to the study of the problem at hand. On reduction of *l*-bornylene with hydrogen, camphane VII results, inactive due to the symmetry of the molecule; on the other hand, the reduction of *l*-bornylene with deuterium leads to the formation of camphane-2,3-d_2, VIII, which if deuterium differs properly from hydrogen should still be optically active.


VII VI VIII

Although *l*-bornylene represents, from a theoretical standpoint, a most ideal type of structure for the study of this problem, its use involves several experimental difficulties. Due to its extreme volatility, purification is by no means an easy task. Furthermore there seems to be no practical method of preparing the substance in a pure state. The decomposition of methyl bornylxanthate,[5] although the most practical and convenient method of preparation, is accompanied by the formation of a rearrangement product, tricyclene,[5,6] from which *l*-bornylene cannot be separated easily. Henderson and Caw[7] described a method for the purification of bornylene containing this impurity by the preferential oxidation of the tricyclene by hydrogen peroxide. However, this was not found to be entirely satisfactory[8] due to the poor yields and incompleteness of the purification. Fortunately, however, the presence of tricyclene as an impurity in the bornylene does not interfere with the results of the following experiments, since by its symmetry, it is optically inactive.

It has been shown previously by Henderson

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(4) McLean and Adams, THIS JOURNAL, **58**, 804 (1936).

(5) Tschugaeff, *Ber.*, **32**, 3332 (1889); *Ann.*, **388**, 280 (1912).

(6) Bredt and co-workers, *Ann.*, **366**, 1 (1909); *J. prakt. Chem.*, (ii) **131**, 137 (1931).

(7) Henderson and Caw, *J. Chem. Soc.*, **101**, 1416 (1912).

(8) Sutherland, private communication.

and Pollock[9] that the catalytic nickel–hydrogen reduction of bornylene to camphane proceeds without rearrangements, even at temperatures of 170–190°. The *l*-bornylene obtained in the present investigation by the decomposition of methyl bornylxanthate was completely reduced catalytically by both hydrogen and deuterium at room temperature and practically atmospheric pressure, yielding camphane and camphane-2,3-d_2, respectively. Although pure camphane is optically inactive, the sample obtained by the reduction with hydrogen was found to have an observed rotation of $\alpha^{25}\text{D} + 0.02°$ (±0.01) (Table I). This small degree of activity could not have been due to incomplete reduction, as the rotation of the original bornylene was negative and the final product was shown to be completely saturated. It is to be explained by the presence of some dextro rotatory impurity. Camphane-2,3-d_2 resulting from the reduction of bornylene with deuterium gave an observed rotation of $\alpha^{25}\text{D} + 0.02°$ (±0.01) (Table I) under identical conditions. Care was exercised to run control experiments with blank samples and the rotations of the hydrogen and deuterium analogs were each checked in triplicate. In every case there was an observable but identical rotation.

A density determination (Table I), using the method of McLean and Adams,[4] on both camphane and camphane-2,3-d_2 definitely distinguished these two substances.

It is to be conceded that the above evidence, due to its qualitative nature, should not be accepted as definite proof of the inactivity of the RR′CHD structure. It is certain, however, that the effect of the deuterium atom on the optical activity of this structure is of an extremely small order of magnitude. Further studies along these lines are in progress; in particular a similar investigation is being conducted on menthene and a further attempt is being made to obtain pure bornylene in order to repeat the experiments reported here.

Experimental

***l*-Bornylene.**—*d*-Borneol was converted into *d*-methyl bornylxanthate as described by Tschugaeff.[5] After two recrystallizations from alcohol, the xanthate melted at 57–58°; rotation in dioxane was $[\alpha]^{24}\text{D} + 31.5°$ (c = 2.00). The rotation and melting point checked those previously reported and were unchanged by further purification. *l*-Bornylene was obtained from methyl bornylxanthate by dry distillation[5] at 170–190° and freed from sulfur impurities by repeated sublimations from metallic sodium. The sample of *l*-bornylene prepared in this manner melted at 105–106.5°; rotation was $[\alpha]^{25}\text{D} - 10.66°$ (c = 4.627 in toluene), $[\alpha]^{25}\text{D} - 9.57°$ (c = 16.00 in ethyl acetate); density, $d^{131}{}_4$ 0.7666. As the first two constants indicate and as was earlier pointed out by Bredt and co-workers,[6] bornylene prepared in this manner is contaminated by a rearrangement product, tricyclene, from which it cannot be completely separated by ordinary methods of purification. Bredt and Sandkuhl[10] obtained a sample of bornylene melting at 113° and having a rotation of $[\alpha]\text{D} - 21.69°$ which they believed to be essentially pure. The presence of tricyclene as an impurity should have no effect, however, on the optical inactivity of camphane formed by the reduction of the impure bornylene.

Camphane.—The apparatus employed for the reduction of bornylene by hydrogen (or deuterium) was the same as that previously described by McLean and Adams.[4] Two reduction tubes were used, the charge in each tube being 1.36 g. of *l*-bornylene, 0.05 g. of platinum catalyst and 8 cc. of ethyl acetate (dry and acid and alcohol free). One-half of the theoretical amount of hydrogen was absorbed in one and one-half hours. There was no further absorption in an additional hour. That complete reduction had been obtained was substantiated by the settling of the catalyst in the reduction tubes.

The contents from the reduction tubes, after separation from the catalyst, were shaken with 1 liter of cold water in order to precipitate the crude camphane. The crude material was separated by filtration, dried for a short time over phosphorus pentoxide, and finally allowed to sublime at room temperature from metallic sodium. The camphane obtained in this manner gave no test for unsaturation as shown by bromine in glacial acetic acid and had the physical constants listed in Table I.

The rotations recorded in Table I were checked in triplicate, care being taken to maintain a constant temperature of ±0.2° during the observations and to use a blank control in each case. In every instance there was evidence of slight activity due to the presence of some dextro-rotatory impurity.

Camphane-2,3-d_2.—Practically 100% deuterium was prepared as earlier described[4] by the electrolysis of deuterium oxide. This deuterium was employed for the reduction of *l*-bornylene, using conditions identical to those given above for the hydrogen analog. Complete reduction was attained in two hours as compared with one and

TABLE I

CONSTANTS ON CAMPHANE AND CAMPHANE-2,3-d_2

Compound	M. p., °C.[a]	Density[b] obs., $d^{15}{}_4$	$\alpha^{25°}\text{D}^{\pm 0.2}$ [c]
Camphane	145	0.7458	+0.02 (±0.01)
Camphane-2,3-d_2	143	0.7552	+0.02 (±0.01)

[a] These low melting points for camphane indicate the presence of the impurity of tricyclene carried through from bornylene.

[b] The method employed for the density determination was that described in a previous paper.[4]

[c] Concentration = 0.85 g. in 5 cc. of ethyl acetate. l = 1.

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[9] Henderson and Pollock, *J. Chem. Soc.*, **97**, 1620 (1910).

[10] Bredt and Sandkuhl, *Ann.*, **366**, 11 (1909).

one-half hours for the absorption of an equivalent amount of hydrogen. The product, camphane-2,3-d_2 (plus impurity from the bornylene) was isolated in the same manner used for camphane and gave no test for unsaturation. The physical constants are listed in Table I. In measuring the rotation and in making comparisons with the hydrogen analog, care was exercised to maintain identical conditions throughout. In no instance was there any observable difference between the optical activity of the samples of camphane and camphane-2,3-d_2.

Summary

l-Bornylene upon reduction with hydrogen gives a camphane having a rotation of +0.02 (±0.01) due to some impurity. Reduction with deuterium results in a molecule of identical rotation. The densities of camphane and camphane-2,3-d_2 were shown to be markedly different.

URBANA, ILLINOIS RECEIVED JUNE 8, 1936

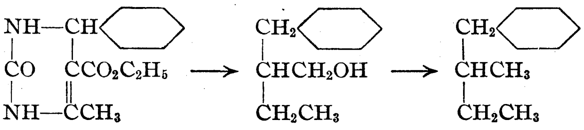
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, AND THE RESEARCH LABORATORY OF MERCK AND CO., INC.]

Hydrogenation and Hydrogenolysis of a 2-Keto-1,2,3,4-tetrahydropyrimidine Derivative to 2-Benzyl- and 2-Hexahydrobenzylbutanol-1[1]

BY KARL FOLKERS[2]

The action of hydrogen on 2-keto-1,2,3,4-tetrahydropyrimidines over nickel and copper–barium–chromium oxide catalysts at approximately 200 atmospheres pressure and at temperatures up to 200° was recently described.[3] It was shown that 2-keto-4-phenyl-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidine, I, was reduced to a mixture of at least two isomeric hexahydropyrimidine derivatives. The reduction of the pyrimidine 5,6-double bond took place at 200°, and the yield of the isolated hexahydropyrimidines was 77%. There was evidence for the presence of side products resulting from further reactions with hydrogen. It was to be expected that a higher temperature would increase the extent of these reactions, and this paper summarizes the results of allowing the 2-keto-1,2,3,4-tetrahydropyrimidine derivative, I, to react with hydrogen at 250° over a copper–barium–chromium oxide catalyst.

It could be predicted that, as the temperature of the reaction neared 250°, a rather complex combination of hydrogenation and hydrogenolysis reactions would occur. Thus, the pyrimidine 5,6-double bond and the carbethoxy group would be definitely susceptible to reduction. The formed carbinol group would be somewhat susceptible to reduction to a methyl group. The ring 3,4-bond and the 1,6-bond would be susceptible to cleavage because of the neighboring activating influences. Theoretically, it could be said that the initial reaction of hydrogen might follow four courses leading to four different products. These four products, on further reaction with hydrogen, could lead to seven new products, and these, in their turn, could lead to seven more. These last seven molecules could lead to four products, and these four would lead to a single molecule, 2-benzylbutane, III. Thus, in this theoretical stepwise transformation of I to III, there are twenty-two intermediates to be considered, exclusive of stereoisomers, and exclusive of change in the -NH-CO-NH-grouping.


I II III

It was never possible, in this hydrogenation at 250°, to obtain full hydrogen absorption, and there was isolated a small amount of a low boiling fraction which appeared to be the product II, 2-benzylbutanol-1. After repeated purifications, only traces of impurities containing nitrogen remained, and the carbon and hydrogen analyses were not quite satisfactory for 2-benzylbutanol-1.

For further identification, the alcohol, II, was synthesized in order that comparable derivatives, etc., could be made. It was readily obtained by the following series of reactions

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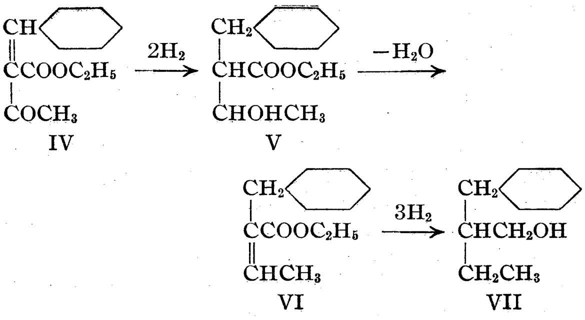
(1) Researches on Pyrimidines CLII.

(2) Post-doctorate Research Fellow, 1933–1934, Yale University. The greater part of this study was made at Yale University under the administration of Professor Treat B. Johnson. The courtesy of Dr. Randolph T. Major for permission to complete the investigation in the Merck Laboratory is gratefully acknowledged.

(3) Folkers and Johnson, THIS JOURNAL, **56**, 1180 (1934).



In carrying out the last step, VI ⟶ VII, the second stage, or carbethoxy group reduction, reached completion very readily, and if the reaction were not stopped, further hydrogenation slowly took place.

Apparently, the benzenoid nucleus was slowly undergoing reduction. Analysis of the product showed a low percentage of carbon and a high percentage of hydrogen, such as would be expected; and when this product was hydrogenated completely over nickel, a low amount of hydrogen was absorbed as calculated for 2-benzylbutanol-1, and analysis of the product indicated that it was 2-hexahydrobenzylbutanol-1.

Interpreting the pyrimidine hydrogenation in accord with the above results, the alcohol product undoubtedly was essentially a mixture of 2-benzyl- and 2-hexahydrobenzylbutanol-1. There were fractions which might have contained the corresponding butane derivatives, but the quantity was much smaller than that of the alcohol fraction.

These experiments contributed toward the knowledge of a characteristic of the copper–barium–chromium oxide catalyst. It has been generally expressed that copper–chromium oxide catalyst is inactive for true benzenoid nuclei reduction.[4] This study would suggest that it is probably a question of relative activity for these catalysts. In other words, there is usually a tremendous difference in the rates of phenyl group reduction with respect to the other many reactions for which these catalysts are valuable, and the control of the reactions and isolation of pure phenyl substituted products is entirely practicable. However, when certain factors (temperature, time, catalyst amounts and ratios, etc.) are forced, advertently or not, the amount of phenyl group reduction may become appreciable, as in the case of ethyl α-benzylcrotonate. In the case of complex heteronuclear phenyl substituted compounds, such as the pyrimidine I, the extent of phenyl group reduction may be sufficient as to make impracticable the isolation of pure phenyl substituted products, when rather drastic conditions must be employed in order to secure appreciable conversion of the hydrogen acceptor.

Experimental Part[5]

Hydrogenation of the Pyrimidine, I.—The literature citations on apparatus, catalysts, and special methods have already been recorded.[3] The preparation of 2-keto-4-phenyl-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidine, I,[6] and the corresponding hexahydropyridine have been described.[3]

When 10 g. (0.038 mole) of the pyrimidine I was hydrogenated at 250° for 7.25 hours over 5 g. of copper–barium–chromium oxides in 100 ml. of ethanol solvent, the resulting solution was colorless and practically free from volatile ammonia or amines. The catalyst, to all appearances, was in an active state. The hydrogen absorption was not over 0.176 mole. The residue, after ethanol removal, was distilled: Fraction I, b. p. essentially 77–79° at 2.5 mm., 1.8 g. (approximately 28.6%); Fraction II, b. p. 80–160° continuous, and large resinous residue.

When the hydrogenation was conducted over 3 g. of catalyst, first for two hours at 200°, then for four hours at 250°, there was isolated only 0.5 g. (8.0%) of Fraction I boiling essentially at 70–72° at 1.5 mm.

Fraction I was also obtained in small yield from the hydrogenation of 2-keto-4-phenyl-5-carbethoxy-6-methylhexahydropyrimidine under similar conditions.

The residues from distillation of Fraction I (or Fraction II, continuous b. p. of 80–160–200° plus its residue) were dissolved in alcoholic sodium hydroxide solution and the mixture refluxed for two to three hours. After removal of the ethanol, there were no basic or neutral substances present other than an occasional trace of Fraction I. On acidification there precipitated carboxy acids. The properties of the acid indicated a complex mixture, and, in one instance, some impure 2-keto-4-phenyl-5-carboxy-6-methylhexahydropyrimidine was isolated.

When the product from the hydrogenation of 20 g. of pyrimidine I under similar conditions was directly saponified, etc., there was obtained 2.6 g. (20.6%) of Fraction I, and the distillation residue of 4.3 g. comprised the remaining basic or neutral products.

The various Fractions I were combined and fractionated. The forerun of b. p. 47–74° at 2 mm. darkened in color on standing and was found to contain 2–3% nitrogen. The greater amount of the material boiled at 75–78° at 2 mm., and, after treatment with acid and alkali, was found to distil at 77–77.2° at 2 mm. Undoubtedly, this liquid was essentially 2-benzylbutanol-1. *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.42; H, 9.82. Found: C, 79.25, 79.20; H, 9.38, 9.33; N, trace (0.1–0.2%). The discrepancy on carbon

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(4) Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931); **54**, 4689 (1932); Wojcik and Adkins, *ibid.*, **56**, 2421 (1934).

(5) Acknowledgment is made to Mr. D. Hayman and Mr. S. Adler for the greater part of the analytical work.

(6) Folkers, Harwood and Johnson, THIS JOURNAL, **54**, 3751 (1932); see also Folkers and Johnson, *ibid.*, **55**, 3784 (1933).

and hydrogen content was probably due in part to the presence of 2-hexahydrobenzylbutanol-1, as explained elsewhere, and to the nitrogen containing impurities.[7]

Ethyl α-Benzalacetoacetate.—This ester was made by the method of Knoevenagel.[8] It was finally distilled through a Widmer column, b. p. 129–130° at 2.5 mm.

Ethyl α-Benzyl-β-hydroxybutyrate.—The ethyl α-benzalacetoacetate was hydrogenated at 150° and 160 atm. in absolute ethanol solvent, and over copper–barium–chromium oxide catalyst. The yield of ethyl α-benzyl-β-hydroxybutyrate was 90%, b. p. 124–126° at 3 mm. *Anal.* Calcd. for $C_{13}H_{18}O_3$: C, 70.22; H, 8.16. Found: C, 70.14, 69.96; H, 8.12, 8.34.

Ethyl α-Benzylcrotonate.—To 20 ml. of dry benzene and 8 g. of phosphorus pentoxide in a distilling flask and cooled in an ice-bath was added 22.8 g. of ethyl α-benzyl-β-hydroxybutyrate. Benzene was now slowly distilled by immersing the flask in an oil-bath and heating slowly to a temperature of 140°. The pressure was then reduced to 15 mm., and, after removal of the last benzene, the dehydrated ester distilled at 133–138° (bath temp. 190–200°), yield 17.1 g. or 81.4%. The ester was purified by washing its ethereal solution with a sodium carbonate and chloride solution and then a sodium chloride solution. The ester after ether removal, on distillation yielded a few drops of a yellow low boiling fraction and then distilled at 125–127° at 13 mm. *Anal.* Calcd. for $C_{13}H_{16}O_2$: C, 76.42; H, 7.89. Found: C, 76.38, 76.29; H, 7.80, 7.67.

2-Benzylbutanol-1.—A solution of 15.5 g. of ethyl α-benzylcrotonate and 25.5 ml. of absolute ethanol was hydrogenated over 4 g. of copper–barium–chromium oxide at 250° and 190 atm. for five minutes. The product was dissolved in alcoholic sodium hydroxide solution and refluxed for five hours. The alcohol, on ether extraction, etc., distilled at 81–81.5° at 2 mm. It was a rather viscous liquid and its odor was not so characteristic or pleasant as that of the hexahydrobenzylbutanol. *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.42; H, 9.82. Found: C, 80.65, 80.55; H, 9.75, 9.64.

2-Benzylbutyric Acid.—The alkaline solution of the above experiment, freed from 2-benzylbutanol, was acidified and ether extracted. A few drops of acid were obtained and distilled in a minute flask, b. p. 123–124° at 2 mm. *Anal.* Calcd. for $C_{11}H_{14}O_2$: C, 74.11; H, 7.92. Found: C, 74.17, 73.88; H, 8.12, 8.14.

2-Hexahydrobenzylbutanol-1.—When 15.3 g. of ethyl α-benzylcrotonate was hydrogenated as described above, except for a period of five and one-half hours, the product, on fractionation, gave a forerun, undoubtedly containing the corresponding butane derivatives, and then the principal fraction, b. p. 86–87.5° at 3 mm. This fraction was, nevertheless, taken in three parts, and the middle one, representing 21% of the total, was estimated to contain 44% of 2-hexahydrobenzylbutanol-1 and 56% of 2-benzylbutanol-1. *Anal.* Calcd. for $C_{11}H_{22}O$: C, 77.56; H, 13.02. Found: C, 79.30, 79.16; H, 11.32, 11.14.

When this mixture of butanols was hydrogenated to completion over Raney nickel catalyst at 180°, 2-hexahydrobenzylbutanol-1 was obtained, b. p. 83–84° at 2 mm. *Anal.* Found: C, 77.01, 77.09; H, 12.94, 12.67. This completely saturated alcohol had a very characteristic and perfume-like odor, and there seemed no doubt but that the odor of Fraction I from the pyrimidine hydrogenation was due to the presence of this alcohol.

Summary

The principal final product of hydrogenation of 2-keto-4-phenyl-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidine over copper–barium–chromium oxides at 250° under elevated pressures was a mixture of 2-benzyl- and 2-hexahydrobenzylbutanol-1. These two alcohols were synthesized by other reactions. It appears that copper–barium–chromium oxide catalyst has a very weak activity for hydrogenation of the phenyl group, and that this slight activity is exhibited only under certain forced conditions.

RAHWAY, N. J. RECEIVED JUNE 11, 1936

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[7] Guerbet [*Compt. rend.*, **146**, 1406 (1908); *Bull. soc. chim.*, [4] **3**, 944 (1908)] described 2-benzylbutanol as an oil of lilac odor, as obtained from the reaction of *n*-butanol and sodium benzylate. The above analytical product had a very characteristic and pleasant odor.

[8] Knoevenagel, *Ber.*, **29**, 172 (1896); **31**, 730, note 4 (1898); see also Claisen and Matthews, *Ann.*, **218**, 178 (1883).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HYNSON, WESTCOTT & DUNNING, INC., AND WASHINGTON AND LEE UNIVERSITY]

The Halogenation of Ortho-Sulfobenzoic Anhydride

BY DANIEL TWISS AND LARKIN HUNDLEY FARINHOLT

The preparation of polyhalogenated *o*-sulfobenzoic anhydrides seemed interesting in several respects. In the first place, as starting materials for the preparation of new sulfonphthaleins, in view of their possible use as indicators, certain of these compounds have since been described by Harden and Drake.[1] Second, with regard to the possibility that the neutral sodium salts of some of these halogenated *o*-sulfobenzoic acids, in particular the tetraiodo derivative, might be useful as radiographic mediums: this phase of the investigation has been discussed by Macht and Twiss,[2] and by Keller.[3]

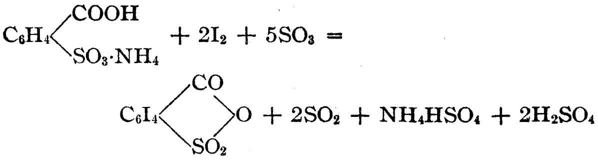
To date little is known concerning the halogenated *o*-sulfobenzoic acids. The 4-chloro acid was prepared by Roode[4] and the 4-bromo acid by Hübner, Post and Weiss[5] and by Remsen and Bayley,[6] by oxidizing the corresponding toluene sulfonic acid or sulfonamide.

In the present investigation, halogenated *o*-sulfobenzoic anhydrides were prepared by the halogenation of *o*-sulfobenzoic acid or its anhydride dissolved in fuming sulfuric acid, with or without the presence of some iodine as a catalyst.[7] This method of halogenation has also been used by Juvalta[8] in the preparation of di- and tetrahalogenated phthalic anhydride.

Without impairing the yield, it proved to be more convenient to use the acid ammonium salt of *o*-sulfobenzoic acid as the starting material since it is more readily available than the acid or anhydride. The acid ammonium salt may be obtained by the hydrolysis of saccharin with dilute hydrochloric acid.

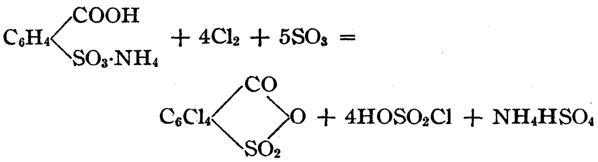
By the method described above, di-, tri-, tetraiodo-; mono-, di-, tri-, tetrabromo-; and di- and tetrachloro-*o*-sulfobenzoic anhydrides were prepared.

Concerning the mechanism of this halogenation nothing is known, but it is probable that *o*-sulfobenzoic anhydride forms an unstable addition complex with sulfuric acid or sulfur trioxide, which facilitates the substitution of halogen. The bromination and iodination take place according to analogous equations. The hydrogen iodide and bromide produced in the reactions are oxidized by sulfur trioxide, and the halogen thus made available again for further substitution. The formation of tetraiodo-*o*-sulfobenzoic anhydride, for example, may be represented by the equation



$$C_6H_4\left\langle\begin{matrix}COOH\\SO_3\cdot NH_4\end{matrix}\right. + 2I_2 + 5SO_3 = C_6I_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle O + 2SO_2 + NH_4HSO_4 + 2H_2SO_4$$

The chlorination differs from the bromination and iodination only by the fact that the hydrogen chloride, generated in the chlorination process, is not oxidized by sulfur trioxide, but combines with it to form chlorosulfonic acid



$$C_6H_4\left\langle\begin{matrix}COOH\\SO_3\cdot NH_4\end{matrix}\right. + 4Cl_2 + 5SO_3 = C_6Cl_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle O + 4HOSO_2Cl + NH_4HSO_4$$

The anhydrides of the halogenated *o*-sulfobenzoic acids are crystalline substances. With the exception of the tetraiodo derivative, they react very readily with water and are converted, even by moisture in the air, into the corresponding acids.

From a theoretical point of view, it seemed important to determine in what order the halogen atoms enter the available positions. The general procedure which was followed in order to settle this question consisted in eliminating the sulfonic acid group by hydrolysis and identifying the resulting halogenated benzoic acid. The removal of the sulfonic acid group was accomplished by heating the halogenated *o*-sulfobenzoic acid with sulfuric acid containing enough water to cause the mixture to boil between 200 and 210°. This procedure could not be applied to the iodinated acids,

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[1] Harden and Drake, THIS JOURNAL, **51**, 562, 2278 (1929).

[2] Macht and Twiss, *Proc. Soc. Exptl. Biol. Med.*, **27**, 850 (1930).

[3] Keller, *Int. J. Med. Surg.*, **44**, 78 (1931); **45**, 258 (1932); *Med. Record*, **141**, 76 (1935); also editorial, *J. Am. Med. Assn.*, **95**, 1749 (1930).

[4] Roode, *Am. Chem. J.*, **13**, 227, 231 (1891).

[5] Hübner, Post and Weiss, *Ann.*, **169**, 26 (1873).

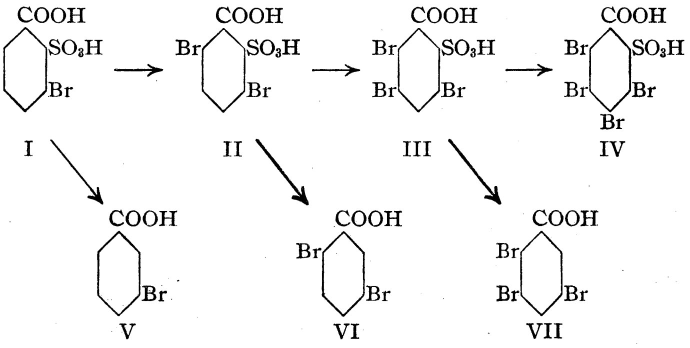
[6] Remsen and Bayley, *Am. Chem. J.*, **8**, 230 (1886).

[7] U. S. Patent 1,760,328 (1930).

[8] German Patent 50,177 (1889), *Frdl.*, **2**, 93 (1889).

owing to the fact that iodine was split off and the compound destroyed. The positions assigned to the iodine atoms have therefore been based on the analogy between these compounds and the corresponding chlorinated and brominated acids.

The elimination of the sulfonic acid group from monobromo-*o*-sulfobenzoic acid yielded 3-bromobenzoic acid (V), while the dibrominated acid produced 2,5-dibromobenzoic acid (VI). From this it may be concluded that the sulfonic acids were 3-bromo- (I) and 3,6-dibromo-2-sulfobenzoic acid (II). Tribromo-*o*-sulfobenzoic acid yielded 2,3,5-tribromobenzoic acid (VII), so that the sulfonic acid was 3,5,6-tribromo-2-sulfobenzoic acid (III). Tetrabromo-*o*-sulfobenzoic acid should naturally be represented by formula IV.



By the same method dichloro-*o*-sulfobenzoic acid yielded 2,5-dichlorobenzoic acid, besides a small quantity of *p*-dichlorobenzene. The formation of the latter compound is due to the fact that not only is the sulfonic acid group removed, but in addition the carboxyl group is also partly split off.

The above facts show that the first halogen atom substitutes in the position meta to the carboxyl and ortho to the sulfonic acid group, and the second halogen atom in the position meta to the sulfonic acid and ortho to the carboxyl group. The third halogen atom enters in the second position meta to the carboxyl group, and the fourth in the remaining second meta position with regard to the sulfonic acid group. In the preparation of the mono-, di- and tri-halogenated *o*-sulfobenzoic anhydrides by direct halogenation, no evidence of the formation of isomers has been found.

It was noted that when an aqueous 10% solution of the neutral sodium salt of tetraiodo-*o*-sulfobenzoic acid was exposed to sunlight, a slow decomposition took place with liberation of iodine and formation of some sodium iodide. A small deposit of crystals consisted of the acid sodium salt of tetraiodo-*o*-sulfobenzoic acid, while the supernatant liquid contained a mixture of the sodium salts of tri- and tetraiodo-*o*-sulfobenzoic acids. The salt of the triiodo acid was converted into the anhydride, which was shown to be identical with 3,5,6-triiodo-*o*-sulfobenzoic anhydride, obtained by direct iodination of *o*-sulfobenzoic acid.

The neutral ammonium salt of the same triiodo acid was precipitated when a concentrated ammoniacal solution of tetraiodo-*o*-sulfobenzoic acid was treated with hydrogen sulfide. The filtrate contained, besides some sulfur and ammonium iodide, the neutral ammonium salt of a diiodo-*o*-sulfobenzoic acid. Its anhydride, obtained by the action of thionyl chloride, forms colorless crystals which are different from the 3,6-diiodo-*o*-sulfobenzoic anhydride prepared by direct iodination of *o*-sulfobenzoic acid. The position of the iodine atoms has not been determined.

Experimental

Halogenation of *o*-Sulfobenzoic Acid

The preparation of each of the following *o*-sulfobenzoic anhydrides was carried out in a three-necked flask provided with a monel metal stirrer and a reflux condenser. The latter was connected with an absorption tower through which circulated water, in order to remove escaping sulfur dioxide and trioxide as well as small quantities of halogen.

3,4,5,6-Tetraiodo-*o*-sulfobenzoic Anhydride.—In 1000 g. of 60% fuming sulfuric acid, 160 g. of *o*-sulfobenzoic acid was dissolved by heating in an oil-bath kept at 60–70°. To this solution, while stirring vigorously, 400 g. of iodine was gradually added. This caused foaming, especially during the latter part of the reaction. After the addition of the iodine, the temperature of the oil-bath was raised slowly to 110–120° and the heating continued for twenty-four hours. The reaction was finished by raising the temperature to 170–175° for one hour. By this time the reaction mass had become too thick for further stirring. After cooling, the reaction mass was mixed with 600 cc. of glacial acetic acid and, after cooling again, filtered by suction on a glass wool pad and washed with glacial acetic acid.

3,4,5,6-Tetraiodo-*o*-sulfobenzoic anhydride was thus obtained as a yellow substance, having no melting point but gradually decomposing in the neighborhood of 300°. The yield of the crude product was 400 g., or 75%.

In a similar manner, the anhydride of *o*-sulfobenzoic acid and its acid ammonium salt were both iodinated with the same results, the yield being approximately 70% in each case.

Free *o*-sulfobenzoic acid may be obtained from the anhydride by boiling with water, which slowly hydrolyzes it. The acid is very soluble in water. Its mono- and disodium salts are prepared by adding the calculated quantities of sodium hydroxide solution to the aqueous solution of the acid. The acid sodium salt is pale yellow and fairly insoluble in water, while the neutral sodium salt is dark yellow and quite soluble. Both are obtained in crystalline form. The acid salt precipitates when the aqueous solution of the neutral salt is acidified with hydrochloric acid.

A good method for preparing pure tetraiodo-*o*-sulfobenzoic anhydride from the sodium salts is to heat either the mono- or disodium salt of the acid with an excess of concentrated sulfuric acid in an oil-bath at 150–165° for one hour. The mixture is then poured on cracked ice and the anhydride filtered off. It is first washed thoroughly with water to free the anhydride of sulfuric acid, then with glacial acetic acid, and finally with a mixture of equal volumes of acetic anhydride and glacial acetic acid, and dried in an oven. It may also be obtained readily from the free acid by treating with acetic anhydride.

The anhydride is very insoluble in most solvents. It can, however, be crystallized from acetic anhydride, in which it is very sparingly soluble.

Anal. Calcd. for $C_7I_4SO_4$: I, 73.81; S, 4.66. Found: I, 73.78; S, 4.58.

3,4,5,6-Tetrabromo-*o*-sulfobenzoic Anhydride.—In the same manner as described above, 165 g. of *o*-sulfobenzoic acid was dissolved in 1000 g. of 60% fuming sulfuric acid. The bromination was carried out by heating the oil-bath to 80–100° and slowly adding 100 cc. of bromine below the surface while stirring. In order to avoid loss of bromine, the rate of addition was regulated according to the rate of absorption. The absorption of bromine went very slowly so that the reaction required a long period of time, between two or three days. In several experiments 10 g. of iodine was added as a catalyst. It has not definitely been established whether this increases the rate of reaction, but it is certain that good results were also obtained when the catalyst was omitted. After all the bromine had been added, the temperature of the oil-bath was slowly raised to 160–170°. On cooling, tetrabromo-*o*-sulfobenzoic anhydride crystallized out and was separated from the sulfuric acid by filtration on a glass wool pad. It was washed free of sulfuric acid with glacial acetic acid containing 25% acetic anhydride. The yield of crude anhydride thus obtained was about 75%. It was crystallized from glacial acetic acid containing 25% acetic anhydride.

3,4,5,6-Tetrabromo-*o*-sulfobenzoic anhydride forms colorless crystals melting at 216–217°.

Anal. Calcd. for $C_7Br_4SO_4$: Br, 63.97; S, 6.42. Found: Br, 63.44; S, 6.42.

It is much less stable toward water than the tetraiodo derivative and even takes up moisture from the air to change into tetrabromo-*o*-sulfobenzoic acid with considerable evolution of heat. The latter substance is extremely soluble in water. The addition of acetic anhydride will convert the acid back into the anhydride.

Instead of using *o*-sulfobenzoic acid as the starting material in the above preparation, the acid ammonium salt of *o*-sulfobenzoic acid and *o*-sulfobenzoic anhydride were used in several experiments with the same results.

3,5,6-Tribromo-*o*-sulfobenzoic Anhydride.—As a by-product in the preparation of the tetrabromo derivative, some 3,5,6-tribromo-*o*-sulfobenzoic anhydride was obtained. It is less soluble in the acetic acid–acetic anhydride mixture than the tetrabromo derivative and was separated from the latter by fractional crystallization. It forms colorless crystals melting at 224°.

Anal. Calcd. for $C_7HBr_3SO_4$: Br, 56.97; S, 7.62. Found: Br, 56.87; S, 7.57.

3,4,5,6-Tetrachloro-*o*-sulfobenzoic Anhydride.—To a solution of 51 g. of *o*-sulfobenzoic acid in 300 g. of 60% fuming sulfuric acid, 2 g. of iodine was added as a catalyst and a slow current of chlorine was passed through the solution, the oil-bath being kept at a temperature of 70–90°. After no more chlorine was absorbed, the reaction was completed by raising the temperature of the oil-bath to 150–160°. Tetrachloro-*o*-sulfobenzoic anhydride crystallized from the ice-cooled solution and was separated from the mother liquor by filtration. The crude anhydride was washed with an acetic acid–acetic anhydride mixture and was crystallized from a mixture of the same composition. Concentration of the liquids used for washing and crystallization gave a second crop of crystals. The total yield was 67%.

The anhydride was also obtained in about the same yield when the preparation was carried out with *o*-sulfobenzoic anhydride or the acid ammonium salt of *o*-sulfobenzoic acid.

3,4,5,6-Tetrachloro-*o*-sulfobenzoic anhydride forms colorless crystals, melting at 158–159°. It is even more sensitive toward the action of water than the tetrabromo derivative.

Anal. Calcd. for $C_7Cl_4SO_4$: Cl, 44.06; S. 9.96. Found: Cl, 43.83; S, 9.75.

3,5,6-Triiodo-*o*-sulfobenzoic Anhydride.—Using the same procedure as described above, 191 g. of iodine was added to a solution of 92 g. of *o*-sulfobenzoic anhydride in 500 g. of 60% fuming sulfuric acid while the oil-bath was kept at a temperature of 60–70°. The reaction was terminated by raising the temperature to approximately 170° for one hour. The yield of the crude triiodo-*o*-sulfobenzoic anhydride, thus obtained, was about 65%. This product contained a small amount of tetraiodo-*o*-sulfobenzoic anhydride.

A pure sample of triiodo-*o*-sulfobenzoic anhydride was obtained by boiling some of the crude anhydride with acetic acid to which a small amount of water had been added. It dissolved to form the free acid and the anhydride was then precipitated by adding an excess of acetic anhydride. The triiodo-*o*-sulfobenzoic anhydride was crystallized from a glacial acetic acid–acetic anhydride mixture, the relatively insoluble tetraiodo derivative remaining behind.

3,5,6-Triiodo-*o*-sulfobenzoic anhydride is obtained as yellow crystals melting at 287–288°.

Anal. Calcd. for $C_7HI_3SO_4$: I, 67.77; S, 5.71. Found: I, 67.75; S, 5.67.

3,6-Diiodo-*o*-sulfobenzoic Anhydride.—In a mixture of 400 g. of 60% fuming sulfuric acid and 200 g. of 95% sulfuric acid (which gives about a 40% fuming sulfuric acid), 109.5 g. of the dry acid ammonium salt of *o*-sulfobenzoic acid was dissolved. In the course of three days, at an oil-bath temperature of about 80°, 127 g. of iodine was added. The temperature was then raised to 105–110° and stirring continued for forty-eight hours in order to ensure complete reaction of the iodine. Finally, the temperature was gradually raised to 180° to eliminate part of the excess sulfur trioxide. The cooled reaction mixture was poured on cracked ice and the anhydride allowed to hydrolyze to the acid form. The amount of sulfate ions was determined quantitatively in a small sample, and the calculated amount of barium hydroxide, dissolved in hot water, added to the main solution. The filtrate from this then contained the acid ammonium salt of diiodo-*o*-sulfobenzoic acid. By evaporating to dryness in the presence of an excess of ammonia, the neutral ammonium salt was obtained in a yield of about 85%.

In order to convert the neutral ammonium salt into the anhydride, it was refluxed for four hours with a solution of an excess of thionyl chloride in benzene. The precipitate of ammonium chloride was extracted several times with hot benzene containing some thionyl chloride. The combined filtrates yielded mainly 3,6-diiodo-*o*-sulfobenzoic anhydride along with small amounts of the triiodo derivative as well as a product of lower iodine content which could not be purified. The 3,6-diiodo compound was obtained by fractional crystallization in a 55% yield. No isomeric diiodo-*o*-sulfobenzoic anhydride could be isolated.

Crystallized from dry benzene, or a mixture of glacial acetic acid and acetic anhydride, 3,6-diiodo-*o*-sulfobenzoic anhydride forms faintly yellow crystals melting at 243–245°.

Anal. Calcd. for $C_7H_2I_2SO_4$: I, 58.23; S, 7.35. Found: I, 58.19; S, 7.29.

The anhydride may also be prepared from the neutral as well as from the acid ammonium salt by heating with concentrated sulfuric acid at 150° for one hour. It is isolated by pouring the cooled solution on cracked ice, filtering off the anhydride rapidly, dissolving the moist product in glacial acetic acid and precipitating it by addition of acetic anhydride.

3,6-Dibromo-*o*-sulfobenzoic Anhydride.—At an oil-bath temperature of 50–60°, 109.5 g. of the acid ammonium salt of *o*-sulfobenzoic acid dissolved in 600 g. of 60% fuming sulfuric acid was brominated by adding 80 g. of bromine in the course of fifty hours. The reaction was finished by raising the temperature to 170–180° for one hour. The cooled reaction mass was poured on ice and the neutral ammonium salt isolated by the same procedure as that described for the 3,6-diiodo anhydride. It was obtained in a yield of 80%. The anhydride was prepared by the action of thionyl chloride in benzene solution in the same manner as above. 3,6-Dibromo-*o*-sulfobenzoic anhydride hydrolyzes readily, even in moist air.

3,6-Dibromo-*o*-sulfobenzoic anhydride crystallizes from benzene containing a little thionyl chloride as colorless crystals, melting at 167–168°.

Anal. Calcd. for $C_7H_2Br_2SO_4$: Br, 46.75; S, 9.38. Found: Br, 46.93; S, 9.05.

3,6-Dibromo-*o*-sulfobenzoic acid is not changed back into its anhydride under the influence of acetic anhydride, unlike most of the other halogenated *o*-sulfobenzoic acids, but the conversion may be accomplished by the action of thionyl chloride.

3,6-Dichloro-*o*-sulfobenzoic Anhydride.—A slow current of chlorine was passed into a solution of 109.5 g. of the acid ammonium salt of *o*-sulfobenzoic acid dissolved in 400 g. of 60% fuming sulfuric acid at an oil-bath temperature of 60–65°. The reaction was completed when the increase in weight of the reaction mass had reached 70 g. The excess of sulfur trioxide was converted into chlorosulfonic acid by passing dry hydrogen chloride gas into the solution and was eliminated by distillation from a retort. On cooling, 3,6-dichloro-*o*-sulfobenzoic anhydride crystallized from the remaining solution. Recrystallized from a glacial acetic acid–acetic anhydride mixture, it forms colorless crystals melting at 121–122°. It may also be purified by adding ligroin to the solution of the crude product in dry toluene. The compound was obtained in a yield of 40–45%. It hydrolyzes very readily when exposed to moist air.

Anal. Calcd. for $C_7H_2Cl_2SO_4$: Cl, 28.03; S, 12.67. Found: Cl, 27.80; S, 12.59.

3-Bromo-*o*-sulfobenzoic Anhydride.—In the course of fifty hours, 40 g. of bromine was added to a solution of 109.5 g. of the dry acid ammonium salt of *o*-sulfobenzoic acid in 600 g. of 60% fuming sulfuric acid at an oil-bath temperature of 50–60°. The temperature was then gradually raised to 180°, and then allowed to cool. After standing for one week, 17 g. of 3,6-dibromo-*o*-sulfobenzoic anhydride had separated. The remaining solution was poured on cracked ice and the neutral ammonium salt isolated in the same manner already described for the diiodo derivative. The reaction yielded 130 g. of neutral ammonium salt from which 34 g. of 3-bromo-*o*-sulfobenzoic anhydride was obtained. In view of the low yield, the possibility that an isomeric monobromo derivative is formed in the reaction should be taken into account. None was isolated, however.

3-Bromo-*o*-sulfobenzoic anhydride crystallizes from benzene containing some thionyl chloride to form colorless needles, melting at 175–176°. It is very sensitive toward moisture.

Anal. Calcd. for $C_7H_3BrSO_4$: Br, 30.39; S, 12.19. Found: Br, 30.16; S, 12.04.

Determination of the Positions of the Halogen Atoms

The method of determining the positions of the halogen atoms in the halogenated *o*-sulfobenzoic acids consisted in the elimination of the sulfonic acid groups to form halogenated benzoic acids of known constitution. These reactions were carried out in the following manner.

The halogenated *o*-sulfobenzoic anhydride was converted into the corresponding acid by heating with some water, an equal volume of concentrated sulfuric acid was then added and water distilled off until the boiling point of the mixture had reached a temperature of 200–210°. It was then refluxed for several hours at this temperature and again distilled, this time collecting the distillate. The halogenated benzoic acid was carried over with the water.

By the above method, tribromo-*o*-sulfobenzoic acid yielded 2,3,5-tribromobenzoic acid, m. p. 185–187°. The methyl ester of the latter was prepared and gave a melting point of 77°. Dibromo-*o*-sulfobenzoic acid gave 2,5-dibromobenzoic acid, m. p. 151–152°, and monobromo-*o*-sulfobenzoic acid gave 3-bromobenzoic acid, m. p. 155°. Dichloro-*o*-sulfobenzoic acid yielded 2,5-dichlorobenzoic acid, m. p. 151–152°, along with a small quantity of *p*-dichlorobenzene, m. p. 53°.

Attempts to convert the iodinated *o*-sulfobenzoic acids into the corresponding iodobenzoic acids were unsuccessful since the acids were destroyed completely under the conditions of the reaction.

Action of Ammonium Sulfide on Tetraiodo-*o*-sulfobenzoic Acid

A concentrated solution of tetraiodo-*o*-sulfobenzoic acid was prepared by boiling 22.4 g. of the corresponding anhydride with 50 cc. of water. Fifty cc. of concentrated aqueous ammonia was then added (causing the neutral ammonium salt to precipitate partially), the solution was saturated with hydrogen sulfide and allowed to stand for twenty-four hours. The white precipitate thus obtained in a yield of 11.5 g. was the neutral ammonium salt of triiodo-*o*-sulfobenzoic acid. It was crystallized from water.

Anal. Calcd. for $C_7H_9O_5I_3N_2S$: I, 62.02; S, 5.22; N, 4.56. Found: I, 61.98; S, 5.26; N, 4.80.

When heated with concentrated sulfuric acid at 160° for one hour, the neutral ammonium salt was converted into the anhydride of triiodo-*o*-sulfobenzoic acid. The cooled sulfuric acid mixture was poured on cracked ice and, after washing with water, the moist yellow solid was dissolved in hot glacial acetic acid. The anhydride was precipitated again by adding acetic anhydride. It is a pale yellow substance, melting at 287–288°, and identical with the 3,5,6-triiodo-*o*-sulfobenzoic anhydride obtained by direct iodination. A mixed melting point with the latter substance did not show a depression.

After the white crystals of the neutral ammonium salt of 3,5,6-triiodo-*o*-sulfobenzoic acid were filtered off, a yellow solution remained. It was evaporated to dryness and extracted with water. The residue consisted of 1.3 g. of sulfur. The evaporated extract yielded 6.4 g. of an alcohol-soluble portion, which was shown to be ammonium iodide. The analysis of the alcohol-insoluble fraction, consisting of 5.7 g. of a white substance, showed it to be the diammonium salt of a diiodo-*o*-sulfobenzoic acid.

Anal. Calcd. for $C_7H_{10}O_5I_2N_2S$: I, 52.02; S, 6.57; N, 5.74. Found: I, 51.78; S, 6.79; N, 5.9.

Treatment with concentrated sulfuric acid at 150° did not produce an anhydride as in the case of the 3,6-diiodo derivative, but a diiodo-*o*-sulfobenzoic anhydride was apparently obtained by refluxing the diammonium salt with thionyl chloride for several hours. It dissolved in the excess of thionyl chloride and was isolated by separating the solution from the precipitate of ammonium chloride and evaporating the thionyl chloride. It was dissolved in water, the solution decolorized with charcoal, and again evaporated to dryness. The residue was treated with acetic anhydride and recrystallized several times from that solvent. In this manner, a diiodo-*o*-sulfobenzoic anhydride was isolated, different from the one obtained by direct iodination. The compound melted at 221–223°. The position of the iodine atoms was not determined.

Anal. Calcd. for $C_7H_2I_2SO_4$: I, 58.23; S, 7.35. Found: I, 57.97; S, 7.27.

Our thanks are due to Mr. Grant Spurrier for carrying out much of the analytical work.

Summary

1. Mono-, di-, tri- and tetrahalogeno substitution products of *o*-sulfobenzoic anhydride were prepared by halogenation in fuming sulfuric acid.

2. The positions of the halogen atoms were determined by eliminating the sulfonic acid group by hydrolysis and identifying the resulting halogenated benzoic acids.

BALTIMORE, MARYLAND
LEXINGTON, VIRGINIA

RECEIVED JUNE 1, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

A Study of Some Substituted Hydroxybenzyl Alcohols[1]

BY BROWN DUNNING, JR., FITZGERALD DUNNING AND E. EMMET REID

As saligenin (*o*-hydroxybenzyl alcohol) has three distinct types of physiological action, anesthetic, antispasmodic, and antiseptic, it seemed desirable to prepare a number of its derivatives in which one or more of these might be accentuated and to study these in connection with the derivatives, homologs and analogs already known to see how these properties are altered by changes of structure and composition. It was also of interest to find out how far the physiological activities of these compounds can be correlated with their physical properties, particularly their solubilities and partition coefficients. Eight new compounds have been prepared and studied along with ten that were already known. These include halogen and alkyl substituted saligenins and halogen substituted *m*- and *p*-hydroxybenzyl alcohols.

The unsubstituted hydroxybenzyl alcohols were made by the reduction of the corresponding hydroxybenzaldehydes through the use of the Adams platinum catalyst.[2] The halogen derivatives of these were prepared by direct halogenation. The alkyl derivatives were synthesized from various

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[1] From the Ph.D. dissertation of Brown Dunning, Johns Hopkins University, 1934. Original manuscript received November 26, 1935.

[2] Adams, "Organic Syntheses," Vol. VIII, Wiley and Sons, Inc., New York, 1928.

substituted phenols by means of the well-known Reimer–Tiemann reaction,[3] which gave hydroxyaldehydes which were subsequently reduced. In those cases where the alkyl phenols were not available, they were obtained by reduction of the appropriate hydroxyphenones, using the Clemmensen reduction method.[4]

The partition coefficients were determined indirectly for each compound by dividing the solubility in olive oil by the water solubility.

The water solubility was determined by weighing the residue from evaporation of a known volume of a saturated solution in distilled water. For the oil solutions since the refractive index was found to be practically a straight line function of the concentration for each individual compound, it was possible to determine the concentration of a saturated solution by comparing its refractive index with the refractive indices of solutions of known concentration.

There was found to be a very definite relationship between partition coefficients and bactericidal power in each series, but changing the relative positions of the functioning groups, as in the case of the analogs (*o*-, *m*- and *p*-hydroxybenzyl alcohols) changes the physiological properties without regard to partition coefficients. The pharmacological results, although of necessity only roughly comparative, in most cases support the bacteriological results.

Experimental

The preparation of 5-ethyl-2-hydroxybenzyl alcohol may be taken as an example of the general method of preparing the compounds.

p-Hydroxyacetophenone was reduced by the Clemmensen method[4] using amalgamated zinc and hydrochloric acid. The *p*-ethylphenol obtained was purified by steam distillation and the aldehyde group introduced by treating with sodium hydroxide and chloroform according to the method of Reimer and Tiemann.[3] The 5-ethyl-2-hydroxybenzaldehyde was purified by making the sodium bisulfite addition compound which was washed with alcohol and ether, dried, and decomposed with warm dilute acid to liberate the aldehyde. Yields from most of the Reimer–Tiemann reactions were about 30%.

The purified aldehyde was reduced in alcohol solution by passing in hydrogen under about 500 mm. excess pressure in the presence of 1% of the Adams platinum oxide catalyst[2] while shaking on a mechanical shaker. After removal of the catalyst by filtration, the alcohol was evaporated off on a water-bath and the product of the reduction purified by crystallization from carbon tetrachloride.

The purified product of the Reimer–Tiemann reaction on *m*-cresol is a heavy yellow oil which is a mixture of two isomers, 2-hydroxy-4-methyl-benzaldehyde and 6-hydroxy-2-methyl-benzaldehyde. These were separated as suggested by Chuit and Bolsing[5] by steam distilling the mixture with a solution of sodium carbonate from which the former less acidic isomer distils leaving the latter behind. Upon reduction the two corresponding isomeric benzyl alcohols are obtained which melt at 103 and 80°, respectively. These are incidentally isomers of the alcohol obtained by starting with *p*-cresol.

Analyses of the new compounds are included in Table I.

Bacteriological

All the compounds prepared were tested for their bacteriological activity. The organism used was *Staphylococcus aureus*. A modification of the F. D. A. test was employed, which was essentially as follows: 0.5 cc. of a standard twenty-four hour culture was added to 5 cc. of diluted antiseptic. Transfers were made at the end of forty-five minutes with a 4-mm. platinum loop made from No. 23 B. and S. gage wire. The culture media used was a sterile nutrient, beef extract broth, 10 cc. being used in each subculture tube. All dilutions were made with 20% alcohol, the use of which was necessary in order to dissolve some of the compounds. Although the presence of the alcohol has a slight effect on the killing power, it was, however, used throughout all the tests and the results are therefore comparable.

The results of the bacteriological tests are contained in Table I. The figures show the relative bactericidal strengths of equimolar quantities of the respective compounds calculated from their maximum killing dilutions, saligenin being given an index value of 1. In Fig. 1 these are plotted against the partition coefficients for the mono substituted saligenins. Figure 2 shows the same for the di-halogenated compounds. No attempt has been made to compare these two series with each other.

Attention is called to the analogs of saligenin, 3-hydroxy- and 4-hydroxybenzyl alcohol and their respective bromo derivatives. As was expected, the partition coefficient relationship holds between each analog and its derivative, but not between the members of the different series, in which the relative positions of the functioning groups are different.

Pharmacological

Most of the compounds have been tested for anesthetic and antispasmodic action and also for toxicity.

The best method of obtaining comparable values of the anesthetic efficiency was by the frog-skin method in which a 1% hydrochloric acid solution was used as the stimulus on the skin of a pithed frog, both before and after soaking the skin in various concentrations of the anesthetic. The factors taken into consideration in calculating the figures are the time of the normal reflex, the time of immersion in the anesthetic solution, the concentration of the solution, the time of the reflex after anesthesia and the duration of anesthesia. The anesthetic effects on mice and on goldfish were also studied and while they confirm the results of the frog-skin tests, the type of data obtained

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[3] Reimer and Tiemann, *Ber.*, **9**, 423, 824 (1876); **10**, 1562 (1877); etc.

[4] Clemmensen, *ibid.*, **46**, 1837 (1913); **47**, 53 (1914).

[5] Chuit and Bolsing, *Bull. soc. chim.*, [3] **35**, 129, 134 (1906).

TABLE I

Benzyl alcohol derivatives	Solubility in water, %	Solubility in olive oil, %	Partition coefficient	Relative bactericidal strength	Relative anesthetic efficiency	Relative antispasmodic action	M. p., °C.	Analyses Calcd.	Analyses Found
3,5-Diiodo-2-hydroxy-[a]	0.015	9.0	600	91	30	50	107	I, 67.53	67.70
3-Iodo-5-bromo-2-hydroxy-	.05	14.8	296	53			86	I, 38.6	39.2
								Br, 24.3	24.1
3,5-Dibromo-2-hydroxy-[b]	.11	11.4	103	45.4	15	25	89	Br, 56.6	56.4
3-Chloro-5-bromo-2-hydroxy-	.12	7.1	59	34.4			93	Br, 33.6	32.6
								Cl, 14.9	14.5
3,5-Dichloro-2-hydroxy-[c]	.28	10.6	37	15.6	7.5	2.7	83	Cl, 36.75	36.86
5-Propyl-2-hydroxy-	.27	4.1	15.1	16	20	10	73	C, 72.2	71.7
								H, 8.5	8.9
5-Iodo-2-hydroxy-[a]	.11	1.5	13.6	14.1	10	25	138	I, 50.77	50.72
5-Bromo-2-hydroxy-[a]	.70	4.8	6.8	9.8	5	16.5	109	Br, 39.4	39.47
5-Chloro-2-hydroxy-[a]	1.46	7.4	5.0	7.6	2	6	90	Cl, 22.37	22.17
5-Ethyl-2-hydroxy-	0.80	3.0	3.7	4.9	3.4	5	83	C, 71.0	70.5
								H, 7.9	7.7
5-Methyl-2-hydroxy-[d]	.95	1.1	1.1	1.1	2.5	4	105		
2-Hydroxy-[d]	6.0	1.8	0.3	1	1	1	87		
6-Methyl-2-hydroxy-	1.6	3.6	2.2	2.2	0.9	5.5	80	C, 69.5	69.5
								H, 7.3	7.3
4-Methyl-2-hydroxy-	1.5	2.7	1.8	2.2	1.8	6	103	C, 69.5	69.0
								H, 7.3	7.3
6-Bromo-3-hydroxy-	0.78	4.0	5.1	9.8	2	25	124	Br, 39.4	38.8
3-Hydroxy-[e]	43.4	1.1	0.02	0.5	0.2	1.1	71		
3-Bromo-4-hydroxy-	1.0	1.1	1.1	22.9	.8	1.5	128	Br, 39.4	39.8
4-Hydroxy-[c]	2.0	1.0	0.5	0.5	.03	0.75	124		

[a] Visser, *Arch. Pharm.*, **235**, 547 (1897). [b] Auwers and Buttner, *Ann.*, **302**, 131 (1898). [c] Mettler, *Chem. Centr.*, **77**, II, 1790 (1906). [d] Manasse, *Ber.*, **27**, 2411 (1894). [e] Mettler, *ibid.*, **38**, 1752 (1905).

does not well lend itself to comparison on a numerical basis. These results have been in part reported elsewhere.

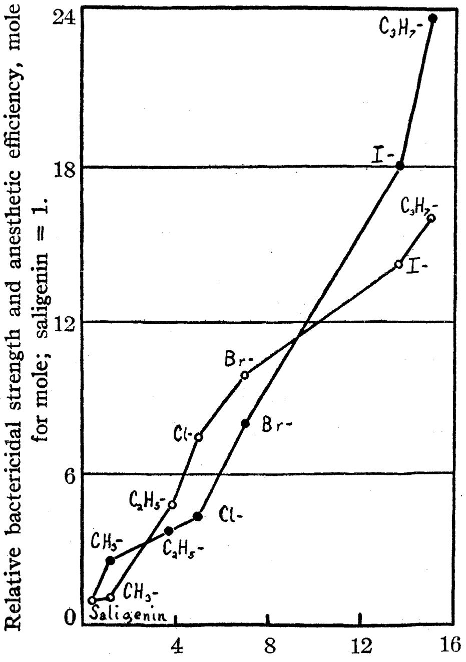

Fig. 1.—Mono-substituted saligenins: ○, relative bactericidal strength; ●, relative anesthetic efficiency.

The figures in Table I represent the relative local anesthetic efficiency of the compounds obtained by the frog-skin method on a weight for weight basis, saligenin being given an index value of 1. It was found that a molecule for molecule comparison would give a relationship more nearly corresponding to the partition coefficients, and a comparison of this kind may be seen in Fig. 1 for the mono substituted saligenins.

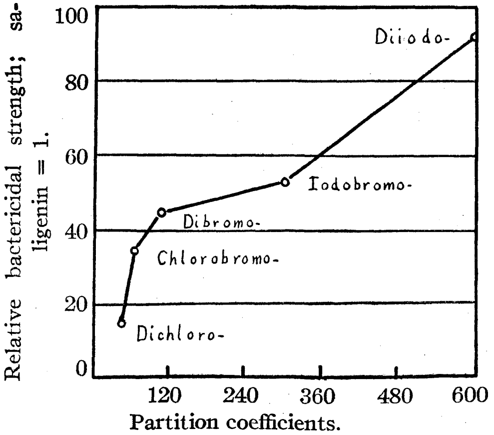

Fig. 2.—Di-halogen derivatives of saligenin.

Also included in Table I are figures for the antispasmodic activity of the compounds. These were calculated from the amounts required to produce antispasmodic action on the smooth muscle of cat's intestine in 50 cc. of Locke's solution oxygenated at 38°, saligenin again being given an index value of 1. No attempt has been made to relate these figures with the partition coefficients since there is no obvious reason why lipoid solubility should be related to effects of this kind.

The toxicity of the compounds was determined on cats and on the seedlings of lupinus albus. No relationship was expected in these figures, since such an effect as toxicity could hardly be predicted from any one set of physical properties; hence they are not included in this paper.

Discussion

It is felt that from the preceding data it may be stated that there has been demonstrated herein a definite relationship between physical and physiological properties of hydroxybenzyl alcohols. It is interesting to note how the actions of the mono-alkyl and mono-halogen derivatives are related according to their partition coefficients without regard to the great difference in chemical nature of the substituent groups, as may be seen in Fig. 1.

The question of the position of the substituent group in the parent molecule has also been considered in the case of the three isomeric methyl saligenins. It is seen that the bactericidal power depends more on the physical properties of the molecule than on the position of the inert group.

As mentioned previously, shifting the relative positions of the functioning group changes the nature of the molecule, so that there can be no comparison between saligenin and its analogs. It is to be noted, however, that in comparing each analog to its respective derivatives, the relation of physical to physiological properties holds good.

Summary

The partition coefficients between oil and water of a series of derivatives, analogs and homologs, of saligenin (*o*-hydroxybenzyl alcohol) have been determined and compared with the bacteriological and pharmacological properties of the compounds. A definite relationship exists, even in cases where the structures of the inert substituent groups differ greatly.

BALTIMORE, MARYLAND RECEIVED JUNE 4, 1936

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Studies in the Phenanthrene Series. XI. Propanolamines of the Type $C_{14}H_9CHOHCH_2CH_2NR_2$[1]

BY JACOB VAN DE KAMP AND ERICH MOSETTIG

The pharmacological study of a number of amino alcohols in the phenanthrene series[2] has shown that some of these compounds, carrying the side chain $-CHOHCH_2NR_2$ (type I)[3] and $-CHOHCH(CH_3)NR_2$ (type II),[4] exhibit a decided analgesic action. In both types of compounds the nitrogen atom is located in the side chain in the β-position to the phenanthrene nucleus. Through the systematic investigations by Barger and Dale and associates[5] of the amines $Ar(CH_2)_xNH_2$ (Ar being the phenyl, hydroxyphenyl or iminazolyl group), it became evident that almost universally the greatest physiological action (in particular with respect to blood pressure) is exerted by the compounds in which $x = 2$. As Barger points out, compounds of this type occur frequently in nature and are probably in some instances intermediates in the phytosynthesis of isoquinoline derivatives. In the compounds with $x < 2$ or $x > 2$, the physiological action is greatly diminished. It was of interest to determine, by comparison of the phenanthrene alkamines of type I and II[6] on the one hand with the compounds of the type $C_{14}H_9CHOHCH_2CH_2NR_2$ on the other, whether or not a similar regularity may be observed with the phenanthrene derivatives of these series, particularly in respect to their analgesic action.

The propanolamines described in this communication were prepared essentially by the Mannich method,[7] starting from 2-, 3- and 9-acetylphenanthrenes: $C_{14}H_9COCH_3 + CH_2O + HNR_2\cdot$

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[1] The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

[2] Eddy, *J. Pharmacol.*, **55**, 419 (1935).

[3] Mosettig and van de Kamp, THIS JOURNAL, **55**, 3448 (1933).

[4] Mosettig and Czerwin, unpublished results.

[5] Barger, "Some Applications of Organic Chemistry to Biology and Medicine," McGraw-Hill Book Co., Inc., New York City, 1930, pp. 73–100.

[6] The comparison of type I and type II has shown that the compounds of type II are generally slightly weaker analgesics than those of type I.[2]

[7] Mannich, *Arch. Pharm.*, **255**, 261 (1917); Mannich and Braun, *Ber.*, **53**, 1874 (1920); Mannich and Heilner, *ibid.*, **55**, 356 (1922); Mannich and Lammering, *ibid.*, **55**, 3510 (1922).

TABLE I

COMPOUNDS, PROPERTIES AND ANALYSES

Phenanthrene derivatives	Solvent	Appearance	M. p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2-(3-(Dimethylamino)-1-oxo-propyl)-	Et_2O	Colorless plates	104.5–105	$C_{19}H_{19}ON$	82.26	82.70	6.91	6.95
Hydrochloride	EtOH-Et_2O	Colorless plates	193 –193.5	$C_{19}H_{20}ONCl$			Cl, 11.31	11.48
Perchlorate	EtOH	Colorless plates	167 –167.5	$C_{19}H_{20}O_5NCl$			N, 3.71	3.85
3-(3-(Dimethylamino)-1-oxo-propyl)-·HCl	EtOH-Et_2O	Colorless needles	177.5–178	$C_{19}H_{20}ONCl$			Cl, 11.31	11.02
Picrate	EtOH	Yellow needles	175.5–176	$C_{25}H_{22}O_8N_4$			N, 11.07	11.30
9-(3-(Dimethylamino)-1-oxo-propyl)-·HCl	EtOH-Et_2O	Colorless leaflets	171 –171.5	$C_{19}H_{20}ONCl$			Cl, 11.31	11.46
Picrate	EtOH	Yellow blades	175 –175.5	$C_{25}H_{22}O_8N_4$			N, 11.07	11.08
2-(3-Diethylamino)-1-oxo-propyl-·HCl	EtOH	Colorless plates	167 –167.5	$C_{21}H_{24}ONCl$			Cl, 10.38	10.49
3-(3-(Diethylamino)-1-oxo-propyl)-·HCl	EtOH-Et_2O	Colorless blades	155.5–156	$C_{21}H_{24}ONCl$			Cl, 10.38	10.35
Picrate	EtOH	Yellow prisms	108 –109	$C_{27}H_{26}O_8N_4$			N, 10.49	10.48
9-(3-(Diethylamino)-1-oxo-propyl)-·HCl	EtOH-Et_2O	Colorless leaflets	135 –136	$C_{21}H_{24}ONCl$			Cl, 10.38	10.35
Salicylate	EtOH-Et_2O	Colorless prisms	113 –113.5	$C_{28}H_{29}O_4N$			N, 3.16	3.31
2-(3-(Piperidino)-1-oxo-propyl)-	Et_2O-pet. ether	Colorless plates	88.5– 89	$C_{22}H_{23}ON$			N, 4.42	4.50
Hydrochloride	H_2O	Colorless plates	220 –220.5	$C_{22}H_{24}ONCl$			Cl, 10.03	9.78
3-(3-(Piperidino)-1-oxo-propyl)-·HCl	H_2O	Colorless plates	201 –201.5	$C_{22}H_{24}ONCl$			Cl, 10.03	10.29
Picrate	EtOH	Yellow leaflets	162.5–163.5	$C_{28}H_{26}O_8N_4$			N, 10.26	10.35
9-(3-(Piperidino)-1-oxo-propyl)-·HCl	EtOH-Et_2O	Colorless prisms	184 –185	$C_{22}H_{24}ONCl$			Cl, 10.03	10.21
Picrate	EtOH	Yellow plates	138 –139	$C_{28}H_{26}O_8N_4$			N, 10.26	10.43
2-(3-(1,2,3,4-Tetrahydroisoquinolino)-1-oxo-propyl)-	EtOH	Colorless leaflets	133.5–134	$C_{26}H_{23}ON$	85.44	85.50	6.35	6.14
Hydrochloride	EtOH	Colorless prisms	208 –209	$C_{26}H_{24}ONCl$			Cl, 8.83	9.28
3-(3-(1,2,3,4-Tetrahydroisoquinolino)-1-oxo-propyl)-	$CHCl_3$-Et_2O	Colorless prisms	118.5–119	$C_{26}H_{23}ON$	85.44	85.23	6.35	6.60
Hydrochloride	EtOH	Colorless needles	219 –220	$C_{26}H_{24}ONCl$			Cl, 8.83	9.01
9-(3-(1,2,3,4-Tetrahydroisoquinolino)-1-oxo-propyl)-·HCl	EtOH	Colorless needles	228.5–229	$C_{26}H_{24}ONCl$	77.68	77.72	6.02	6.38
2-(3-(Dimethylamino)-1-hydroxy-*n*-propyl)-	[a]	Colorless plates	97.5– 98	$C_{19}H_{21}ON$	81.67	81.61	7.58	7.87
Picrate	EtOH	Yellow blades	156 –157	$C_{25}H_{24}O_8N_4$			N, 11.03	10.96
2-(3-(Dimethylamino)-1-benzoxy-*n*-propyl)-·HCl	EtOH-Et_2O	Colorless needles	219 –219.5	$C_{26}H_{26}O_2NCl$			Cl, 8.45	8.26
3-(3-(Dimethylamino)-1-hydroxy-*n*-propyl)-	[a]	Colorless needles	99 –100	$C_{19}H_{21}ON$	81.67	81.84	7.58	7.81
9-(3-(Dimethylamino)-1-hydroxy-*n*-propyl)-	[b]	Colorless oil		$C_{19}H_{21}ON$	81.67	81.91	7.58	7.74
Perchlorate	EtOH-Et_2O	Colorless plates	142.5–143	$C_{19}H_{22}O_5NCl$			N, 3.69	3.67
Picrate	EtOH	Yellow prisms	167.5–168	$C_{25}H_{24}O_8N_4$			N, 11.03	11.07
2-(3-(Diethylamino)-1-hydroxy-*n*-propyl)-	[a]	Colorless prisms	91 – 92	$C_{21}H_{25}ON$	82.03	82.45	8.20	8.24
2-(3-(Diethylamino)-1-benzoxy-*n*-propyl)-·HCl	EtOH-Et_2O	Colorless prisms	166 –167	$C_{28}H_{30}O_2NCl$			Cl, 7.92	8.05
3-(3-(Diethylamino)-1-hydroxy-*n*-propyl)-	[a]	Colorless liquid		$C_{21}H_{25}ON$	82.03	81.74	8.20	8.25
Hydrochloride	EtOH-Et_2O	Colorless prisms	141 –143	$C_{21}H_{26}ONCl$			N, 4.08	3.95
9-(3-(Diethylamino)-1-hydroxy-*n*-propyl)-	[a]	Colorless oil		$C_{21}H_{25}ON$	82.03	82.21	8.20	7.82
2-(3-(Piperidino)-1-hydroxy-*n*-propyl)-	[b]	Colorless rods	128 –128.5	$C_{22}H_{25}ON$	82.71	82.47	7.89	7.49
Hydrochloride	EtOH	Colorless prisms	184 –185	$C_{22}H_{26}ONCl$			Cl, 9.97	9.81
3-(3-(Piperidino)-1-hydroxy-*n*-propyl)-	[b]	Colorless liquid		$C_{22}H_{25}ON$	82.71	82.73	7.89	7.50
Hydrochloride	EtOH-Et_2O	Colorless plates	185 –185.5	$C_{22}H_{26}ONCl$	N, 3.94	3.76	Cl, 9.97	9.85
3-(3-(Piperidino)-1-acetoxy-*n*-propyl)-·HCl	EtOH-Et_2O	Colorless leaflets	237.5–238	$C_{24}H_{28}O_2NCl$			Cl, 8.92	8.94
9-(3-(Piperidino)-1-hydroxy-*n*-propyl)-	[c]	Colorless prisms	126 –126.5	$C_{22}H_{25}ON$	82.71	82.62	7.89	8.12
Picrate	EtOH	Yellow prisms	193.5–194	$C_{28}H_{28}O_8N_4$			N, 10.22	10.19
2-(3-(1,2,3,4-Tetrahydroisoquinolino)-1-hydroxy-*n*-propyl)-	EtOH	Colorless prisms	132.5–133	$C_{26}H_{25}ON$	84.97	84.83	6.86	7.10
Hydrochloride	EtOH-Et_2O	Colorless plates	212.5–213	$C_{26}H_{26}ONCl$			Cl, 8.78	8.79
3-(3-(1,2,3,4-Tetrahydroisoquinolino)-1-hydroxy-*n*-propyl)-	EtOH	Colorless plates	117 –117.5	$C_{26}H_{25}ON$	84.97	85.04	6.86	7.15
Hydrochloride	EtOH	Colorless plates	208 –208.5	$C_{26}H_{26}ONCl$	77.29	77.51	6.49	6.72
							N, 3.47	3.60
9-(3-(1,2,3,4-Tetrahydroisoquinolino)-1-hydroxy-*n*-propyl)-		Colorless oil	[b]	$C_{26}H_{25}ON$	84.97	84.90	6.86	6.99

[a] Distilled at 100° (0.01 mm.). [b] Distilled at 130° (0.01 mm.). [c] Sublimed at 100° (0.01 mm.).

$HCl \longrightarrow C_{14}H_9COCH_2CH_2NR_2 \cdot HCl \xrightarrow{\text{cat. red.}} C_{14}H_9CHOHCH_2CH_2NR_2 \cdot HCl$, where $-NR_2$ represents the dimethylamino-, diethylamino-, piperidino- and tetrahydroisoquinolino group.

We wish to express our gratitude to Merck and Co., Rahway, N. J., for their generous coöperation in the large scale preparation of the 2- and 3-acetylphenanthrenes.

Experimental

A mixture of 2-, 3-[8] or 9-acetylphenanthrene[9] (0.1 mole), paraformaldehyde (0.15 mole), and the secondary amine hydrochloride (0.15 mole) (dimethylamine-, diethylamine, piperidine- and 1,2,3,4-tetrahydroisoquinoline hydrochloride) in 60 to 80 cc. of isoamyl alcohol was kept at a gentle boil for five to twenty minutes. The advantage of using the higher boiling solvent, isoamyl alcohol, in this

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(8) Mosettig and van de Kamp, THIS JOURNAL, **52**, 3704 (1930).

(9) Mosettig and van de Kamp, *ibid.*, **55**, 3442 (1933).

condensation is that the reaction proceeds much quicker, whereas in ethyl alcohol, the solvent used by Mannich, the condensation takes place very slowly. By prolonged boiling in ethyl alcohol, furthermore, the yield of the expected amino ketone is considerably lowered, on account of the formation of by-products. These are both neutral and basic in nature and in part crystalline. In the preparation of most of the piperidino and tetrahydroisoquinolino ketones the hydrochlorides crystallized out after five to ten minutes. They were filtered off from the cooled reaction mixture and recrystallized. In the cases where the hydrochlorides did not precipitate, the reaction mixture was cooled, after having been kept boiling for fifteen to twenty minutes. After the addition of a few drops of concentrated hydrochloric acid, in order to depolymerize unchanged paraformaldehyde, unreacted ketone and formaldehyde were taken up in ether. The aqueous layer was alkalified and extracted with ether and the residue left from evaporation of the ether was warmed slightly in a vacuum in order to remove aliphatic amines. The amino ketones subsequently were purified through the hydrochlorides.

The amino ketones were reduced in the form of the hydrochlorides, in 50–70% ethyl alcohol, using platinum oxide as a catalyst. In two cases where the free amino ketones were reduced, namely, in the cases of the 3-dimethylamino ketone and the 9-(1,2,3,4-tetrahydroisoquinolino) ketone, two moles of hydrogen were absorbed, and in the case of the 2-dimethylamino ketone, approximately three moles of hydrogen were taken up. The reduction of the 3-(1,2,3,4-tetrahydroisoquinolino) ketone was effected with good results either by hydrogenating the free base in 95% ethyl alcohol, or by reducing the hydrochloride in 60% ethyl alcohol.

Summary

1. A series of amino ketones of the type $C_{14}H_9COCH_2CH_2NR_2$ (NR_2 representing the dimethylamino-, the diethylamino-, the piperidino- and tetrahydroisoquinolino group) has been prepared by the Mannich method from 2-, 3- and 9-acetylphenanthrene.

2. By catalytic hydrogenation the corresponding amino alcohols $C_{14}H_9CHOHCH_2CH_2NR_2$ have been prepared. These substances will be investigated to determine the result pharmacologically of lengthening the carbon chain of amino alcohols of the phenanthrene series.

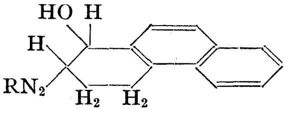
UNIVERSITY, VIRGINIA RECEIVED JUNE 22, 1936

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Studies in the Phenanthrene Series. XII.[1]
Amino Alcohols Derived from 1,2,3,4-Tetrahydrophenanthrene[2]

BY ALFRED BURGER AND ERICH MOSETTIG

Among the synthetical substances which have been prepared in this Institution in the attempt to find morphine substitutes, 2-piperidino-1-hydroxy-1,2,3,4-tetrahydrophenanthrene (type I), and 3-(1,2,3,4-tetrahydroisoquinolino)-4-hydroxy-1,2,3,4-tetrahydrophenanthrene (type II) proved to have the strongest analgesic action (minimal effective doses administered orally to cats, 20 and 15 mg. per kilogram, respectively, comparable with doses of 20 mg. for pseudocodeine, 10 mg. for codeine, and 1 mg. for morphine).[2] Experiments are under way to resolve these compounds and eliminate or "muzzle" their alcoholic hydroxyl in the hope of increasing their physiological activity.[3]



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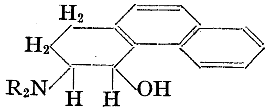
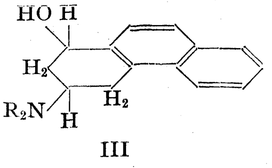
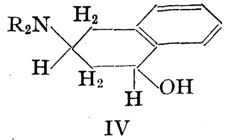


II

We are reporting in the present communication the preparation of compounds which differ from those of types I and II principally through the position of the nitrogen group. Compounds which may be represented by type formulas III and IV, analogs of the propanolamines reported in the foregoing communication, are obviously not readily accessible.



III



IV

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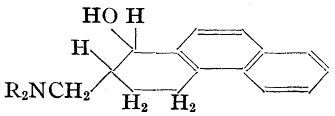
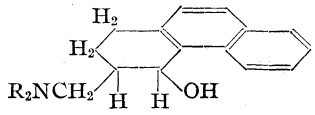
[1] The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

[2] First communication on amino alcohols derived from 1,2,3,4-tetrahydrophenanthrene, Mosettig and Burger, THIS JOURNAL, **57**, 2189 (1935).

[3] Elimination and muzzling of the alcoholic group in morphine and its derivatives produce generally a marked increase in analgesic action. Eddy, *J. Pharmacol.*, **55**, 127 (1935); Eddy and Howes, *ibid.*, **55**, 257 (1935).



V



VI

The compounds of type V and VI, however, carrying the nitrogen group in the same relative position to the alcoholic hydroxyl group as in the propanolamines and in types III and IV could be conveniently prepared, essentially by the Mannich method,[4] that is, by the action of the hydrochlorides of secondary amines (dimethylamine, diethylamine, piperidine and tetrahydroisoquinoline) and paraformaldehyde on 1- and 4-ketotetrahydrophenanthrenes, and subsequent reduction of the amino ketones.[5]

We have not proved experimentally formulas V or VI for the new amino alcohols described in this communication, but the formation of the corresponding amino ketones by the method of Mannich hardly leaves any doubt as to the constitution of the amino alcohols, since the formulas of the amino ketones prepared by Mannich and Braun[4,6] from cyclohexanone, amine hydrochloride and formaldehyde appear to be well established. In the reduction of our amino ketones to the amino alcohols, only one of the possible diastereomeric forms is obtained.

It was observed that two of the amino alcohols (V and VI, NR_2 represents the diethylamino- and tetrahydroisoquinolino group) split off water with ease when an attempt was made to acetylate them with acetic anhydride in pyridine. This loss of water also takes place under the influence of alcoholic hydrogen chloride. The resulting unsaturated amine readily can be reduced catalytically. We have not sufficient experimental data to make any conjecture concerning the structural features upon which the tendency to split out water is dependent. This question will be investigated in another connection.

The 1- and 4-tetanthrenones are also convenient starting materials for the synthesis of 1- and 4-aminotetanthrenes, which are obtained in good yields by reduction of the corresponding ketoximes.

Experimental

Preparation of Amino Ketones.—A mixture of 1- or 2-ketotetrahydrophenanthrene (1 mole), the amine hydrochloride (1.2 moles), and paraformaldehyde (2.5 moles) in isoamyl alcohol was heated under reflux for ten to fifteen minutes. Generally portions of 5 to 10 g. of ketone in 50 to 100 cc. of isoamyl alcohol were used. A clear solution resulted after two or three minutes. The excess of paraformaldehyde was depolymerized by addition of a few drops of alcoholic hydrogen chloride. The solution was cooled, diluted with ether and extracted with dilute aqueous hydrochloric acid. The amino ketones were liberated, extracted into ether and purified by crystallization or in the form of their salts. The secondary amines used in the reaction were dimethylamine, diethylamine, piperidine and tetrahydroisoquinoline. No definite reaction was observed with tetrahydroquinoline. In the case of the two tetrahydroisoquinolino ketones, the hydrochlorides crystallized directly from the reaction mixtures. They were filtered and washed with a little cold water.

Preparation of Amino Alcohols.—The amino ketones were hydrogenated as hydrochlorides in solution in 90% alcohol, using a platinum oxide catalyst. In most of the cases the reductions stopped when one mole of hydrogen had been absorbed.

1,2-Dihydro-3-[(1,2,3,4-tetrahydroisoquinolino)-methyl]-phenanthrene.—In the attempt to acetylate 4-hydroxy-3-[(1,2,3,4-tetrahydroisoquinolino)-methyl] - 1,2,3,4-tetrahydrophenanthrene with acetic anhydride and pyridine at room temperature, the unsaturated amine was formed. The same substance was obtained by allowing 4-hydroxy-3-[(1,2,3,4-tetrahydroisoquinolino)-methyl] - 1,2,3,4-tetrahydrophenanthrene to stand with alcoholic hydrogen chloride overnight. The base crystallized from dilute alcohol; m. p. 81–82°.

Anal. Calcd. for $C_{24}H_{23}N$: C, 88.56; H, 7.13; N, 4.31. Found: C, 88.55; H, 7.39; N, 4.40.

The hydrochloride was crystallized from alcohol–ether and melted at 227–228°.

Anal. Calcd. for $C_{24}H_{24}NCl$: C, 79.62; H, 6.69; N, 3.87. Found: C, 79.41; H, 6.84; N, 4.09.

The hydrochloride readily absorbs one mole of hydrogen (platinum oxide catalyst).

3,4-Dihydro-2-[(diethylamino)-methyl]-phenanthrene.—1 - Keto-2 - [(diethylamino) - methyl] - 1,2,3,4 - tetrahydrophenanthrene hydrochloride readily absorbed one mole of hydrogen, but neither the free amino alcohol nor any of its derivatives could be obtained in a crystalline state. On treatment with either acetic anhydride or alcoholic hydrogen chloride as described above, a colorless hydrochloride was obtained; recrystallized from alcohol–ether, m. p. 231–232°.

Anal. Calcd. for $C_{19}H_{24}NCl$: C, 75.58; H, 8.02; N, 4.64. Found: C, 75.88; H, 8.52; N, 4.88.

The free base from the hydrochloride was oily. The hydrochloride absorbed one mole of hydrogen on catalytic reduction.

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(4) Mannich and Braun, *Ber.*, **53**, 1874 (1920).

(5) By employing 1,2,3,4-tetrahydroquinoline no definite reaction could be initiated. The same observation was made by Mannich in the case of aryl methyl ketones [Mannich and Lammering, *Ber.*, **55**, 3510 (1922)]. It should be recalled that it was impossible to obtain definite reaction products in the attempt to exchange the bromine in the bromotetanthrenones with tetrahydroquinoline.[2]

(6) See also Bodendorf and Koralewski, *Arch. Pharm.*, **271**, 101 (1933).

TABLE I

Derivatives of 1,2,3,4-tetrahydrophenanthrene	Appearance	Solvent	Yield, %	M. p., °C.,	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
1-Keto-2-((dimethylamino)-methyl)-	Colorless blades	Pet. ether		66–82	$C_{17}H_{19}ON$					5.53	5.22
Hydrochloride	Colorless	EtOH	65	199–200	$C_{17}H_{20}ONCl$					4.84	4.87
1-Keto-2-((diethylamino)-methyl)-	Leaflets	Pet. ether		60–61	$C_{19}H_{23}ON$					4.98	4.44
Hydrochloride	Colorless	EtOH-Et_2O	59	137–138	$C_{19}H_{24}ONCl$					4.41	4.49
Picrate	Yellow	EtOH		163–164	$C_{25}H_{26}O_8N_4$					10.98	11.08
1-Keto-2-(piperidinomethyl)-	Leaflets or needles	MeOH	40	97–98	$C_{20}H_{23}ON$					4.78	5.11
Hydrochloride	Colorless	EtOH-Et_2O		170–220	$C_{20}H_{24}ONCl$					4.25	4.26
1-Keto-2-((1,2,3,4-tetrahydro-isoquinolino)-methyl)-	Colorless needles	MeOH		121–123	$C_{24}H_{23}ON$					4.11	4.37
Hydrochloride	Shining leaflets	EtOH-Et_2O	61	148–150	$C_{24}H_{24}ONCl$					3.71	3.76
4-Keto-3-((dimethylamino)-methyl)-·HCl	Shining leaflets	EtOH	77	178–179	$C_{17}H_{20}ONCl$					4.84	4.85
4-Keto-3-((diethylamino)-methyl)-·HCl	Colorless	EtOH-Et_2O	51	153–154	$C_{19}H_{24}ONCl$					4.41	4.38
Picrate	Yellow	EtOH		149–151	$C_{25}H_{26}O_8N_4$					10.98	11.28
4-Keto-3-(piperidinomethyl)-	Yellow leaflets	Dil. acetone	37	106–107	$C_{20}H_{23}ON$					4.78	4.90
Perchlorate	Colorless	EtOH		163–164	$C_{20}H_{24}O_5NCl$					3.56	3.88
4-Keto-3-((1,2,3,4-tetrahydro-isoquinolino)-methyl)-.HCl	Glitt. prisms	EtOH-Et_2O	34	159–161	$C_{24}H_{24}ONCl$					3.71	3.80
1-Hydroxy-2-((dimethyl-amino)-methyl)-	Colorless	MeOH		146–147	$C_{17}H_{21}ON$	79.94	80.29	8.30	8.33	5.49	5.63
Hydrochloride	Colorless	EtOH-Et_2O	70	236	$C_{17}H_{22}ONCl$					4.80	4.87
1-Hydroxy-2-(piperidino-methyl)-	Fine needles	MeOH		133–134.5	$C_{20}H_{25}ON$	81.30	81.31	8.54	8.59	4.75	4.87
Hydrochloride	Needles	EtOH-Et_2O		227–228	$C_{20}H_{26}ONCl$					4.22	4.27
1-Hydroxy-2-((1,2,3,4-tetra-hydroisoquinolino)-methyl)-	Colorless	EtOH		159–160	$C_{24}H_{25}ON$	83.91	83.67	7.34	7.53	4.08	4.28
Hydrochloride	Colorless	EtOH-Et_2O		217	$C_{24}H_{26}ONCl$					3.69	3.80
4-Hydroxy-3-((dimethylamino)-methyl)-·HCl	Colorless	EtOH-Et_2O		186–187	$C_{17}H_{22}ONCl$	69.95	69.66	7.61	7.74	4.80	4.85
4-Acetoxy-3-((dimethylamino)-methyl)-·HCl	Colorless	EtOH-Et_2O		200	$C_{19}H_{24}O_2NCl$					4.20	4.32
4-Hydroxy-3-((diethylamino)-methyl)-·HCl	Colorless	EtOH-Et_2O	86	172–173	$C_{19}H_{26}ONCl$	71.32	71.42	8.20	8.39	4.38	4.52
Picrate	Yellow	EtOH		177–179	$C_{25}H_{28}O_8N_4$					10.94	11.26
4-Hydroxy-3-(piperidino-methyl)-·HCl	Colorless	Acetone	71	178–179	$C_{20}H_{26}ONCl$	72.36	72.51	7.90	8.14	4.22	4.20
4-Hydroxy-3-((1,2,3,4-tetra-hydroisoquinolino)-methyl)-	Colorless	Dil. MeOH		149.5–151	$C_{24}H_{25}ON$	83.91	83.92	7.34	6.92		
Hydrochloride	Colorless	EtOH-Et_2O		181–182	$C_{24}H_{26}ONCl$	75.85	75.50	6.90	6.76		
1-Amino-[a]	Colorless		86	61–63	$C_{14}H_{15}N$					7.07	7.23
Hydrochloride	Colorless	EtOH-Et_2O		256–257	$C_{14}H_{16}NCl$	71.92	71.81	6.90	6.90	6.00	6.09
Benzal 1-amino-[b]	Colorless	EtOH		103–105	$C_{21}H_{19}N$					4.91	4.96
1-(Methylamino)-·HCl[b]	Colorless	EtOH-Et_2O	54	258	$C_{15}H_{18}NCl$	72.70	72.31	7.33	7.31	5.66	5.84
Hydriodide[b]	Glitt. leaflets	EtOH		243	$C_{15}H_{18}NI$					4.13	4.25
1-(Dimethylamino)-·HCl[c]	Colorless	EtOH-Et_2O		216	$C_{16}H_{20}NCl$	73.39	73.47	7.71	7.82		
Picrate	Yellow	EtOH		177–178	$C_{22}H_{22}O_7N_4$					12.34	12.59
4-Amino-·HCl[d]	Colorless	EtOH-Et_2O		267–268	$C_{14}H_{16}NCl$	71.92	71.70	6.90	7.00	6.00	5.96
4-(Dimethylamino)-·HCl[c]	Colorless	EtOH-Et_2O		202	$C_{16}H_{20}NCl$	73.39	73.46	7.71	8.05		

[a] Prepared by reduction of 1-tetanthrenone oxime [Schroeter, Müller and Huang, *Ber.*, **62**, 645 (1929)] with 2.5% sodium amalgam in alcohol solution, acidified with acetic acid, or with aluminum amalgam in moist ether. [b] Prepared by the method of Decker, *Ann.*, **395**, 362 (1913). [c] Prepared by heating the primary amine with methyl iodide and sodium acetate at 100° for five hours and separating the reaction mixture by the Hinsberg method. [d] Prepared by reduction of 4-tetanthrenone oxime with aluminum amalgam in moist ether.

Summary

1. The synthesis of a series of amino alcohols derived from 1,2,3,4-tetrahydrophenanthrene is described. The synthesis is effected by condensing 1-keto-1,2,3,4-tetrahydrophenanthrene and 4-keto-1,2,3,4-tetrahydrophenanthrene, respectively, with paraformaldehyde and the hydrochlorides of dimethylamine, diethylamine, piperidine and 1,2,3,4-tetrahydroisoquinoline, respectively, by the method of Mannich, and subsequent catalytic hydrogenation of the resulting amino ketones.

2. By reduction of the oximes of the above-mentioned tetanthrenones with sodium amalgam or aluminum amalgam, 1- and 4-aminotetanthrene can be prepared in satisfactory yields. The amino alcohols will be investigated for comparison of their physiological action with that of the next lower homologs.

UNIVERSITY, VIRGINIA

RECEIVED JUNE 22, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NEBRASKA AND WALLA WALLA COLLEGE]

The Reactivity of Nuclear Chlorine in the Isomeric 1,2- and 2,1-Chloronaphthalenearsonic Acids

BY GEORGE W. BOWERS AND CLIFF S. HAMILTON

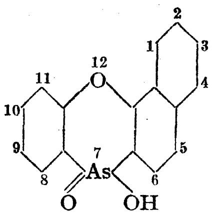
In the benzene nucleus the reactivity of chlorine ortho or para to the arsono group has been investigated[1,2,3] in this Laboratory. The object of this study was to extend the work to naphthalenearsonic acids.

In the preparation of the parent chloronaphthalenearsonic acids, the methods worked out previously[4] were found helpful. β-Naphthylamine was used in the production of both the isomers and 1-chloro-2-naphthalenearsonic acid was prepared readily. However, the synthesis of 2-chloro-1-naphthalenearsonic acid presented several difficulties and experimental methods finally developed must be followed carefully particularly in the arsonation reaction in order to obtain workable yields.

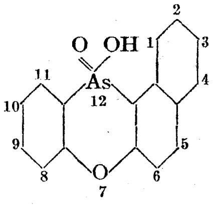
The most favorable conditions for the condensation reactions were determined by a series of experiments in which variations were made in the temperature, solvent, catalyst, time and proportion of reactants. Nitrobenzene proved the best solvent and the optimum temperature was approximately 140°. A small piece of bright copper foil was found the best catalyst and the reaction time was ten to twelve hours.

The reactivity of chlorine in these naphthalenearsonic acids is less than that found in the benzenearsonic acids, for neither the aliphatic nor the aromatic amines showed any evidence of reaction and, in general, the yields are smaller for the condensation product with phenols. Of the two chloroarsonic acids, the 1-chloro-2-naphthalenearsonic acid is apparently more reactive but due to the formation of tars the ethers were very difficult to isolate.

When the ethers resulting from the reactions of these chloronaphthalenearsonic acids and the phenols were boiled with glacial acetic acid they, without exception, lost the elements of water and two series of heterocyclic naphthalene arsenicals were produced. The following structures and names are proposed



α-Benzophenoxarsinic acid



γ-Benzophenoxarsinic acid

These structures are assigned for the following reasons: (1) the arsenic and oxygen atoms are in the same relative positions as in the parent ether compounds. (2) The arsenic analyses indicate the loss of water from the parent ethers. (3) These arsinic acids do not hydrolyze even by treatment with hot sodium hydroxide solution. They certainly would do so if the arsono group alone were involved in the dehydration. (4) The parent chloroarsonic acids are not dehydrated by the action of glacial acetic acid. This fact indicates again that the dehydration is not due to the arsono group alone. (5) It is assumed that ortho hydrogen of the phenolic group is involved because of the stability of six-membered rings. (6) The insolubility of the sodium salt of the similar phenoxyphenylarsinic acid in an excess of sodium carbonate has previously been observed.[5]

Experimental

1-Chloro-2-naphthalenearsonic Acid.—Twenty-one and two-tenths grams of 1-amino-2-naphthalenearsonic acid, prepared according to Saunders and Hamilton's[4] directions, was precipitated in a finely divided state by dissolving the pulverized compound in 2 *N* sodium hydroxide and acidifying to Congo red paper with 2 *N* hydrochloric acid. The mixture was diluted to 400 cc., 30 cc. of concentrated hydrochloric acid added, and diazotization carried out at −5° by adding dropwise 8 g. of sodium nitrite in 32 cc. of water over a period of one hour.

Meanwhile a cuprous chloride suspension was prepared in the usual way from 25 g. of crystallized copper sulfate and was dissolved in 72 cc. of concentrated hydrochloric acid. To this solution the diazotized amine was added in small portions. The resulting mixture was made alkaline by the addition of solid sodium carbonate and then filtered. Upon acidification of the filtrate to Congo red paper with hydrochloric acid, a light red precipitate of 1-chloro-2-naphthalenearsonic acid separated; purified by dissolving in sodium carbonate and reprecipitating by hydrochloric

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[1] Etzelmiller and Hamilton, THIS JOURNAL, **53**, 3085 (1931).

[2] Maclay and Hamilton, *ibid.*, **54**, 3310 (1932).

[3] Hall and Hamilton, *ibid.*, **56**, 1779 (1934).

[4] Saunders and Hamilton, *ibid.*, **54**, 636 (1932).

[5] Roberts and Turner, *J. Chem. Soc.*, 2004 (1925).

TABLE I

1-Arsono-2-( )-naphthalene	Yield, %	M. p., °C.	Formula	Arsenic analyses, % Calcd.	Found	
-(Phenoxy)	51	211–295[a]	$C_{16}H_{13}O_4As$	21.78	21.82	21.85
-(2′-Methylphenoxy)	48	295	$C_{17}H_{15}O_4As$	20.93	20.95	20.96
-(4′-Methylphenoxy)	30	225–273[b]	$C_{17}H_{15}O_4As$	20.93	20.95	20.99
-(2′-Chlorophenoxy)	42	230–231	$C_{16}H_{12}O_4ClAs$	19.80	19.76	19.82
-(4′-Chlorophenoxy)	24	217–219	$C_{16}H_{12}O_4ClAs$	19.80	19.80	19.82

[a] Substance partially melts at 211° then solidifies and finally melts at 295°. [b] Substance partially melts at 225° then solidifies and finally melts at 273°.

TABLE II

2-Arsono-1-( )-naphthalene	Yield, %	M. p., °C.	Formula	Arsenic analyses, % Calcd.	Found	
-(Phenoxy)	66.5	322	$C_{16}H_{13}O_4As$	21.78	21.80	21.78
-(2′-Methylphenoxy)	18	181	$C_{17}H_{15}O_4As$	20.93	20.88	20.90

acid, followed by recrystallization from 50% acetic acid; white needles; m. p. 317°; yield 82%; soluble in methyl and ethyl alcohols, but insoluble in water and benzene.

Anal. Calcd. for $C_{10}H_8O_3ClAs$: As, 26.16; Cl, 12.38. Found: As, 25.99, 26.10;[6] Cl, 12.21, 12.20.[7]

2-Chloro-1-nitronaphthalene.—From α-nitro-β-naphthylamine in 82% yields following the method of Hodgson and Walker,[8] for diazotization.

2-Chloro-1-aminonaphthalene.—Five grams of 2-chloro-1-nitronaphthalene was dissolved in 100 cc. of 95% alcohol, about 1 g. of Raney nickel added and the mixture exposed with shaking to molecular hydrogen under 40 lb. (2.66 atm.) pressure. Reduction was complete in twenty minutes. The catalyst was filtered from the mixture, the filtrate evaporated to 25 cc., 10 cc. of water was added and the solution placed in the refrigerator. The amine separated in long white needles; yield, quantitative; m. p. 56°.

2-Chloro-1-naphthalenearsonic Acid.—In a 600-cc. beaker was placed 17.7 g. of crude 2-chloro-1-aminonaphthalene and 196 cc. of 6 *N* hydrochloric acid. The mixture was cooled to 0° and 8 g. of sodium nitrite dissolved in 47 cc. of water was added dropwise over a period of two hours. Meanwhile in a 2-liter beaker an arsenite solution was made up by dissolving 50 g. of sodium metarsenite in 206 cc. of water in which was dissolved 2 g. of copper sulfate. This solution was cooled to 5°. The 2-liter beaker was fitted with a mechanical stirrer, and two funnel tubes extending to the bottom. A dropping funnel was adjusted at the top of each funnel tube. In one was placed 146 cc. of 6 *N* sodium hydroxide and in the other the filtered diazotized amine. With stirring the two solutions were dropped in rapidly at such a rate that the mixture in the beaker was always slightly basic. After the diazotized amine had all been added, stirring was continued for fifteen minutes longer and the mixture filtered through a carbon mat. Upon acidification to Congo red paper with hydrochloric acid the 2-chloro-1-naphthalenearsonic acid separated as an almost white precipitate. After dissolving in a sodium carbonate solution and reprecipitating with hydrochloric acid, the arsonic acid was used in this state of purity for subsequent condensations; purified by dissolving in 50% acetic acid and decolorizing with activated charcoal. Upon cooling colorless needles appeared, m. p. 296°; yield 56%; soluble in ethyl alcohol but insoluble in ether and benzene.

Anal. Calcd. for $C_{10}H_8O_3ClAs$: As, 26.16; Cl, 12.38. Found: As, 25.99, 26.10; Cl, 12.48, 12.38.

Phenyl Ether Derivatives

General Procedure.—A mixture of 5 g. of 2-chloro-1-naphthalenearsonic acid or 1-chloro-2-naphthalenearsonic acid, 10 g. of phenol or substituted phenol, 5 g. of anhydrous potassium carbonate, 25 cc. of nitrobenzene and a small piece of bright copper foil was placed in a 125-cc. Erlenmeyer flask fitted with ground-glass connections. The mixture was agitated by means of a stirrer extending through the length of the reflux condenser. The flask and its contents were heated in an oil-bath at 140° for ten to twelve hours. The resulting mixture was steam distilled to remove the nitrobenzene and excess phenol, and treated with activated charcoal. After filtering, the mixture was acidified to Congo red paper with hydrochloric acid, whereupon the phenyl ether derivatives of the arsonic acid precipitated. The crude products were charcoaled and crystallized from 50% acetic acid. The melting points are high, and more or less decomposition takes place as indicated by darkening.

Benzophenoxarsinic Acids and Derivatives

General Procedure.—The corresponding phenoxynaphthalenearsonic acids were boiled with glacial acetic acid and an equal volume of water was added. A portion of the arsinic acids precipitated and sufficient 50% acetic acid was added to bring them into solution at the boiling temperature. Upon cooling, the benzophenoxarsinic acids crystallized out in quantitative yields. No further puri-

TABLE III

	M. p., °C.	Formula	Arsenic analyses, % Calcd.	Found	
α-Benzophenoxarsinic acid[9]	319	$C_{16}H_{11}O_3As$	22.98	23.02	23.05
11-Methyl-α-benzophenoxarsinic acid	177	$C_{17}H_{13}O_3As$	22.04	22.00	22.02

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[6] The potentiometric method of Cislak and Hamilton [THIS JOURNAL, **52**, 638 (1930)] was used for the quantitative determination of arsenic in all of the compounds prepared.

[7] The Carius method was used for the quantitative determination of chlorine in this arsonic acid and its isomer.

[8] Hodgson and Walker, *J. Chem. Soc.*, 1620 (1933).

[9] Aeschlimann, *J. Chem. Soc.*, 811 (1925).

TABLE IV

-Phenoxarsinic acid	M. p., °C.	Formula	Arsenic analyses, % Calcd.	Found	
γ-Benzo	278–280	$C_{16}H_{11}O_3As$	22.98	23.04	23.00
8-Methyl-γ-benzo	205–270[a]	$C_{17}H_{13}O_3As$	22.04	22.04	22.08
10-Methyl-γ-benzo	215–217	$C_{17}H_{13}O_3As$	22.04	22.04	22.06
8-Chloro-γ-benzo	216–218	$C_{16}H_{10}O_3ClAs$	20.79	20.90	20.92
10-Chloro-γ-benzo	214	$C_{16}H_{10}O_3ClAs$	20.79	20.78	20.76

[a] Substance partially melts at 205°, then solidifies and finally melts sharply at 270°.

fication was necessary if the corresponding phenoxynaphthalenearsonic acids used were pure. All were insoluble in sodium carbonate and cold sodium hydroxide solutions, but were soluble in hot sodium hydroxide solutions.

Summary

1. The isomeric 1,2- and 2,1-chloronaphthalenearsonic acids have been prepared for the first time. The synthesis of the latter involved the developing of methods for the quantity production of the intermediates 2-chloro-1-nitronaphthalene and 2-chloro-1-aminonaphthalene and the necessary modifications of the Bart reaction.
2. Two new series of naphthyl phenyl ether derivatives have been prepared by the condensation of the parent compounds with phenol and substituted phenols. 1-Chloro-2-naphthalenearsonic acid has been condensed with phenol and *o*-cresol. 2-Chloro-1-naphthalenearsonic acid has been condensed with phenol, *o*- and *p*-cresols, and *o*- and *p*-chlorophenols.
3. By the elimination of water, heterocyclic benzophenoxarsinic acids have been prepared from all the above naphthyl phenyl ethers. No benzophenoxarsinic acids have been reported previously.
4. No condensations were possible, under the conditions employed, with either aniline, the aliphatic amines or the aliphatic alcohols.
5. Chlorine in these naphthalenearsonic acids was found less reactive than chlorine in a similar position in the benzene nucleus.

LINCOLN, NEBRASKA RECEIVED JUNE 5, 1936

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Normal Potential of the Silver–Silver Bromide Electrode from 5 to 40°[1]

BY BENTON BROOKS OWEN AND LOUISE FOERING

Experimental difficulties inherent in the direct comparison of certain electrodes with the hydrogen standard have led to the extensive use of secondary standards such as the familiar calomel half-cells. Because of the thermodynamic objections to the estimation of liquid junction potential involved in the ordinary use of such standards, it is important to be able to perform the comparison in cells without liquid junctions. It has recently been shown[2] that cells containing dilute borax buffers can be very conveniently employed in this connection. Although the method is general in principle, the use of borax solutions, under certain prescribed conditions, has the peculiar advantage of eliminating the need for an extrapolation to infinite dilution. This labor-saving feature and the convenience of borax as a buffering agent make it desirable to test the accuracy and reliability of the method by investigating a system which can be readily checked by more orthodox procedures.

For this purpose we have measured the electromotive forces of cells of the type

$$H_2 \mid HBO_2(m),\ NaBO_2(m),\ KX(m) \mid AgX - Ag$$

in which X represents either bromide or chloride, and $m \eqsim 0.005$ molal. After a small correction[2] to the electromotive forces to make them correspond exactly to $m = 0.005$, the equation

$$E^0_{\mathrm{HBr}} = E^0_{\mathrm{HCl}} + E^{0.005}_{\mathrm{KBr}} - E^{0.005}_{\mathrm{KCl}} \qquad (1)$$

permits the calculation of E^0_{HBr} in terms of known values of E^0_{HCl} taken as standard. Comparison can then be made with values of E^0_{HBr} obtained by direct extrapolation of measurements on cells containing dilute hydrobromic acid. We have employed electrodes containing fused silver bromide because the corresponding normal potentials have

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(1) This communication embodies part of the experimental material to be presented by Louise Foering to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Owen, THIS JOURNAL, **57**, 1526 (1935). Full particulars regarding the calculations are given.

TABLE I

OBSERVED VALUES OF $E^{0.005}_{\mathrm{KBr}}$ AND THE CORRESPONDING VALUES OF $E^0_{\mathrm{HBr}} = -E^0_{\mathrm{AgBr}}$

	$E^{0.005}_{\mathrm{KBr}}$					E^0_{HBr}	
$t°$	(1)	(2)	(3)	(4)	(5)	Average	Δ
5	0.72777	0.72786	0.72775	0.72769	0.72777^b	0.07986	0
10	.73417	.73423	.73417	.73409	.73416^b	.07801	1
15	.74061	.74061	.74071	.74059	.74053^b	.07599	3
20	.74703	.74709	.74714	.74707	.74714	.07372	−2
25	.75362	.75366^a	.75365	.75356	.75377	.07128	−6
30	.76011	.76008^a	.76011	.76006	.76014	.06871	−5
35	.76668	.76661^a	.76661	.76656	.76663	.06600	0
40		.77300^a	.77300	.77312	.77312	.06307	1
$m \times 10^6$	4902	4939	4997	4840	5031		

^{a} $m \times 10^6 = 5061$. ^{b} $m \times 10^6 = 4719$.

recently been reported[3] over a wide temperature range.

Materials and Technique

Since the concordance among some of the earlier estimations of E^0_{HBr} is not very satisfactory, we have paid particular attention to the purity of our materials upon the supposition that the uncertainty in the older measurements may have been due to impurities in the hydrobromic acid.

We employed two samples of potassium bromide. Sample A was prepared from carefully purified potassium oxalate and bromine, and recrystallized three times from conductivity water. The purification of the bromine was essentially the procedure used by Baxter and Grover.[4] Sample B consisted of Baker "analyzed" potassium bromide recrystallized six times from conductivity water. Both samples were dried over solid sodium hydroxide, and then heated in platinum to constant weight at 120°.

The borax was a re-fused Kahlbaum product previously described.[5]

All concentrations were calculated from the weights of the "dry" salts, and expressed as moles per kilogram of solvent weighed *in vacuo*. The effect of the presence of 0.1% of moisture in the borax would be unmeasurable under the conditions of our experiment, but would amount to 0.02 or 0.03 mv. if present in the potassium bromide.

The silver–silver bromide electrodes were prepared by heating a mixture of 90% silver oxide and 10% silver bromate for seven minutes at 650°.[6] Several different samples of silver bromate were employed. One was a recrystallized fresh preparation, and the other two were carried over from previous researches.[6,7] Fresh and old[2] silver oxides were also used. Six electrodes were prepared from a silver bromate–silver oxide mixture left in the laboratory by Dr. Keston. They were used in the measurement marked by the superscript *a* in Table I.

Intercomparison of electrodes prepared from various combinations of these silver compounds showed them to be indistinguishable. They were kept dry until used, and no effort was made to protect them from diffuse daylight.[2]

Special care was taken in washing the hydrogen electrodes free from chlorides of the platinizing bath, and in the exclusion[2,5] of oxygen during the preparation and use of the cell solutions. Solutions were always used within one to four days after their preparation.

Discussion of the Results

The observed electromotive forces of the cells containing borax and potassium bromide were corrected to a partial pressure of hydrogen of one atmosphere, and to the round concentration $m = 0.005$. They are recorded as $E^{0.005}_{\mathrm{KBr}}$ in Table I.

The actual concentrations, *m*, of the solutions used in each series of cells is also included. Each value of $E^{0.005}_{\mathrm{KBr}}$ is the mean value of five or six independently filled cells agreeing within 0.1 mv. The same set of cells was never used over a temperature range greater than 20°.

Solutions (1) and (2) were prepared from sample B of potassium bromide. The others were made from the elaborately purified sample A. It can be seen that no *consistent* difference was observed in the electrochemical behavior of the two samples of potassium bromide. Since the source of the bromate and oxide used in the electrodes was also without noticeable effect upon the results, it is reasonable to conclude that the silver bromide electrode is not sensitive to such traces of impurities as may have remained in *any* of our chemicals.

In the calculation of E^0_{HBr} by equation (1), we employed the smoothed values of E^0_{HCl} given by equation (7) of Harned and Ehlers,[8] the mean values of $E^{0.005}_{\mathrm{KCl}}$ previously reported,[2] and the mean values of $E^{0.005}_{\mathrm{KBr}}$ derivable from the data given in Table I. The resulting values of E^0_{HBr} are recorded in the next to last column. Their temperature variation can be represented empirically by the quadratic equation

$$E^0_{\mathrm{HBr}} = 0.07134 - 498 \times 10^{-6}(t - 25) - 3.6 \times 10^{-6}(t - 25)^2 \quad (2)$$

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[3] Harned, Keston and Donelson, THIS JOURNAL, **58**, 989 (1936).

[4] Baxter and Grover, *ibid.*, **37**, 1027 (1915).

[5] Owen, *ibid.*, **56**, 1695 (1934).

[6] Keston, *ibid.*, **57**, 1671 (1935).

[7] Owen, *ibid.*, **55**, 1922 (1933).

[8] Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

The "fit" of this equation is indicated by the deviation in millivolts ($\Delta = E^0$ (obsd.) $- E^0$ (Eq. 2)) given in the last column.

Comparison with the corresponding values reported by Harned, Keston and Donelson[3] shows that our results are higher by two or three tenths of a millivolt, the agreement being best at the higher temperatures. In view of the indirect nature of our method and the combined uncertainties of the extrapolations for E^0_{HCl} and E^0_{HBr} involved in the comparison, it is probable that the agreement obtained is as good as could be expected. Nevertheless it should be remarked that Donelson's data for the 0.01 molal hydrobromic acid cell (fused silver bromide) are also two or three tenths of a millivolt higher than Keston's at the same concentration.[9]

Upon this basis we regard the reliability of electrode comparisons in borax buffers as established, and the accuracy of the method as limited only by the reproducibility of the measurements and the absolute accuracy of the electrode employed as standard.

Summary

1. The normal electrode potential of the silver–silver bromide (fused) electrode has been determined from 5 to 40° by comparison with the silver–silver chloride electrode in borax solutions without liquid junctions.

2. The reliability of the method is indicated by satisfactory agreement with results obtained with similar electrodes in hydrobromic acid solutions.[3]

3. By using materials from a variety of sources and subjected to different degrees of purification, it was shown that the silver–silver bromide (fused) electrode is highly reproducible.

NEW HAVEN, CONN. RECEIVED JUNE 22, 1936

[9] In a private communication Mr. Donelson informs us that the extrapolation of his data on the cells $H_2 \mid HBr(0.01), LiBr(m) \mid AgBr - Ag$ leads to values of E^0_{HBr} in excellent agreement with our own—maximum difference about 0.1 mv.

Contribution to the Chemistry of Europium

BY HERBERT N. MCCOY

Introduction.—The easy preparation of bivalent europium salts which, though powerful reducing agents, are sufficiently stable to be handled, invited further study of these unique rare earth compounds. This work has included determination of the velocity of oxidation by air of such europous compounds, the measurement of their reduction potential, the development of new methods of electrolytic reduction, the observation of the absorption spectrum of europous solutions, and the discovery that this spectrum is wholly different from that of trivalent europium solutions. As no method for the determination of europium in both of its stages of oxidation had been described, the first necessity for the work was the development of such a method.

Determination of Europium.—In a preliminary note[1] it was mentioned that europium may be determined iodometrically. The method may be illustrated by the following example.

A solution of europium chloride was made by dissolving 2.1619 g. of nearly pure europium oxide in 8.2 ml. of 6 *N* hydrochloric acid and diluting to 250 ml. Standard iodine and thiosulfate solutions, approximately 0.04 *N*, were prepared. The Jones reductor used[1] contained 150 g. of 20 to 30 mesh amalgamated zinc which gave a column 1.7 cm. in diameter and 21 cm. high. Immediately before each series of titrations 0.05 *N* hydrochloric acid was poured into the reductor tube and the zinc and acid were well shaken together. The reductor was then thoroughly flushed with more of the dilute acid, leaving sufficient barely to cover the top of the zinc column. The nozzle of the reductor dipped into a measured volume (usually 20 ml.) of standard iodine solution in a 400-ml. covered beaker into which a stream of carbon dioxide was passed to exclude air. For an analysis, 20 ml. of the europium chloride solution was run through the reductor, followed by a wash of 150 ml. of approximately 0.05 *N* hydrochloric acid. Reduction and washing required about twenty minutes.

The excess iodine was titrated with standard thiosulfate. The reactions are $2EuCl_3 + Zn \longrightarrow 2EuCl_2 + ZnCl_2$ and $Eu^{++} + I \longrightarrow Eu^{+++} + I^-$. In four determinations the net volumes of iodine solution required were 18.12, 18.05, 18.08 and 18.11 ml., mean 18.10 ml. indicating 0.1685 g. of europium oxide (Eu = 152.0) while the amount of oxide taken was 0.1730 g. The purity of the oxide was therefore 97.5%. In determinations, when no carbon dioxide was used, the results were 1 to 3% too low, due, doubtless, to partial oxidation of reduced europium by air.

Using this technique, the europium content of rare earth mixtures containing 1% or even less of this element may be determined if other reducible substances are

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[1] McCoy, THIS JOURNAL, **57**, 1756 (1935).

absent. A chloride solution of the rare earths of monazite in nearly their natural proportions was freed from iron, phosphate and sulfate. This material had been precipitated previously as double sodium sulfate and in consequence was nearly free from ytterbium, which may react like europium. The solution had a density of 1.13 and contained 0.11 g. of oxides per ml. Fifty ml. of this solution was reduced and titrated. Its titer indicated a europium oxide content of 0.0033 g., assuming no other reducing substances present. To two further 50-ml. portions of this solution known amounts of europium were added. Analyses gave the following results.

	I	II
Eu_2O_3 in 50 ml. sol., g.	0.0033	0.0033
Eu_2O_3 added, g.	.0625	.0424
Total	0.0658	0.0457
Found	0.0659	0.0440

Oxidation of Europium by Air.—The observation of Urbain[2] that a dilute solution of europous chloride can be kept and that it is not oxidized by iodine or nitric acid even at 100° can only mean that complete oxidation by air had occurred before the small amount of material in hand was tested. A like explanation may be made regarding the statement of Jantsch, Alber and Grubitsch[3] who were unable to titrate with iodine a solution thought to contain europous chloride and concluded that a state of equilibrium was reached. Yntema[4] and also Selwood[5] found no difficulty in oxidizing solid europous sulfate with nitric acid.

On exposure to air a solution of europous chloride is oxidized more or less rapidly depending on conditions. A few ml. of a dilute solution in an open beaker may be oxidized completely in an hour or less, but 300 to 400 ml. of a 30% solution has often stood three or four days under similar conditions without being wholly oxidized. When thus oxidized, solutions with excess hydrochloric acid remain clear, europium trichloride being formed. If there is a deficiency of acid, white basic material precipitates.

A rough determination of the speed of oxidation of europous chloride by air was made. A 30 to 50-fold excess of air was blown through dilute solutions under such conditions that the concentrations of the dissolved oxygen remained nearly constant. The set-up used comprised a 70-ml. wide-mouthed jar with a rubber stopper carrying a small zinc reductor, the tip of a buret for standard iodine solution, a tube through which either carbon dioxide or air could be led to the bottom of the jar, and a narrow vent for the escape of gases. The solutions used were half molar europium chloride, normal and decinormal hydrochloric acid, and 0.04 N iodine and thiosulfate; only the last two were standardized. In making a run, 5 ml. of N acid was put in the jar, the stopper with attached tubes adjusted, and the air displaced by carbon dioxide. Two ml. (exactly) of the europium solution followed by 25 ml. of decinormal acid were run through the reductor in five or six minutes while a slow stream of carbon dioxide was passed into the jar.

This finished, the latter gas stream was replaced at zero time by 8 or 10 bubbles of air per second for an exactly measured interval. Next a measured excess of iodine solution was run in rapidly and, after waiting a few minutes for the completion of the ensuing reaction, the excess of iodine was titrated with thiosulfate. A fresh 2-ml. portion of europium solution was used for each oxidation run. The results lead to a fair constant for a first order reaction.

Speed of Oxidation of $EuCl_2$ Solutions by Air at 23°

Interval, min.	Net ml. $N/25$ I	$K \times 10$
0	26.33	..
1	21.99	1.80
2	18.32	1.81
3	15.09	1.85
5	11.53	1.65
7	7.31	1.83
9	4.62	1.93
	Mean	1.81

It is thus seen that a 0.04 molar solution is half oxidized in about four minutes in a solution kept saturated with oxygen from air. The speed of oxidation by air of a concentrated solution standing in a beaker is very much slower for obvious reasons.

Electrolytic Reduction of Europium.—In the electrolytic reduction of a europium chloride solution Yntema[4] used a two-compartment cell which required 65 volts to give a current of 0.18 amp. Its high resistance was due to the great separation of the electrodes. A one compartment cell having electrodes close together fails to give much reduction because of the reverse change at the anode.

The electrolysis of europium formate (made from the oxide and acid) overcomes these difficulties. The cathode is mercury, the anode a short stout platinum wire. At the anode carbon dioxide and hydrogen from the formate ion come off steadily. In a one-compartment cell with 50 ml. of 0.1 molar formate 6 volts (4 no. 6 dry cells) give an almost steady current of 0.08 amp. Practically no hydrogen is liberated at the cathode, which remains bright and mirror-like until the larger part of the europium is reduced. Finally when 75 or 80% has been reduced hydrogen begins to be liberated at the cathode and the current efficiency falls off. Europous formate so made shows the typical reactions of europous solutions, including the immediate formation of the insoluble sulfate when treated with a solution of sulfuric acid or a sulfate. Europium may be separated from other rare earths by the electrolysis of formate solutions containing some sulfate.

The electrolysis of the acetate works well. It is also possible to reduce a chloride solution in a one-compartment cell, using a silver anode.

The Reduction Potential of the Eu^{++}/Eu^{+++} Electrode.—The many indications that a solution of Eu^{++} has a high reducing potential were confirmed by direct measurement which led to a value of E_0 of about 0.43 volt. The arrangement of the cell was as follows: $Pt/Eu(COOH)_3 + Eu(COOH)_2 + HCOOH + N\ KCl/ + N\ KCl/N\ KCl + Hg_2Cl_2/Hg$. For the potential measure-

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[2] Urbain, *Compt. rend.*, **153**, 1155 (1911).

[3] Jantsch, Alber and Grubitsch, *Monatsh.*, **53–54**, 305 (1929).

[4] Yntema, This Journal, **52**, 2782 (1930).

[5] Selwood, *ibid.*, **57**, 1145 (1935).

ments the following Leeds and Northrup instruments[6] were used: potentiometer, galvanometer, double throw switch, Eppley standard cell and Hildebrand (normal) calomel electrode. The total concentration of the europium was approximately 0.1 molar, the concentration of the free formic acid was small and variable, being sufficient only to prevent precipitation of the base by reason of oxidation by air during the measurements. A 150-ml. tall form beaker (without lip) with a fiber board cover and rubber band seal served both for the partial electrolytic reduction of the europium formate solution and later for the measurement of the electrode potential. In the beaker were placed 20 ml. of pure mercury and 50 ml. of approximately 0.1 molar europium formate containing a small excess of formic acid. The cover had seven holes, one central, the others peripheral. The central hole carried the glass insulated anode for the electrolysis, 1.5 cm. of stout platinum wire. Three glass-insulated platinum wires passed through other holes—one led to the mercury, the others, 3 mm. exposed lengths of small wires, served as alternate electrodes for the potential measurements. These electrodes were made of new wire carefully cleaned and kept in acidified europous chloride solution for twenty-four hours before being used. They quickly came to definite potentials during measurements. A salt bridge with normal potassium chloride connecting with a normal calomel electrode and a glass mechanically operated reciprocating stirrer passed through two holes while the seventh hole, closed by a plug, permitted the introduction of a 5-ml. pipet. The electrolysis was carried out as already described with four dry cells. The current of 0.07 to 0.08 amp. ran for two to two and one-half hours and reduced half or more of the europium to the bivalent state. The electrolyzing circuit was now disconnected and sufficient solid potassium chloride was dissolved in the reduced solution to make the concentration of this salt exactly one molar. If this addition is made prior to the electrolysis several difficulties arise.

During the series of potential measurements requiring about one hour, a little oxidation of the bivalent europium by air took place. For this reason potentiometric readings for each of the alternate platinum electrodes in the reduced solution were made immediately before and after removal of a 5-ml. sample for titration. This sample was run into a small (measured) excess of 0.04 *N* iodine. The excess was titrated with thiosulfate a few minutes later. Following the second pair of potential readings 5 ml. of a solution of europium trichloride and potassium chloride was run into the reduced solution. The former solution had exactly the same composition as the latter excepting that the europium of the solution added was entirely in the trivalent form. The ratio of Eu^{+++} to Eu^{++} of the solution in the cell was thus increased by stages. Following this addition, the titration of the excess iodine was made.

The solution in the cell was now stirred well for a few minutes and another series of potential measurements and another analysis were made, etc.

The two consecutive readings for the alternate electrodes usually agreed within 0.1 millivolt while the pair made before drawing the sample differed from those afterward by about one millivolt. The mean of the four readings of a set and the time of drawing the sample are given in the following table.

After the measurements were completed the total europium concentration was found by reduction of four 5-ml. portions in the zinc reductor and titration with standard iodine. The potential of a platinum electrode in the Eu^{+++} and Eu^{++} solution with normal potassium chloride was calculated by the equation

$$E_0 = (V - 0.2805) + 0.05915\ (\log_{10} Eu^{+++}/Eu^{++})$$

V being the observed e. m. f. including the normal calomel electrode. The reaction is $Eu^{++} = Eu^{+++} + e$. The platinum electrode in the europium solution is charged negatively.

POTENTIAL OF THE Eu^{+++}, Eu^{++} ELECTRODE

Temp. 25°. Total Eu concn. 0.0900 Molar

Time, min.	E. m. f., v.	Molar concn. Eu^{++}	Molar concn. Eu^{+++}	E_0, v.
0	0.7100	0.0437	0.0463	0.4310
19	.7007	.0358	.0542	.4309
30	.6933	.0289	.0611	.4321
40	.6864	.0239	.0661	.4321
50	.6797	.0201	.0699	.4312
65	.6720	.0162	.0738	.4304
			Mean	.4313

Another set of similar measurements gave $E_0 = 0.4283$ volt.

In these experiments liquid potentials have not been entirely eliminated, but it is thought that they have been made quite small by reason of the preponderating concentration of potassium chloride in all solutions. The value found for E_0, about 0.43 volt, is one of the highest reducing potentials so far observed.[7] It is in good accord with the powerful reducing properties of europous solutions.

Europous Sulfate.—Progress in the work of isolation of europium by the europous sulfate method[1,4,5] is easily followed by titration of this salt with standard permanganate. In a typical case the sulfate was made from a chloride solution which showed but faintly the strongest absorption bands of neodymium in addition to those of europium. After being well washed on the filter with dilute hydrochloric acid and methyl alcohol and dried at 75°, portions of about 0.1 g. were covered with 30 ml. of 3 *N* sulfuric acid and titrated with 0.04 *N* permanganate, 0.6 to 0.8 ml. excess being added and the excess titrated with standard ferrous solution after the difficultly soluble europous sulfate had completely dissolved.

	I	II
$EuSO_4$ taken, g.	0.1113	0.1119
0.04 *N* $KMnO_4$, ml.	10.83	10.86
Purity of $EuSO_4$, %	96.6	96.3

It is possible to titrate the sulfate with iodine but the solid dissolves so slowly that the method is tedious.

Europous sulfate exists in two forms: (α) tufts of minute needles which are feathery and bulky; and (β) still smaller crystals, appearing nearly globular when highly magnified, of high density and settling to a very

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(6) All kindly loaned by Professor L. D. Roberts, Univ. of Southern California.

(7) "Int. Crit. Tables," Vol. VI, p. 332.

compact mass. The α-form is frequently obtained when a solution of europous chloride from a zinc reductor is run into a solution of magnesium sulfate or dilute sulfuric acid. It soon passes into the stable β-form. The latter is but slightly soluble in 3 *N* sulfuric acid, while the former is dissolved by acid of this concentration. The analyses quoted were of the β-form.

The dry β-form keeps surprisingly well. In one case a sample, kept in a corked vial, showed the same permanganate titer after two, sixteen and fifty-five days and but 2.8% less after one hundred and forty-three days. Another sample, known to contain some rare-earth contamination, showed a purity of 94.7% after sixty-four days. The resistance of europous sulfate to oxidation by air is doubtless in large measure due to its marked insolubility.

Europous sulfate can be oxidized by and dissolved in nitric acid.[4,5] It can also be oxidized by chlorine, bromine, bromic acid and other active oxidizing agents. When europous sulfate is boiled for a few minutes with a solution of one equivalent of sodium carbonate and 0.4 equivalent of sodium hydroxide it forms a yellow, compact, easily filtered carbonate (probably $EuCO_3$). The carbonate dissolves readily in most acids.

The Absorption Spectrum of Europous Chloride.—The chloride ($EuCl_2$) solution of 20 to 30% concentration has a greenish yellow color like that of a concentrated solution of chlorine. The absorption spectrum of this solution, in the visible range, differs in a remarkable way from one of the trichloride. It does not show any of the several bands of the latter.[8] Instead, below approximately 4480 Å. all visible light is absorbed. The exact maximum wave length at which complete absorption begins depends upon the concentration of the solution and the thickness of the layer. Characteristic results are obtained when 30 ml. of a 1.2 molar solution of europium trichloride is run through a zinc reductor and viewed in a 20-cm. tube. The spectrometer used was a Bausch and Lomb instrument Cat. no. 2700. The light was that of a 75-watt Mazda bulb. It thus appears that the shift of the valence electron in the change $Eu^{+++} \rightleftharpoons Eu^{++}$ is responsible for a profound change in the absorption spectrum.

Summary

1. New methods permit the electrolytic reduction of trivalent europium to bivalent in simple cells at 6 volts or less.

2. Solutions of bivalent europium do not show any of the bands of the absorption spectrum of the trivalent salts; instead, complete absorption of visible light occurs below 4480 Å.

3. The reduction potential E_0 of Eu^{++}, Eu^{+++} solutions is approximately 0.43 volt.

4. Dilute europous solutions are half oxidized by a rapid stream of air bubbles in about four minutes. Crystalline europous sulfate, $EuSO_4$, is quite stable in air.

5. Iodometric methods for the determination of europium are described.

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[8] If incompletely reduced the two strongest bands of Eu^{+++} may show faintly.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, NO. 368, AND THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, NO. 141]

The Vibrational Levels of Cyclopropane

BY GILBERT W. KING,[1] ROBERT T. ARMSTRONG AND LOUIS HARRIS

Cyclopropane has considerable interest stereochemically and from the point of view of the mechanics of vibration of polyatomic molecules. A unique assignment of frequencies to its normal vibrations is not possible from its Raman spectrum[2] alone; infra-red data, even of a semi-quantitative nature, would aid in such an assignment. Together, the two spectra permit an analysis of the fundamental modes of vibration of cyclopropane.

Infra-red Absorption.—The preparation and purification of the cyclopropane has been described in a previous paper.[3] The infra-red spectrum has been mapped in the following manner.

Region	Method of measurement	State of cyclopropane
I. 0.8 μ to 2.8 μ	Quartz monochromator. 1000 watt projection lamp. 15 mm. length quartz cell.	Liquid at −78°. Gas at 25° and 1 atm. pressure.
II. 0.8 μ to 1.1 μ	Hilger E1 spectrograph (Glass optics); also 21 ft. grating. 1000 watt projection lamp. 1 meter length cell, quartz windows.	Gas at 25° and 1 atm. pressure.

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[1] Present address, National Research Fellow, California Institute of Technology.

[2] L. Harris, A. A. Ashdown and R. T. Armstrong, THIS JOURNAL, **58**, 852 (1936).

[3] A. A. Ashdown, L. Harris and R. T. Armstrong, *ibid.*, **58**, 850 (1936).

Region	Method of measurement	State of cyclopropane
III. 3.3 μ to 10.0 μ	Low dispersion rock salt spectrometer. Nernst glower. 10 cm. length cell. Rock salt windows.	Gas at 25° and 10 mm. to 1 atm. pressure.

The observed infra-red bands and Raman frequencies (previously reported) are presented in Table I.

TABLE I

THE RAMAN AND INFRA-RED ABSORPTION SPECTRA OF CYCLOPROPANE

Raman (liquid) Cm.$^{-1}$	Intensity	Infra-red (gas) Cm.$^{-1}$	Intensity	Infra-red (liquid) Cm.$^{-1}$	Intensity
382	v. w.				
745	w.				
869	v. s.				
1022	m.	1020 ± 10	s.		
1191[a]	v. s.				
1437	m.	1425 ± 20	m.		
1454	m.				
1505	w.				
1873	v. w.	1800 ± 40	m.		
		2020 ± 40	m.		
2856	w.				
2953	w.	2950 ± 100	m.		
3013	m.				
3030	m.				
3079	m.				
		3580 ± 1%	m.		
		4200	m.		
		4450	s.		
				4760 ± 1%	m.
				4980	s.
		5160	w.	5130	s.
		5260	w.		
				5620	w.
		5950	s.	5930	s.
				6730	m.
		7040	m.	7090	m.
				7350	m.
				8060	w.
		9070 ± 0.2%	m.	9070	s.
				11,100	m.
		11,490 ± 0.2%	m.	11,800	w.

[a] 1191 cm.$^{-1}$ was the only Raman line observed from gas.

Selection Rules.—The symmetry of the molecule may be decided definitely from qualitative considerations. The manner of distribution of the twenty-one ($3\,N - 6$) fundamental frequencies of cyclopropane among the representations of the most likely symmetry groups is given in the following table, together with their infra-red (IR) or Raman (R) activity.

C_{3v}			C_{2v}			D_{3h}		
R, IR,	A_1	5	R, IR,	A_1	7	R,	A_1'	3
	A_2	2	R,	A_2	4		A_2'	1
R, IR,	E	7	R, IR,	B_1	5		A_1''	1
			R, IR,	B_2	5	IR,	A_2''	2
						R, IR,	E'	4
						R,	E''	3

C_{3v}.—This symmetry group requires twelve frequencies (seven of the twelve being doubly degenerate) active in both the Raman and infra-red spectra, which is not in agreement with our data.

C_{2v}.—This requires seventeen frequencies active in the infra-red, all of them also active in the Raman spectrum, totaling twenty-one different active fundamentals in the latter spectrum, again not in agreement with observation.

Furthermore, of the three groups given, C_{3v} and C_{2v} require strong Raman frequencies (the totally symmetrical A_1) to be active also in the infra-red. No absorption was detected in the region corresponding to the strongest Raman frequency, 1191 cm.$^{-1}$ (absorption was less than 5% with cyclopropane at one atmosphere pressure in a cell with an effective length of 10 cm.), so that these two symmetry groups are not further considered.

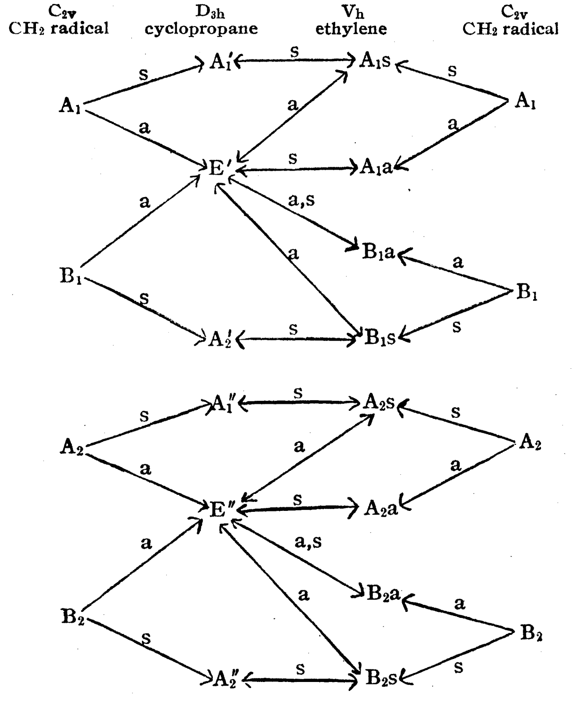
D_{3h}.—This requires six (four doubly degenerate) infra-red active fundamentals, and ten (seven doubly degenerate) Raman active frequencies, which is more compatible with the data. These frequencies may be identified by the following semi-quantitative considerations, pending exact perturbation calculations.

Symmetry Coördinates.—In general there is a correspondence of the representations of a symmetry group of a system and the representations of the symmetry groups of parts of the system, or system under perturbation. If all equivalent bonding energies are permitted to decrease simultaneously (*e. g.*, allow the three CH_2 groups to recede to a large distance yet preserve their geometrical relations) the symmetry of the (enlarged) molecule is unchanged. In the enlarged molecule the normal vibrations are such combinations of the nine orthogonal motions of the isolated radical CH_2 (3 vibrations, 3 rotations, 3 translations) as conform to the symmetry of the group D_{3h}. The fact that the symmetry operators of the combined system (C_3H_6), for example rotation through 120°, must carry any vibration of the enlarged molecule into a linear combination of the vibrations of the same level, indicates that the three isolated CH_2

groups must be vibrating in the same mode, all either in phase (s) or one of the three groups out of phase (a). A more accurate statement concerning the composition of systems from radicals is provided by the resolution of representations into those of component radicals. Table II correlates the representations of CH_2, ethylene and cyclopropane.

TABLE II

CORRELATION OF THE REPRESENTATIONS OF THE SYMMETRY GROUPS OF CYCLOPROPANE, ETHYLENE AND THE CH_2 RADICAL WITH CORRESPONDING RELATIONS FOR THE NORMAL VIBRATIONS



The corresponding relations hold for the actual vibrational states belonging to the various representations. These are described by vector models for CH_2 and $(CH_2)_3$ in Fig. 1.

Figure 1 illustrates the use of the above principles in determining the normal vibrations of cyclopropane from those of its component radicals, $3CH_2$'s. The nine (3 N) normal vibrations of a non-linear tri-atomic molecule (translations, T_z, T_h and $T_\perp$, and rotations, R_z, R_h and $R_\perp$, may be regarded as vibrations of zero frequency) are described by vector models in the center column of Fig. 1. These vibrations are perturbed by the coupling action of the other two CH_2 groups and each frequency (including the translations and rotations) combines anti-symmetrically (doubly degenerate, a-levels) or symmetrically (s-levels) to give the vibrations of cyclopropane as shown on the left and right of the figure, respectively. Similarly the vibrational levels of the symmetrical triangular C_3 molecule (Group D_{3h}), or of a constrained cyclopropane molecule, where the CH_2 groups are rigid, may be resolved into the levels of the actual cyclopropane molecule.

Assignment of Observed Frequencies to Normal Modes of Vibration

a. Carbon Interaction: (T_{zs} and $T_{\perp a}$).—Calculations based on central forces[4,5] of the frequencies of the constrained cyclopropane molecule identify the intense symmetrical vibration (labeled T_{zs} in Fig. 1) at 1191 cm.$^{-1}$ (properly inactive in the infra-red) and a doubly degenerate deformation frequency at 869 cm.$^{-1}$ (labeled $T_{\perp a}$ from its construction from CH_2 levels). The latter was beyond the spectral region (infra-red) investigated (see note 10 at end of paper).

b. CH_2 (Vibration) Interaction: $\sigma_{s,a}$; $\pi_{s,a}$; $\delta_{s,a}$).—The principles used in deriving the normal modes of vibration lead to further definite assignments. Each of the three normal vibrations of CH_2, σ, π, δ, should split slightly to form a- and s-levels of ethylene, and to almost the same degree to form the corresponding a- and s-levels of cyclopropane, in the same region of the energy scale. These frequencies can be identified more precisely by means of Mecke's Rule II.[6] The infra-red spectrum was not resolved enough to decide, by means of selection rules, which of the Raman frequencies (1505, 1437, 1454 and 2953, 3013, 3030 cm.$^{-1}$) are the a- and s-combinations of the δ_a and π_a levels. The doublets (1437–1454 and 3013–3030) may be the doubly degenerate levels δ_a and π_a whose degeneracy has been removed either by interaction of the angular momentum of the doubly-degenerate motions with that of pure rotation[6] (p. 125), or by resonance due to a slight difference in the C–C bonds requiring both components to be active in the Raman and infra-red spectra.

Dr. E. Bright Wilson, Jr., has kindly suggested that these doublets are more likely to be ascribed to accidental degeneracy of δ_s and 2 × 745 (leading to 1437 and 1454) and of π_s with 2 × 1505 (leading to 3013 and 3030). The frequency 745 cm.$^{-1}$ is probably to be assigned to $R_{\perp a}$ of repre-

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[4] S. Bhagavantam, *Indian J. Phys.*, **5**, 73 (1930).

[5] R. Lespieau, M. Bourguel and R. Wakeman, *Bull. soc. chim.*, [4] **51**, 400 (1932).

[6] Eucken-Wolf, "Hand- und Jahrbuch der chemischen Physik," [9] II, 1934, p. 338.

TABLE III

Type	$(CH_2)_2O$ ν cm.$^{-1}$	$(CH_2)_2O$ $\nu_a^2 - \nu_s^2$	$(CH_2)_2$ ν cm.$^{-1}$	$(CH_2)_2$ $\nu_a^2 - \nu_s^2$	$(CH_2)_2$ Calcd.	$(CH_2)_3$ ν cm.$^{-1}$	$(CH_2)_3$ $\nu_a^2 - \nu_s^2$	$(CH_2)_3$ Calcd.
σ_a			3107			3079		
				+0.234	+0.2			
σ_s	3047		3069					
π_a	2970		2988			2957		
		−0.227		−0.186	−0.1		−0.461 to −0.368	−0.4
π_s	3008		3019			3013–30		
δ_a			1444			1505		
				+0.283	+0.3		+0.200 to +0.151	+0.2
δ_s			1342			1437–54		

sentation E″, as indicated below. Thus its overtone belongs to E′ and A′, and so may couple with δ_s of A′, both frequencies being active in the Raman, and the component with symmetry *E′* of the overtone being active in the infra-red. An analogous situation obtains for the π_s level. Much greater resolution than was used here will be required to decide whether one or both components of the doublets appear in the infra-red. The relative positions of the a- and s-levels of cyclopropane and ethylene oxide[7] are the same according to this assignment, as shown in Table III. The separations of the a- and s-levels are computed assuming that the coupling of the CH_2 radicals is due predominantly to central forces between the atoms of one radical and those in the other, whose magnitudes are estimated from the types T_{zs}, R_{ha} and $R_{\perp a}$. (No assumptions are necessary regarding the potential function within the CH_2 radicals, other than a rough estimate of the amplitudes of motion in each vibration.) Since the results for ethylene agree in order of magnitude and sign with observation (Table III) some weight may be given to the values obtained for cyclopropane.

c. **Hydrogen (CH_2 Rotation) Interaction:** ($R_{ha, s}$; $R_{za, s}$; $R_{\perp a, s}$).—All the frequencies of cyclopropane except those that are a and s combinations of the *rotational* modes of the CH_2 radical, have now been assigned and correlated. Of these R_{ha} (of C_3H_6) is to be ascribed to 1022 cm.$^{-1}$, for this is the only vibration of this group that is active in both the infra-red and Raman spectra. Another frequency of this group, $R_{\perp s}$, is also unique since it is the only one predicted to occur in the infra-red alone. The band at 1800 cm.$^{-1}$ was observed only in absorption; but since this is a high frequency for such a (fundamental) mode, it is probably a combination frequency and $R_{\perp s}$ probably lies in the unexplored region < 1000 cm.$^{-1}$. The only permitted combinations and harmonics of appreciable intensity active only in

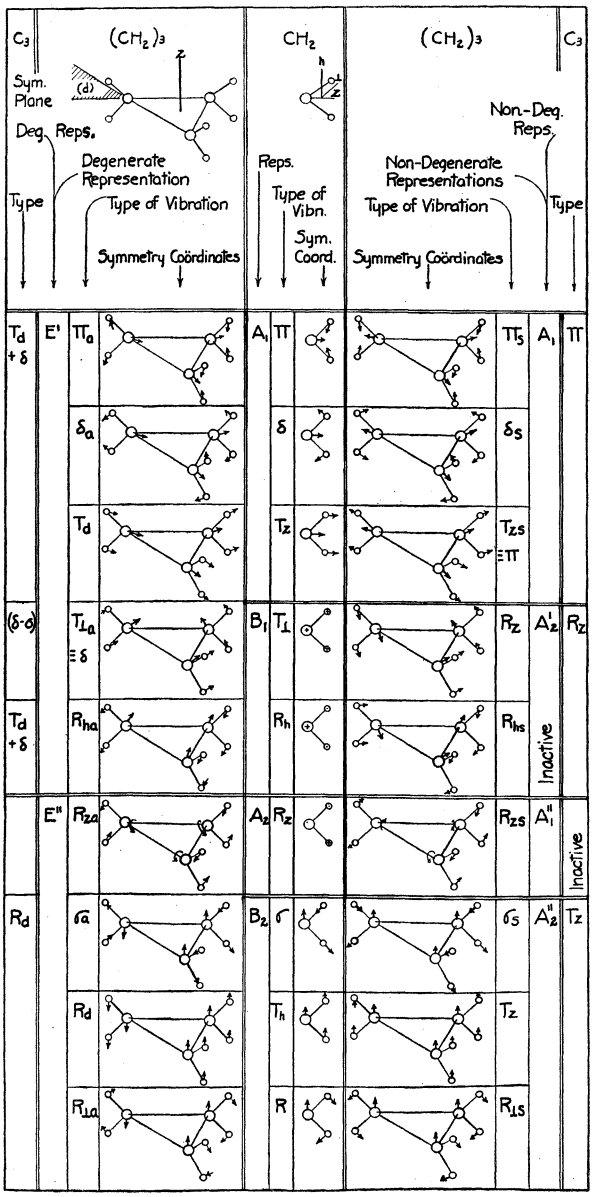

Fig. 1.—Symmetry coördinates and derivation of the fundamental vibrational modes of cyclopropane.

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[7] B. Timm and R. Mecke, *Z. Physik*, **97**, 221 (1935).

absorption are $T_{zs} + R_{\perp s}$ (giving $R_{\perp s} = 1800 - 1191 = 609$ cm.$^{-1}$ + anharmonicity) and the combination $R_{zs} + R_{hs}$. The latter modes should be inactive in both spectra as fundamentals.

The unassigned lines in the Raman spectrum (382, 745 and 1873 cm.$^{-1}$, all of low intensity) are attributed to the two remaining fundamentals, $R_{\perp a}$ and R_{za}. The following tentative assignment is made $R_{\perp a} = 745$ cm.$^{-1}$, $R_{za} = 382$ cm.$^{-1}$, and $R_{ha} + T_{\perp a} = 1873$ cm.$^{-1}$.

Further Confirmation of Assignments.—As indicated in Table II, the anti-symmetrical levels of cyclopropane are composed from the anti- *and* symmetrical levels of ethylene. The anti-symmetrical levels of cyclopropane are, to a first approximation, the mean of the corresponding (squared) frequencies of ethylene

$$\underbrace{\nu_s^2 + \nu_a^2}_{\text{Ethylene}} = \underbrace{2\nu_a^2}_{\text{Cyclopropane}}$$

This formula holds quite well for all the levels except R_{za} (giving 500 cm.$^{-1}$ instead of 382 cm.$^{-1}$) and $R_{\perp a}$ (950 cm.$^{-1}$ instead of 745 cm.$^{-1}$).

Similarly the vibrational modes of cyclopropane can also be constructed from the motions of the "radicals," C_3 and H_3. Due to much larger perturbation here the levels more closely related to CH_2 levels are split to such an extent that this composition is purely formal. However, the π and δ (doubly degenerate) levels of C_3 (whose frequency ratio based on central forces[4,5] would be $\sqrt{2}$) are only slightly perturbed to form T_{zs} and and $T_{\perp a}$ (ratio 1.372) and δ_s and R_{ha} (ratio 1.476). The motions of the hydrogen planes (π and δ) are similar in each pair, but are in opposite phase relative to the carbon motions, accounting for the four per cent. perturbation in each direction from $\sqrt{2}$. These ratios confirm the previous method of assignment and may be extended to modes involving only π and δ vibrations of the hydrogen rings. It is interesting to note that the ratio of 1022 to 745 is also 1.372, but it is difficult to attach significance to this.

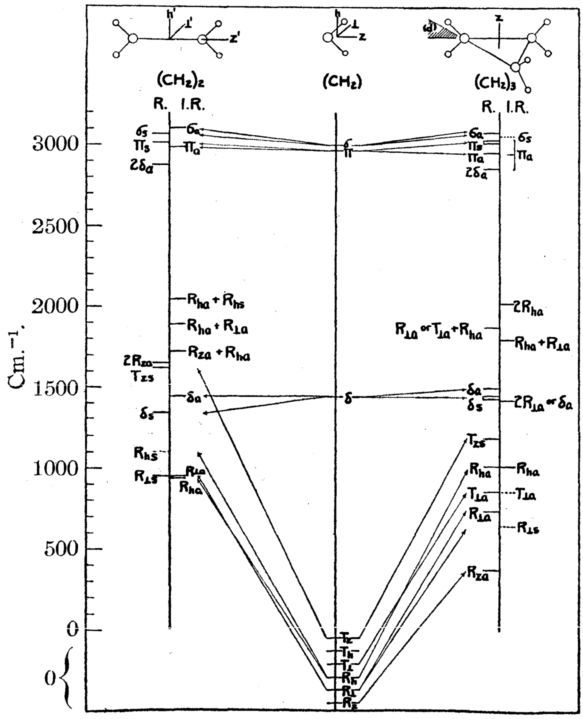

Fig. 2.—Relation of the frequencies of the CH_2 radical, ethylene and cyclopropane.

Acknowledgment

We wish to thank Professor Hoyt C. Hottel for the use of the rock-salt spectrometer.

Summary

The fundamentals of cyclopropane have been identified by group theoretical correlation with the frequencies of ethylene[8] and of the CH_2 radical.[9] The results are summarized in Figure 2. The frequencies predicted but not observed here ($T_{\perp a}$, $R_{\perp s}$) are indicated by dotted lines.[10] Such semi-quantitative analysis should act as a guide in the deduction of a suitable type of potential function for these hydrocarbons.

The measurements reported for the infra-red absorption bands in the 0.8 μ to 3.6 μ region (listed in Table I) are inadequate to justify an assignment of the combination frequencies.

CAMBRIDGE, MASS. RECEIVED MARCH 20, 1936

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[8] L. C. Bonner, THIS JOURNAL, **58**, 34 (1936).

[9] C. B. B. M. Sutherland and D. M. Dennison, *Proc. Roy. Soc.*, **148**, 258 (1935).

[10] Since this paper was submitted we have learned through the kindness of Professor E. F. Barker, of the University of Michigan, of some measurements of the infra-red absorption of cyclopropane made there by Doctor W. W. Sleator. He observed the following: a strong unresolved triplet at about 675 cm.$^{-1}$, another similar one at 870 cm.$^{-1}$, a strong narrow peak at approximately 1400 cm.$^{-1}$ and several weaker ones at higher frequencies, one near 1437 cm.$^{-1}$. Absorption in the 3 μ region was strong, but was not completely resolved.

Infra-red absorption at 870 cm.$^{-1}$ confirms the assignment of T_{zs} and $T_{\perp a}$ given above. Absorption at 675 cm.$^{-1}$ is probably due to $R_{\perp s}$ (predicted at 609 + cm.$^{-1}$).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

A Study of the Preparation and Quantitative Determination of Elementary Fluorine[1]

BY WILLIAM T. MILLER, JR., AND LUCIUS A. BIGELOW

A program of research now in progress in this Laboratory[2] deals with the action of fluorine upon organic compounds. Until recently, the element has been prepared by the electrolysis of molten potassium bifluoride, in an open generator of the Mathers type, and the fluorine produced has been regarded as fairly pure, in common with the views of others.[3] However, it was found that the gas was not completely absorbed by potassium iodide solution, the residue being largely oxygen; and also that it was partly condensable at the temperature of liquid air, which indicated that it contained a good deal of oxygen fluoride. The formation of these impurities was undoubtedly due to the presence of water in the molten electrolyte. The purpose of the present paper is to set forth the general conditions necessary for the production of pure fluorine, and to describe a generator embodying these principles, together with apparatus and methods for analyzing the product.

Apparatus and Methods

As the result of a rather careful survey of the literature,[4] we have considered, first, that fluorine must be generated free from oxygen and other impurities, rather than subjected to later purification; second, that the electrolysis of molten potassium bifluoride is the most promising and convenient method available for the purpose; and finally that the essential requirements for the formation of a pure product are an efficiently closed generator and an anhydrous electrolyte.

We have designed a new closed generator of the U-type, in contrast to the V-type described by Dennis, Veeder and Rochow.[5] It was constructed of heavy cast nickel and is illustrated in Fig. 1. It was strong, efficient and durable, as well as being suitable for pressure work. Nickel was chosen because it was resistant at operating temperatures, and formed a persistent, insoluble coating of nickel fluoride during the electrolysis. The apparatus was cast with flanged ends, and the caps were made by turning and drilling cast nickel forms. Lead washers were placed between the turned surfaces of the caps and the U-tube, and the connections made gas tight and rigid by drawing these parts together with heavy clamps, consisting of 13-mm. steel plates, provided with six 13-mm. steel bolts.

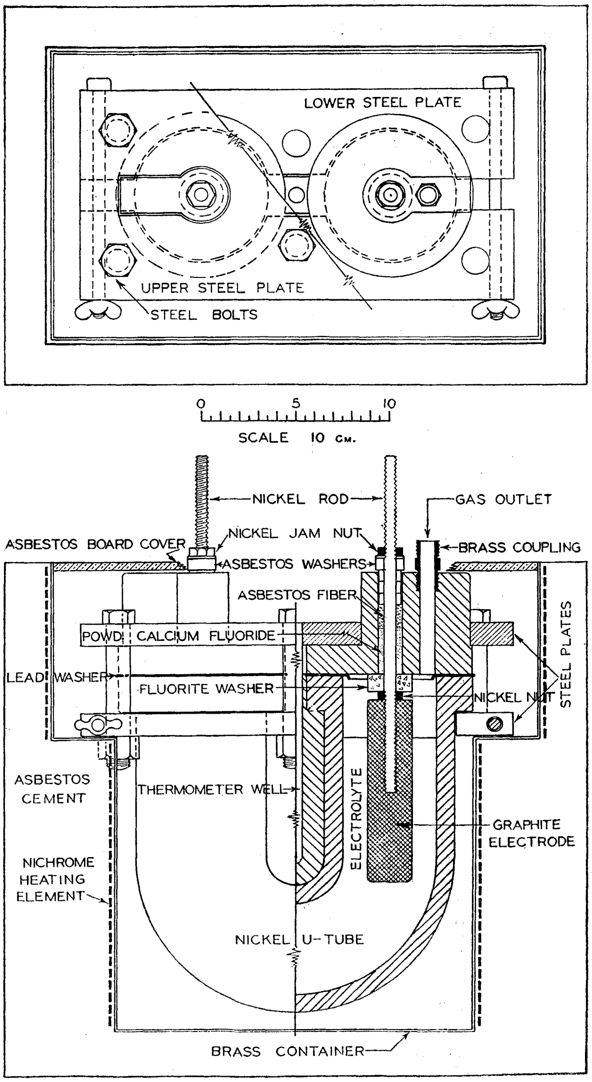

Fig. 1.—The fluorine generator.

Graphite electrodes were used, and threaded directly onto 6-mm. nickel rod supports. These, in turn, were centered in 13-mm. holes in the caps, and were held in place, made gas tight, and also insulated by means of a cement prepared from ground fluor spar and sodium silicate. Handles were made from 6-mm. iron rod, in the form of rectangles, which fitted under the ends of the steel clamp plates, and were folded and grasped together above the generator.

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(1) This paper is abstracted from the Doctorate thesis of William T. Miller, Jr., presented to the Graduate School of Arts and Sciences of Duke University in June, 1935.

(2) Previous papers, THIS JOURNAL, **55**, 4614 (1933); **56**, 2773 (1934).

(3) Simons, *ibid.*, **46**, 2175 (1924).

(4) The leading references describing the work upon which the following conclusions have been based are: (a) purification, Ruff and Menzel, *Z. anorg. Chem.*, **211**, 204 (1933); Ruff, *Z. angew. Chem.*, **46**, 739 (1933); (b) preparation, Ruff, "Die Chemie des Fluors," Julius Springer, Berlin, 1920; Lebeau and Damiens, *Compt. rend.*, **181**, 917 (1925); Ruff, *Z. angew. Chem.*, **47**, 480 (1934); (c) bifluoride melt hygroscopic, Fredenhagen and Krefft, *Z. Elektrochem.*, **35**, 671 (1929); Fredenhagen and Cadenbach, *Z. anorg. allgem. Chem.*, **178**, 289 (1929).

(5) Dennis, Veeder and Rochow, THIS JOURNAL, **53**, 3263 (1931).

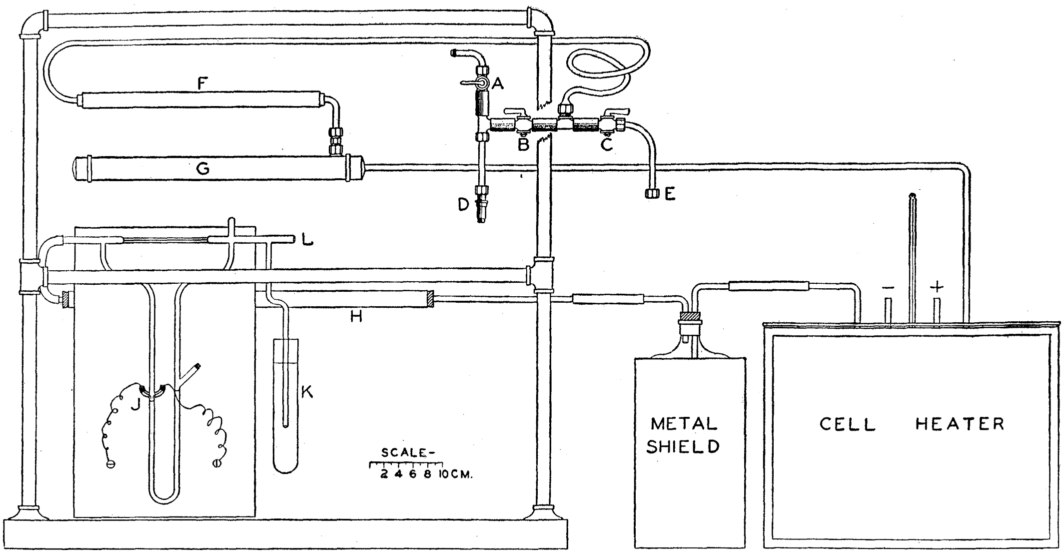

Fig. 2.—The apparatus assembly.

The construction of the heater is shown in Figs. 1 and 2. It consisted, essentially, of a brass container wound with a nichrome wire heating coil having resistance of 20.0 ohms. This unit was packed into an asbestos board box with dry asbestos cement hardened at the surface. The generator was placed in the heater in such a manner that the caps and couplings were kept sufficiently hot to fuse the low-melting sublimate from the electrolyte.

A special apparatus was designed to dehydrate the charge. It consisted essentially of a vertical copper pipe, approximately 48 × 8.3 cm., closed at the lower end, wound with nichrome wire (11.5 ohms), and insulated with asbestos cement. The top was closed by a cover, bolted on, using a lead washer, and carrying a copper exit tube and a thermometer well. From the bottom of the apparatus there extended a length of 13-mm. (i. d.) copper tubing, in the form of a spout, into the upper horizontal surface of which was soldered a 6-mm. brass coupling. In this apparatus, dry air, and finally fluorine gas, were passed through the salt, at an elevated temperature, entering from below. The salt was allowed to stand in contact with the fluorine for some time,[6] to complete the dehydration. Finally, by raising the temperature of the oven to 245° the salt was liquefied, and under these conditions ran down into the uninsulated spout, where it froze. With this arrangement, the dry electrolyte could be transferred very neatly to the generator by placing the latter, in its heater, and at about 260°, directly beneath the spout, and then melting the frozen salt with a Meker burner. The molten charge then flowed rapidly into the generator, which was immediately closed, thus ensuring a minimum exposure of the bifluoride to air and moisture in the process.

The set-up of apparatus which has been used for generating and handling the fluorine is illustrated in Fig. 2. The copper tubes G and H were filled with powdered sodium fluoride, which has been shown[5] to combine quantitatively with hydrogen fluoride. The tube F was filled with copper oxide wire, which, while not affected by the fluorine, would decompose quantitatively any ozone which might possibly be present. The container in the metal shield was a surge bottle in the hydrogen line, leading to a flow meter, which served also as an important safety device. It was arranged by means of a relay so as to sound an alarm whenever the flow of hydrogen was interrupted during the time that the apparatus was in operation. This avoided the danger of building up high pressures inside the generator by continuing the electrolysis with the exit tubes obstructed. However, by closing the hydrogen outlet L with a rubber cap and passing the gas through K, it was possible to apply any desired small pressure to the cathode chamber of the generator, in order to compensate for any such which might be built up in the anode compartment and the fluorine line.

The simplest, reasonably accurate analytical method for determining the efficiency of the generator consisted in allowing the fluorine produced in a measured time, at a definite current density, to react with a potassium iodide solution, and then to titrate the liberated iodine in the usual way. In the absence of oxygen fluoride, this method may be expected to give good results. No apparatus has been described in detail for carrying out this procedure, however, and the set-up which we have used is illustrated in Fig. 3. The U-tube was coated completely on the inside with a thin layer of ceresin wax, which was shown not to be attacked significantly by diluted fluorine (50% in air) at 0°. The rapid counter current flow of the solution produced by the screw pump promoted the complete absorption of the gas, without introducing any appreciable head of liquid. Gas samples, suitably diluted with air, were taken directly from the fluorine line through a slip joint, sealed with ceresin wax, at B. The 50-cc. bulb provided at C effectively prevented splashing, and the mercury seal made it possible to collect any unabsorbed gases quantitatively at A.

The precise determination of the fluorine contained in a gas sample, followed by the analysis of the residual gas,

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(6) Henglein and Stauf, U. S. Patent 1,914,425 (1933).

proved to be no simple problem. However, we have found experimentally that metallic mercury, when shaken, absorbed fluorine quantitatively. Also, we have observed that no significant absorption of the gas took place when it was stored for six hours at room temperature in a Pyrex glass bulb, and confined by means of mercury in a tube of small diameter. This was due to the perfect protective coating formed at the undisturbed surface of the metal, and to the fact that fluorine did not react with the glass under such conditions.

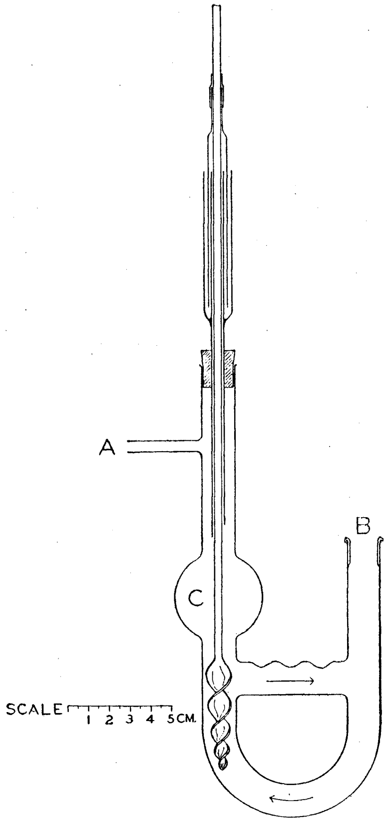

Fig. 3.—Absorption tube for the efficiency measurements.

Accordingly, a Pyrex glass buret, of the constant volume type, using mercury as the absorbent, has been designed, and is illustrated, with the jacket removed, in Fig. 4. Perhaps the most significant feature of this apparatus was the device for sealing in the fluorine sample with mercury at A and C. The arrangement at H and K served as a means of reference, so that manometer readings could be corrected for different positions of the buret, and also as a necessary bubble trap. The most satisfactory way to make clear the advantages and uses of the other connections shown is to describe at this point, in some detail, the method of collecting and measuring a sample of fluorine.

The buret was clamped in position, and the manometer attached at M, Fig. 4, using a little glycerol to prevent this connection from sticking. After lowering the level of the mercury in the manometer about 760 mm. below M, rubber caps were placed over tubes A, B and C, and the apparatus pumped out through J with an oil pump. Stopcocks D and G were both opened alternately in the two possible ways, in order to exhaust their bores as well as the rest of the apparatus, which was rinsed several times with dry air. Stopcock D was then closed and mercury admitted through G and its connecting tubes until the level of the liquid approximately reached F. After closing H and G the pump was shut off and the leveling bulb raised. The vacuum in the apparatus was then released through A or C, and the relative positions of K and F determined on the manometer scale by adjusting the mercury level to the respective marks, with H open. The tube B was filled about three-fourths full of mercury, which was freed from all adsorbed gases by gently warming and tapping the tube, which was exhausted at the same time from above. After again exhausting the apparatus, mercury was allowed to pass through D, in such a way as to fill the capillaries to the bottoms of both U-tubes as shown below C (Fig. 4). Similarly, E and the central tube leading up from F were filled with mercury, as shown in the figure, and the vacuum in the apparatus was then released with dry air. Before collecting the sample to be analyzed, the anode tube system from the generator was swept out for two hours, with a gas flow corresponding to a 5 amp. current. Then capillary C (Fig. 4) was slipped into the Monel metal fitting D (Fig. 2), the connection wrapped tightly with thin copper foil, and painted on the outside with ceresin wax. Fluorine was then passed through the pipet at the usual 5 amp. rate for one hour. The brass stopcock A (Fig. 2)

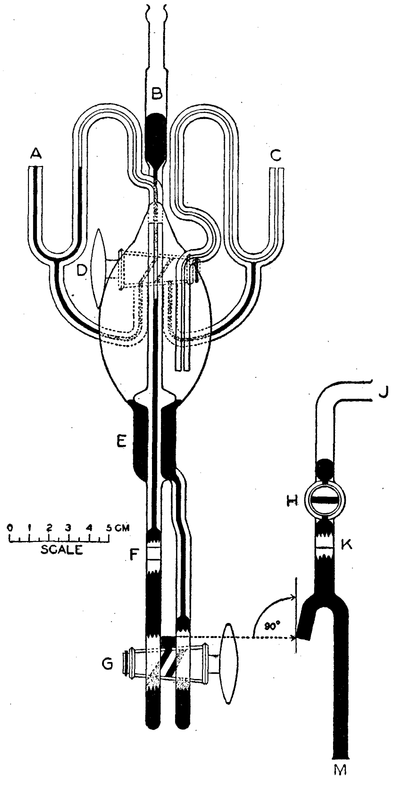

Fig. 4.—Gas buret for the quantitative estimation of fluorine.

was then opened, to by-pass the fluorine, and mercury allowed to fill the outlet U-tube of the absorption apparatus through D (Fig. 4), to the position shown at A in this figure. Then A was warmed with a small flame and a drop of sealing wax melted across the end of the tube and the mercury, taking care to exclude any air bubbles. After allowing the sample to stand in this way for five minutes, the brass stopcock B (Fig. 2) was closed, C opened, and the inlet U-tube likewise filled with mercury, disconnected at D (Fig. 2), and sealed. By passing heated air through the system in place of the generator gas, this method was shown experimentally to give a sample in the buret at the water-jacket temperature, and at atmospheric pressure, after the five-minute period of standing.

When the seals were completely hard, the buret was held in the hands, tilted to an angle of about 45°, with stopcock D leaning backward, and shaken so as to swirl the mercury in a thin film over the back portion of the bulb. A coating was formed at first, which quickly darkened as the fluorine reacted with it. The shaking was continued at short intervals, until this film remained bright for five minutes. The end-point was sharp, and signified the complete absorption of the fluorine. The pressure was then read at F, and the value thus obtained correlated with the atmospheric reading by correcting it to the corresponding position of K (Fig. 4) on the manometer scale.

To remove the residual gas from the pipet, mercury was admitted through G, until the pressure inside the bulb was approximately atmospheric. Then the tube B was connected by means of a section of 1-mm. capillary tubing, to a gas analysis apparatus similar to that described by Ambler.[7] The air was displaced from the tube by passing mercury out through the inlet capillary of the absorption apparatus through D and B. The residual gas was finally led out through the outlet capillary, also through D and B, into the Ambler apparatus, and analyzed in the usual way for carbon dioxide, oxygen and inert constituents.

Discussion of the Results

The new generator, set up and connected as described above, gave excellent results. It was easy to charge, quiet and steady in operation, and gave a closely reproducible product. The unit stood up very satisfactorily in service, being hardly at all corroded after five hundred hours of operation. The current efficiency measurements obtained showed a variation from 89–61%, falling off somewhat with time of electrolysis. The current was measured to 0.5%, the titration to about 0.2% and the time to about 0.3%, making a total of 1%. The error due to pressure changes was negligible. However, it should be noted that when the fluorine from the generator was passed into concentrated neutral potassium iodide solution, some hydrogen ion was formed, presumably due to the direct action of the halogen on the water, and to the extent of about 3% of the oxidizing value of the sample, under our operating conditions. According to Cady[8] when fluorine reacted with cold neutral water, oxidizing agents capable of liberating iodine were formed to the extent of 70% of the halogen absorbed. From this it was indicated that in our work the loss in oxidizing value from this cause should not exceed 0.30×3 = approximately 1%. Consequently, the maximum total error in the efficiency measurements was considered to be not over 2.5%.

The purity of the fluorine generated, as measured by means of the mercury absorption buret described above, varied from 94 to 99% by volume, according to the age of the charge, and its initial moisture content. When the potassium bifluoride was finally dried with fluorine gas, the quality of the product was improved significantly. The best sample measured, prepared from an electrolyte which had been dried in this way, contained 99% fluorine, 0.4% oxygen, 0.2% carbon dioxide plus carbon oxyfluoride, and 0.4% inert gas, presumably carbon fluorides. The end-point of the absorption was sharp, as indicated by the appearance of the mercury. The principal experimental error of this method occurred in making the pressure readings, each of which could be observed to within ±0.2 mm., leading to a possible maximum error of 0.8 mm. This could affect the fluorine value by about ±0.15%, although it was more than likely that the errors would be at least partially compensating. Any variations due to temperature or pressure at the time of sampling, or volume changes due to the formation of mercury fluoride in the buret, have been shown to be entirely negligible. The values obtained for the composition of the residual gas were probably quite accurate, in terms of the total sample, because of the comparatively small portion of the latter which they represented. It should be pointed out, of course, that serious errors in all of these values would have resulted if the gas had contained any significant amounts of oxygen fluoride, which reacted slowly with mercury, with the evolution of oxygen.

From all of these considerations, it was clear that the closed generator described above was dependable, convenient, and yielded a closely reproducible product of a proven high degree of purity.

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[7] Ambler, *Analyst*, **54**, 517 (1929).

[8] Cady, THIS JOURNAL, **57**, 246 (1935).

Experimental Part

The Preparation of Fluorine.—One kilogram of Merck purified potassium bifluoride, free from chloride and sulfate, was placed in the drying oven already described, and the lower opening of the spout closed with a rubber stopper. Then a current of dry air at reduced pressure was drawn through the salt at 150°, and at a rate of about 1.5 liters per hour, for twenty-four hours. After this, fluorine gas was passed into the oven from below until it issued from the top, and the salt allowed to stand in contact with the halogen for twelve hours at 150°. This treatment was repeated twice more with fresh fluorine. Then the bifluoride was melted in the oven by heating it to 245°, and transferred to the generator in the manner already described.

A preliminary electrolysis for one hour at 3 amp., and one-half hour at 5 amp. was carried out, in order to form a good insulating coating on the inside of the U-tube, and after this the generator was connected with the system shown in Fig. 2. It would then produce fluorine smoothly, either continuously or otherwise, for about 125 ampere-hours. Under normal operating conditions at 250°, a current of 5 amperes corresponded to a potential drop across the generator of 18–20 volts, and to a gas flow of approximately 2 liters per hour. In operating the unit, the safety alarm already mentioned was used always, and care taken to avoid any pressure changes which might force the molten electrolyte into either of the outlet tubes. Also between runs, the apparatus was maintained at 175°. It should be noted, in addition, that according to Fredenhagen and Cadenbach[4c] the exhausted electrolyte may be regenerated by treating it with anhydrous hydrogen fluoride, which was readily absorbed by the salt. However, we have not employed this technique up to the present time.

Current Efficiency of the New Generator.—The system was swept out with fluorine by operating the generator for one hour at 5 amp., with A and B closed, C open and E connected to a glass tube extending just under the surface of concentrated sulfuric acid. Meanwhile, the absorption apparatus was charged with 34 cc. of a 50% solution of potassium iodide in water, and attached to the system at D, by means of a metal sleeve, painted on the outside with ceresin wax. It was then surrounded by a small ice-bath, and rigidly clamped to avoid vibration. A right-angled glass tube was connected at A (Fig. 3), and arranged to lead the outlet gases through a little potassium iodide solution, in order to test the completeness of the absorption, although this was always practically quantitative. The stirrer was started at high speed, A (Fig. 2) was opened, and a slow current of air drawn in by applying a slight suction to the supplementary trap, in such a way that the generator gas would be diluted with about twice its volume of air. To do this the system was kept under a pressure of approximately 1–1.5 mm. of mercury less than atmospheric. Then the current was adjusted to a flow of precisely 5.00 amp., the exact time noted and the two stopcocks B and C turned simultaneously, the one on and the other off. The absorption was run for exactly fifteen minutes and was discontinued by again turning B and C simultaneously. The solution was finally washed out of the apparatus and an aliquot portion titrated with sodium thiosulfate in the usual way. The results obtained have been summarized in Table I.

TABLE I

THE CURRENT EFFICIENCY OF THE NEW GENERATOR *vs.* THE TIME OF THE ELECTROLYSIS

No.	Time of electrolysis to start of measurement Hrs.	Min.	Time interval between measurements Hrs.	Min.	Temp. of the electrolyte, °C.	Current eff., %
A-1	1	57	..	..	250	87.1
B-1	1	0	..	..	238	82.1
B-2	8	0	7	0	251	68.5
B-3	15	15	7	15	250	65.2
B-4	20	0	4	45	252	63.5
C-1	2	35	..	..	249	89.3
C-2	8	40	6	5	249	74.8
C-3	19	25	10	45	260	75.5
C-4	23	37	4	12	263	61.4

Analysis of the Gas Produced by the New Generator.—The system was set up as outlined above, and the mercury absorption buret attached at D (Fig. 2). The manipulation has already been described in detail, and the results obtained, including the analyses of the residual gas, are summarized in Table II.

TABLE II

COMPOSITION OF THE GAS PRODUCED BY THE NEW GENERATOR *vs.* THE TIME OF ELECTROLYSIS

No.	Time of electrolysis before sampling Hrs.	Min.	Temp., of electrolyte, °C.	% by volume of F_2	CO_2	O_2	Inert
A-1	11	30	265	95.4	1.1	2.2	1.3
B-1	16	30	250	94.8	0.71	3.7	0.79
C-1	25	0	260	94.4	0.63	2.8	2.17
D-1	7	55	249	97.1	0.97	1.6	0.43
D-2	18	50	256	98.8	..	..	..
E-1	8	25	251	97.4	1.3	0.98	0.32
F-1	3	30	247	96.5	1.8	1.4	.30
F-2	23	20	257	99.0	0.22	0.38	.40

The procedure for drying the charge with fluorine was introduced just before making run D-1, and the resulting improvement is clearly obvious.

Summary

1. A generator suitable for producing pure fluorine has been described. It consists of a heavy nickel U-tube, tightly closed to the air, and proved to be very efficient.

2. A novel apparatus for the quantitative determination of fluorine by absorption in metallic mercury has been designed. This has made possible a precise estimation of the constituents of the gas produced by the new generator.

3. A detailed procedure for the preparation of fluorine of known purity has been described for the first time. The product was found to contain 94–99% of the halogen.

DURHAM, NORTH CAROLINA RECEIVED MARCH 9, 1936

[CONTRIBUTION NO. 523 FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Interatomic Distances in Orpiment, Realgar, Sodium Sulfantimonate Enneahydrate, and Calcium Mercuric Bromide[1]

BY WILLIAM V. MEDLIN

The method of direct determination of radial distribution of atoms from x-ray photographs was first used by Debye and Menke,[2] who applied it to mercury as an example of a monatomic liquid substance. It was extended by Gingrich and Warren[3] to solid substances, both crystalline and amorphous. In this field it has been found to be quite useful in determining distances between heavy atoms as a preliminary step in the determination of crystal structures, and in studying the bonding between atoms without determining complete structures. With the latter purpose in view I have applied the method to orpiment, realgar, sodium sulfantimonate enneahydrate, and calcium mercuric bromide. In all cases an approximate form of the method was used, in which visual estimates of the intensities of the lines of the powder photograph replaced the absolute intensities required by the formula, thus making impossible a quantitative measurement of the scattering power of the atoms concerned. The distances obtained by the rough treatment, however, are quite reliable, as shown by the fact that reasonable changes in the estimates of the intensities do not alter appreciably the positions of the peaks in the resulting distribution curves.

The method of treatment was the same as that used with diphenyliodonium iodide in a previous work.[4] The samples were all mounted with collodion on the outside of fine tubes of low absorbing glass; the radiation used was the Kα line of copper, obtained by passing copper radiation through nickel. The estimated intensities of the lines on the resulting photographs were multiplied by a small arbitrary factor, $e^{-B\sin^2\theta}$ and used directly as I_i in the formula

$$4\pi r^2\rho(r) = 4\pi r^2\rho_0 + \frac{2r}{\pi}\sum_{i=1}^{\infty} s_i I_i \sin s_i r$$

where $s = (4\pi \sin \theta)/\lambda$ and θ is one-half the angle of scattering. ρ_0 is a constant proportional to the number of scattering electrons per unit volume; its value is not known if absolute values of the intensities are unknown. The curves shown in this article do not include this term.

Orpiment and Realgar

Orpiment and realgar are naturally occurring sulfides of arsenic; the stoichiometrical formula of the former is As_2S_3 and that of the latter AsS. Both are monoclinic; measurement of the layer lines on a rotation photograph of orpiment gave b = 11.41 ± 0.05 Å. The axial ratios of orpiment are $a:b:c = 0.5962:1:0.6650$ with β = 90°41′.[5] In orpiment the coördination numbers of arsenic and sulfur can be three and two, respectively, with each arsenic atom bonded to three sulfur atoms and each sulfur bonded to two arsenic atoms. If the same coördination numbers are to prevail in realgar there must be As–As bonds, with each arsenic atom bonded to another arsenic and two sulfur atoms. The normal As–As distance is 2.42 Å., and the As–S distance should be 2.25 Å., from the corresponding covalent radii.[6] We may expect that application of the radial distribution method will disclose those bonds that exist.

Powder photographs of the two substances are quite different in arrangement of their lines; their similarity lies in the fact that the strongest lines of both patterns occur at approximately the same scattering angles. We see from Fig. 1, calculated with the use of 45 and 74 powder lines, respectively, that the resulting radial distribution curves are alike in the interesting region with r less than 5.5 Å. In the case of orpiment the first small peak occurs at r = 2.24 Å., the second peak at 3.46 Å., and a third at 4.39 Å. In the curve for realgar the first peak is at 2.16 Å., the second at 3.54 Å., and the third at 4.52 Å. Only the first peak in each case may be attributed to two atoms that are bonded together; the position of the peaks is correct for the As–S separation. In realgar a peak representing the As–As bond should be one-half as important as the As–S peak, since there must be four As–S bonds for each As–As bond, and the atomic number of arsenic is approximately twice that of sulfur. Hence if there

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[1] Original manuscript received February 20, 1936.

[2] Debye and Menke, *Physik. Z.*, **31**, 419 (1930).

[3] Gingrich and Warren, *Phys. Rev.*, **46**, 368 (1934).

[4] Medlin, THIS JOURNAL, **57**, 1026 (1935).

[5] Groth, "Chemische Kristallographie," Engelmann, Leipzig.

[6] Pauling and Huggins, *Z. Krist.*, [A] **87**, 205 (1934).

are As–As bonds at 2.4 Å. we might observe that a separate peak exists to represent it or that a single peak occurs at a value of r somewhere between the As–S and As–As separations, and closer to the former. Actually the observed peak is at a slightly smaller value of r than expected.[7]

If in orpiment we assume coördination numbers of three and two, respectively, for arsenic and sulfur we must attribute the first peak to the As–S bond and the second peak to unbonded As–As interaction with the x-ray beam. On this basis we can calculate for the bond angle for sulfur the value 97°14′. The third peak represents a distance more than twice that between sulfur and arsenic, and thus it cannot represent the nearest S–S distance. This distance must then be approximately 3.4 Å. and the arsenic bond angle approximately that of sulfur. The comparatively low scattering power of sulfur makes measurement of the S–S distance much less reliable and increases the reliability of the As–As distance obtained. A similar calculation for realgar gives the value 102°32′ for a bond angle, perhaps the average for sulfur and arsenic.

Sodium Sulfantimonate Enneahydrate (Schlippe's Salt)

Sodium sulfantimonate enneahydrate, $Na_3SbS_4 \cdot 9H_2O$, was treated by this method, using 86 powder lines, with the result shown in Fig. 1. The first peak occurs at 2.26 Å., and must be attributed to the Sb–S interaction as being by far the most important at this small distance. The second peak is found at r = 4.31 Å.; this is presumably an average S–S distance, with perhaps other distances involving atoms of smaller atomic numbers also contributing, unresolved from the main peak. It is interesting to note the simplicity of the radial distribution curve for a substance consisting of many light atoms; we see that resolution of distances involving these atoms is quite poor. In order to resolve distances in such cases it would be necessary to use accurate intensities to much larger values of (sin Θ)/λ.

The Sb–S distance found for this substance is appreciably smaller than the sum of the normal covalent radii for sulfur and antimony, 2.40 Å. It was suggested in a similar observation by Brockway and Wall[8] on stannic chloride and similar compounds that differences in residual charge on the atoms act in shortening the bonds between them, and that double bonded structures may be contributing to some extent to the normal state of the molecule. Both suggestions are valid in this case.

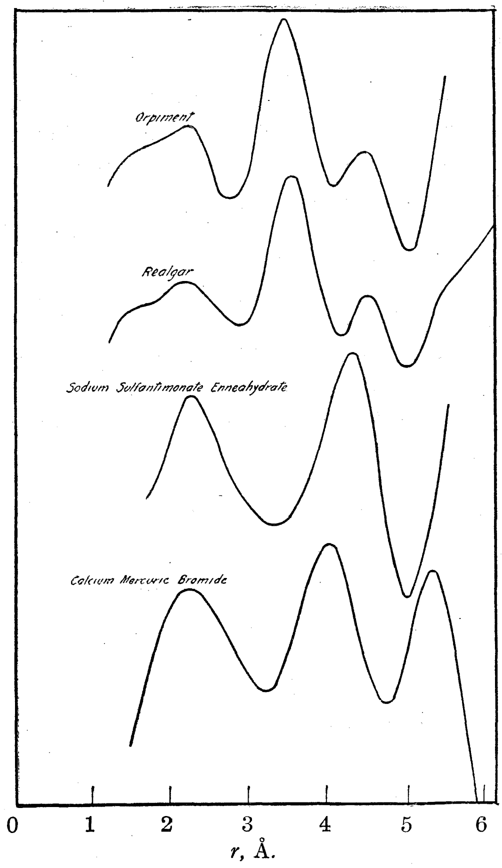

Fig. 1.

Calcium Mercuric Bromide[9]

Figure 1 also shows the density distribution curve obtained for calcium mercuric bromide, $CaHgBr_4$, with the use of 61 powder lines. The three peaks shown occur at 2.24 Å., 4.01 Å. and 5.35 Å. The first peak is rather broad, indicating that several rather widely differing unresolved distances are contributing. It is likely, then, that the value 2.24 Å. does not represent accurately a single Hg–Br distance, but that there are several such distances existing in the crystal. If there are $HgBr_4$ tetrahedra and the position of the second peak is taken to represent the Br–Br distance, the Hg–Br distance is calculated to be 2.47

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(7) M. J. Buerger, *Am. Mineral.*, **20**, 36 (1935) reports a_0 = 9.27 Å., b_0 = 13.50 Å., c_0 = 6.56 Å., β = 73° 22.7′, 16 AsS, space group $C_{2h} - P_2/n$ for realgar.

(8) Brockway and Wall, THIS JOURNAL, **56**, 2373 (1934).

(9) It was shown in 1922 by Professors R. G. Dickinson and L. Pauling that the face-centered cubic unit of structure of this crystal has a_0 = 19.14 Å. and contains 32 $CaHgBr_4$ (unpublished investigation).

Å. If on the other hand the structure is built upon bromide ions in contact, the Br^-–Br^- distance would be expected to be approximately 3.90 Å., the diameter of the bromide ion,[10] agreeing with the observed position of the second peak.

Conclusion

Application of the rough radial distribution method of these four substances shows in a general way to what extent the method may be relied upon. The results seem to be accurate when there is only one distance involving large atoms near a given value; otherwise resolution is poor. In a large number of cases in which the structure is not known it is impossible to state whether or not this condition is being fulfilled. The use of reflections at large values of $(\sin \Theta)/\lambda$ gives increased resolutions; with intense photographs and accurate estimates of intensities of the weak lines being reflected at large angles one could use these important lines to much greater advantage. It is a particularly useful method when applied to large molecules containing a comparatively small number of heavy atoms.

I wish to express my gratitude to Professor Linus Pauling for his valuable coöperation, and to Dr. Sidney Weinbaum for his assistance in preparing the curves for presentation.

Summary

The radial distribution method has been applied to orpiment, realgar, sodium sulfantimonate enneahydrate and calcium mercuric bromide. The environment about the atoms in realgar is shown to be remarkably like that in orpiment, and in both cases the distance between arsenic and sulfur atoms agrees within experimental error with the sum of the corresponding covalent radii. A value for the sulfur bond angle is given, and the *b*-axis of the unit cell of orpiment was measured. The sulfur–antimony distance in sodium sulfantimonate enneahydrate was found to be definitely less than the sum of the covalent radii. Application of the method to calcium mercuric bromide led to indefinite results, consistent either with a closest packing of bromide ions, or with a structure consisting of tetrahedral covalent $HgBr_4$ groups.

PASADENA, CALIFORNIA RECEIVED JUNE 23, 1936

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[10] Pauling, THIS JOURNAL, **49**, 765 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, TEMPLE MEDICAL SCHOOL]

Improvements in Technique for the Determination of Microgram Quantities of Iodine

BY R. H. HAMILTON, JR.[1]

Because a small amount of iodine has to be extracted from a large mass of other salts before determination, and because extraction with alcohol, as advocated by von Fellenberg,[2] requires the iodine to be in the form of iodide, it is necessary to reduce iodates that may be present. Such reduction has been done in the past with sulfites in acid solution. Acidification increases the amount of salts present, and thus increases the difficulty of extraction, because the salt mixture must again be made alkaline before extraction with alcohol.

Harvey[3] used hydrazine sulfate to reduce iodate when purifying potassium hydroxide solutions. He did not show how nearly quantitative such reduction was. In the present investigation hydrazine sulfate was found to give quantitative reduction. Hydrazine hydrate was later tried and found to have the same action. It should be preferable to the sulfate, as the excess is completely volatile when hydrate is used, whereas added sulfate ions remain as potassium sulfate. When an excess of hydrazine sulfate or hydrate has been added, a small drop of carbonate solution produces a dark spot when placed upon paper dipped in a 5% mercuric chloride solution and dried.

The salt mixture from which iodide is to be extracted usually contains much potassium carbonate, since von Fellenberg advocated the use of this substance.[2] The usual practice has been to evaporate the solution until a solid phase of carbonate appeared. Then the two-phase system was extracted by rubbing with alcohol, which formed a third phase. Occlusion of iodide by crystals becomes marked if there is no aqueous phase present. This fact suggested the use of a two-phase system consisting of saturated potas-

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[1] National Research Fellow in the Biological Sciences, 1934–1935.

[2] Th. von Fellenberg, *Biochem. Z.*, **139**, 391 (1923).

[3] C. O. Harvey, *Analyst*, **59**, 479 (1934).

sium carbonate solution and 92% by volume alcohol, without the presence of any solid carbonate. Experiments showed that extraction under these conditions could be made quantitative.

It was noted that when potassium carbonate solutions were boiled for some time in porcelain dishes, silicates dissolved and hindered quantitative extraction of iodides.

Incidentally, it was also noted that sodium fluoride exerted a definite and marked inhibiting action on the re-oxidation of iodide which ordinarily occurs within a few minutes to a few hours if the titration flask is allowed to stand after the end-point is reached. This observation is of theoretical interest, but it will probably not find application in titration methods, as re-oxidation is not a serious factor when they are properly carried out.

Experimental

In all cases, the method of determination of iodine present, after separation from salt masses, was that described by Reith.[4] In no case did the amount of iodide ion in the aliquot taken for analysis exceed 5 micrograms.

Quantitative Reduction of Iodate in Alkaline Solution by Means of Hydrazine Sulfate.—To 2 cc. of saturated potassium carbonate solution (expt. A, Table I) was added 50 micrograms of iodine as potassium iodate, in 5 cc. of water. The solution was boiled for thirty minutes, water being added to maintain the volume, and was then evaporated to dryness, moistened, and extracted by trituration with 94% alcohol, three 5-cc. portions of alcohol being used.

TABLE I

REDUCTION OF IODATE BY HYDRAZINE SULFATE

Expt.	Satd. K_2CO_3, cc.	Iodine as iodate, γ	Hydrazine sulfate, mg.	Time of boiling before starting evaporation, min.	Total iodine extracted, γ
A	2	50	..	30	1.6
B	2	50	10	30	48.8
C	2	50	10	30	50.5
D	2	1	10	30	1.16
E	2	50	10	..	49.1
F	2	1	10	..	1.04

In expts. B, C and D, a similar procedure was followed, except that each time 10 mg. of hydrazine sulfate was added before the carbonate–iodate solution was boiled for thirty minutes. In expts. E and F, the thirty-minute boiling period was omitted, and extraction was carried out as described below.

Two-phase Extraction of Iodide from Potassium Carbonate Solution.—In expts. E to J, inclusive, a glass-stoppered test-tube was used for the extraction. In expts. G and H, the tube, containing iodide, saturated carbonate solution, and 92% (by volume) alcohol, was stoppered and shaken vigorously 200 times, and laid on its side until the emulsion settled out.

TABLE II

TWO-PHASE EXTRACTION OF IODIDE

Expt.	Satd. K_2CO_3, cc.	Iodine as KI γ	Extraction no.	Alcohol used, cc.	Residue, mg.	Iodine in aliquot, γ	Iodine in whole extract, γ	Total iodine found, γ
G	2	50	1	10	6.3	4.76	47.6	
			2	10	6.8	0.3	1.5	49.1
H	2	50	1	10	5.7	4.91	49.1	
			2	10	6.5	0.66	1.6	50.7
I	1	50	1 and 2	10 + 10		4.96		49.6
J	2[a]	50	1	10	21.7	4.48	44.8	
			2	10	21.6		3.0	
			3	10	18.6		..	47.8

[a] See text.

Separation of the layers was effected by means of a pipet shaped like, and about the dimensions of, a 10-cc. graduated pipet. The tubing at the top of the pipet should have a small lumen (about 2 mm.), to prevent alcohol from wetting the finger upon inversion, and should be 5 or 6 cm. long. The pipet was wet inside with alcohol before use; otherwise the additional partial pressure of alcohol vapor would cause some of the contents to be spilled upon inversion. The alcoholic layer was sucked up into the pipet along with some of the aqueous layer. The latter was allowed to run back into the extraction tube, and the pipet was inverted, the alcoholic contents being allowed to run into an evaporating dish through the top of the pipet. By this procedure, admixture of aqueous phase was avoided. A second extraction was made similarly, without rinsing of the pipet between extractions of the same sample.

In expt. I, 1 cc. of carbonate solution was used, and the two extracts were analyzed together.

A test of this method of extraction was made when other ions than carbonate were present (expt. J). In a platinum dish were placed, in solution, 100 mg. each of potassium nitrate, potassium sulfate and potassium chloride, 50 micrograms of iodine as potassium iodide, and 2 cc. of saturated potassium carbonate, containing about 1.46 g. of the anhydrous salt. The solution was heated gently on an asbestos-covered wire gauze until crepitation ceased, and the salt mixture was transferred mechanically to a glass-stoppered test-tube. The platinum dish was rinsed several times with water, the rinsings being added to the test-tube until the volume of salt solution was slightly over 2 cc. This material was extracted as above with alcohol. Two more extractions were made, no iodine being found in the third extract.

Discussion

After hydrazine sulfate or hydrate is added to the carbonate solution, the latter should be evaporated to dryness over a low flame in order to drive off excess hydrazine, which will otherwise reduce bromine at a later step.

The proposed method of extraction is not usable unless the salt mass is mostly potassium carbonate, as so much water is required to dissolve other salts that the alcohol used is diluted, and interfering ions will be extracted by the dilute alcohol. As

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[4] J. F. Reith, *Biochem. Z.*, **216**, 249 (1929).

will be noted in Table II, the salt extracted by alcohol when carbonate alone is present amounts to only 0.6 to 0.7 mg. per cc. of alcohol. After careful trituration of crystals of potassium carbonate and saturated solution with 94% alcohol, the amount of carbonate extracted was found, as an average of nine determinations, to be about 1.09 mg. per cc. of alcohol.

Much of this work was done in the Rijksinstituut voor de Volksgezondheid, Utrecht, Holland. The author's sincere thanks are due Dr. J. F. Reith, Head of the Chemical Division there, who demonstrated his methods, and offered valuable suggestions and criticisms.

Summary

1. Iodate can be quantitatively reduced in hot alkaline solution by means of hydrazine sulfate.

2. Efficient extraction of iodide can be made with alcohol from a saturated solution of potassium carbonate, without danger of occlusion by crystals.

3. Alkaline solutions containing iodide should not be boiled in porcelain dishes before extraction of the iodide.

4. Fluoride delays the re-oxidation of iodide which takes place after a titrimetric determination of iodine.

PHILADELPHIA, PENNA. RECEIVED JUNE 15, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reduction of Aromatic Compounds with Hydrogen and a Platinum Oxide–Platinum Black Catalyst in the Presence of Halogen Acid

BY J. H. BROWN, H. W. DURAND AND C. S. MARVEL

While reducing hot alcoholic solutions of some bromophenylolefins to the corresponding paraffins by hydrogen in the presence of Adams, Voorhees and Shriner's platinum catalyst,[1] we observed that in some runs more than the expected amount of hydrogen was absorbed, and hydrogen bromide was formed. Further investigation showed that this reaction involved not only removal of bromine from the benzene ring, but also reduction of the benzene ring to a hexahydro derivative. Since Adams and Marshall[2] have found that, in general, aromatic compounds are very slowly reduced in alcohol and only with moderate rapidity in glacial acetic acid, with platinum oxide–platinum black as a catalyst, it has seemed worth while to investigate our chance observation in greater detail.

When bromobenzene was dissolved in alcohol at about 55° and shaken with the catalyst in the presence of hydrogen, rapid absorption of hydrogen occurred, and cyclohexane was formed. By interrupting the reduction when one equivalent of hydrogen per molecule of bromobenzene had been absorbed, the product obtained was an impure sample of benzene, but the reaction did not seem to offer a satisfactory scheme for removal of halogen from a benzene derivative. Other aryl halides, such as *o*-, *m*- and *p*-bromotoluene, *p*-dibromobenzene, chlorobenzene and *p*-dichlorobenzene, were also readily reduced to halogen acid and the cyclohexane derivative. However, not all aryl halides could be reduced readily, as shown by the fact that iodobenzene, *o*-bromobenzoic acid, α-chloronaphthalene and α-bromonaphthalene were not affected in our experiments.

Since the reduction of an aryl halide apparently was taking place in two steps—first, removal of halogen acid, and then reduction of the ring—and more rapidly than the usual reduction of the ring alone, it seemed probable that the liberated halogen acid must be an activator for the platinum catalyst for reduction of aromatic compounds. This was verified by reducing various aromatic compounds in alcoholic solution in the presence of various concentrations of hydrogen chloride and bromide. Some of the first reductions were carried out after preheating the solutions to 50–70°, but later it was found that this was not necessary, as reduction took place rapidly, and the temperature of the mixture soon rose to this point without outside heating. Benzene, toluene, xylene, mesitylene, ethylbenzene, cymene, diphenyl and anthracene were readily reduced, whereas naphthalene and phenanthrene were not affected. There seemed to be no choice between hydrogen chloride and hydrogen bromide as an activator.

When functional groups are present in the aro-

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(1) Adams, Voorhees and Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 452.

(2) Adams and Marshall, THIS JOURNAL, **50**, 1970 (1928).

TABLE I

REDUCTION OF ARYL HALIDES

Compound reduced	Mols of H_2 absorbed[a]	Time, min.	Halogen acid formed, mols	Product of reduction
Bromobenzene	0.185	240	0.0486	Cyclohexane d^{20}_4 0.7767 n^{20}_D 1.4274
Bromobenzene	.06	14	.0422	Benzene
o-Bromotoluene	.17	135	.0479	Methylcyclohexane d^{20}_4 0.7689 n^{20}_D 1.4227
m-Bromotoluene	.2	240	.047	Methylcyclohexane n^{20}_D 1.4362
p-Bromotoluene	.14	300	.044	Methylcyclohexane n^{20}_D 1.4357
p-Dibromobenzene	.22	210	.085	Cyclohexane n^{20}_D 1.4261
Chlorobenzene	.2	210	.049	Cyclohexane n^{20}_D 1.4255
p-Dichlorobenzene	.21	300	.073	[b] Cyclohexane n^{20}_D 1.4282

[a] Calculated roughly from drop in pressure during reduction. [b] Some *p*-dichlorobenzene remained at the end of this run.

matic molecule, there is very little regularity in the effect of halogen acid on the ease of reduction. Phenol and ethyl benzoate were reduced more rapidly in the presence of halogen acid than in its absence. Benzaldehyde and benzoic acid were no more readily reduced in the presence of halogen acid. Anisole, in the presence of halogen acid, gave cyclohexane. It is of interest that, while naphthalene and its α-chloro and α-bromo derivatives were unaffected, α- and β-naphthol both reduced readily in the presence of hydrogen chloride to give the corresponding tetrahydronaphthols. This is the normal course of reduction for α-naphthol, but in the case of β-naphthol sodium and amyl alcohol reduction gives mainly the alcohol[3] and very little phenol.

Adams and Marshall[2] pointed out that alcohol is usually the best solvent for reductions making use of this platinum catalyst, although for aromatic hydrocarbons they had better results with acetic acid. When the catalyst is activated with halogen acid, alcohol again becomes the better solvent, although the activity of the catalyst in acetic acid is slightly improved by hydrogen chloride.

Hamilton and Adams[4] have shown that pyridine derivatives reduce much more readily if they are first converted to the halogen acid salt. This may be due to the same sort of activation of the catalyst which has been observed with hydrocarbons of the benzene series. Zelinsky, Packendorff and Packendorff[5] have reported that ketones can be reduced to the corresponding hydrocarbons over a catalyst of platinized charcoal, provided a little palladium chloride is added to raise the activity of the catalyst. Later Packendorff[6] showed that reduction of chloroplatinic acid in the presence of platinized charcoal gave a catalyst which was effective for the reduction of a carbonyl group to a methylene group. This probably was an activating effect of halogen acid similar to that which we have observed.

Experimental Part

Reduction of Aryl Halides.—A solution of 0.05 mole of the aryl halide in exactly 100 cc. of ethyl alcohol was placed in a reduction outfit[7] and warmed to 55°. To the warm mixture 0.1 g. of platinum oxide catalyst[1] was added and the mixture was reduced under a hydrogen pressure of about 3 atmospheres. The drop in pressure was noted from time to time in order to know when reduction was complete. When no more hydrogen was absorbed, the reaction mixture was removed from the outfit and an aliquot portion of the solution was titrated to show the amount of halogen acid produced. The reaction mixture was then diluted, and the reduction

TABLE II

EFFECT OF HALOGEN ACID ON CATALYTIC REDUCTION OF BENZENE

Halogen acid used	Time for complete reduction, min.	Pressure drop[a]
None	70	None
1 drop alcoholic HCl[b]	49	6.9
0.2 cc. alcoholic HCl	29	7.3
1.0 cc. alcoholic HCl	31	7.0
5.0 cc. alcoholic HCl	30	7.3
6.0 cc. alcoholic HCl	23[c]	7.3
1 drop alcoholic HBr[d]	36	7.4
0.5 cc. alcoholic HBr	34	7.1
5.0 cc. alcoholic HBr	79	5.9
0.02 g. I_2	720	None
0.2 cc. alcoholic HCl[e]	39	7.6

[a] The theoretical absorption of hydrogen should cause a drop in the pressure of 7.1–7.2 lb. [b] This solution was prepared by saturating 95% ethyl alcohol with dry hydrogen chloride at room temperature. [c] In this experiment 0.25 g. of catalyst was used. [d] This solution was prepared by saturating 95% ethyl alcohol with dry hydrogen bromide at room temperature. [e] The solution was not preheated in this reduction.

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(3) Bamberger and Kitschelt, *Ber.*, **23**, 885 (1890).

(4) Hamilton and Adams, THIS JOURNAL, **50**, 2260 (1928).

(5) Zelinsky, Packendorff and Packendorff, *Ber.*, **66**, 872 (1933); **67**, 300 (1934).

(6) Packendorff, *ibid.*, **67**, 905 (1934).

(7) Adams and Voorhees, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 53.

TABLE III

REDUCTION OF AROMATIC HYDROCARBONS

Compound reduced	Amount used	Halogen acid used	Time, hrs.	Product
Benzene	10 cc.	2 cc. aqueous HCl (sp. gr., 1.19)	4	Cyclohexane[a]
Toluene	10 cc.	None	3.5	No reduction
Toluene	10 cc.	1 cc. 48% aqueous HBr	10	Methylcyclohexane[b]
Toluene	10 cc.	5 cc. alc. HCl	3	Methylcyclohexane[b]
Xylene[c]	10 cc.	2 cc. alc. HCl	6	Dimethylcyclohexane[d]
Mesitylene	10 cc.	2 cc. alc. HCl	6	1,3,5-Trimethylcyclohexane[e]
Ethylbenzene	9.25 cc.	1 cc. alc. HBr	5.5	Ethylcyclohexane[f]
Cymene	13.4 g.	0.5 cc. alc. HCl	2.25	Hexahydrocymene[g]
Diphenyl	7.7 g.	5 cc. alc. HCl	10	Dicyclohexyl[h]
Anthracene	4.55 g.	5 cc. alc. HCl	15.5	Octa- and perhydroanthracenes[i]

[a] B. p., 81–81.5°; $n^{20}\mathrm{D}$ 1.4314. [b] B. p., 99–101°; $n^{20}\mathrm{D}$ 1.4359. [c] Technical xylene. [d] B. p., 113–124°; d^{20}_4 0.773; $n^{20}\mathrm{D}$ 1.4258. [e] B. p., 134–136°; $n^{20}\mathrm{D}$ 1.4320. [f] B. p., 131–132°; $n^{20}\mathrm{D}$ 1.4329. [g] B. p., 168–169°; $n^{20}\mathrm{D}$ 1.4395; d^{20}_4 0.8038. Adams and Marshall[2] report $n^{20}\mathrm{D}$ 1.4370; d^{25}_4 0.8061. In their experiment 13.4 g. of cymene in glacial acetic acid was reduced with 0.2 g. of catalyst in seven and one-half hours. [h] B. p., 220–228°; $n^{20}\mathrm{D}$ 1.4792; d^{20}_4 0.8804. [i] Octahydroanthracene, m. p., 73–74°; perhydroanthracene, m. p. 61–62°.

TABLE IV

REDUCTION OF AROMATIC DERIVATIVES

Compound	Amount	Time of reduction	Product	Physical properties of product
Phenol	9.4 g.	32 min.	Cyclohexanol	$n^{22}\mathrm{D}$ 1.4652
Phenol	9.4 g.	3 hrs.[a]	Cyclohexanol	$n^{22}\mathrm{D}$ 1.4652
Ethyl benzoate	7.5 cc.	4 hrs.	Ethyl hexahydrobenzoate	B. p. 190–194°; $n^{15}\mathrm{D}$ 1.4481; d^{20}_4 0.9649
Acetophenone	6 g.	12 hrs.	Ethylcyclohexane[b]	B. p. 130–132°; $n^{20}\mathrm{D}$ 1.4447
Anisole	10.8 g.	6 hrs.	Cyclohexane	B. p. 79–80°; $n^{20}\mathrm{D}$ 1.4272
α-Naphthol	7.2 g.	4 1/2 hrs.	5,6,7,8-Tetrahydronaphthol-1	M. p. 68–69°
β-Naphthol	7.2 g.	10 hrs.	5,6,7,8-Tetrahydronaphthol-2	M. p. 59–60°

[a] No halogen acid has added to this run. [b] This material contained a little ethylbenzene.

product isolated in the usual manner. The results of some of the experiments are summarized in Table I.

Under the same experimental conditions iodobenzene, α-bromonaphthalene, α-chloronaphthalene and *o*-bromobenzoic acid were not affected.

Reduction of Benzene.—A series of experiments, using 5 cc. of freshly distilled, thiophene-free benzene in 100 cc. of 95% ethyl alcohol at 70° with 0.125 g. of platinum oxide catalyst, different amounts of hydrogen chloride and bromide and a hydrogen pressure of about three atmospheres, gave the results shown in Table II.

From these results, it is evident that both hydrogen chloride and hydrogen bromide activate the platinum oxide catalyst for the reduction of benzene. With hydrogen chloride, any amount beyond a trace seems to have little effect. Too much hydrogen bromide seems to be undesirable. Iodine is not an activator for the catalyst. No attempt was made to isolate the product of reduction in these runs.

To test the effect of halogen acid on the catalyst in acetic acid solution, two reductions were carried out, using 5 cc. of benzene, 0.1 g. of platinum oxide and 50 cc. of glacial acetic acid. To one of these batches, 0.5 cc. of alcoholic hydrogen chloride was added. The run without hydrogen chloride was complete in seventy minutes, whereas the run with it was complete in fifty-four minutes.

Reduction of Aromatic Hydrocarbons.—The standard reduction experiment was carried out by dissolving the aromatic hydrocarbon in 100 cc. of alcohol at 70°, using 0.1 g. of platinum oxide catalyst and 45 pounds (3 atm.) of hydrogen pressure. The halogen acid used to activate the catalyst was varied. The reduction products were isolated and identified, although little effort was made to determine exact yields. The results of some of our experiments are collected in Table III.

No evidence of reduction of either naphthalene or phenanthracene could be obtained using the general conditions outlined above, although various amounts of aqueous and alcoholic hydrogen chloride and bromide were added as activators for the platinum catalyst.

Reduction of Some Aromatic Derivatives.—Attempts were made to reduce some phenols, aromatic ethers, acids, esters, aldehydes and ketones, using the platinum oxide catalyst and halogen acids. Some of these derivatives reduced readily, and some not at all. The standard procedure was to use about 0.1 mole of compound, 100 cc. of alcohol, 0.1 g. of catalyst and 0.5 cc. of alcoholic hydrogen chloride at 70° under 3 atmospheres of hydrogen. The results are summarized in Table IV.

Benzaldehyde and benzoic acid were not reduced under the same conditions.

Summary

Small amounts of hydrogen chloride and hydrogen bromide increase the effectiveness of platinum oxide–platinum black as a catalyst for the hydrogenation of most aromatic rings.

URBANA, ILLINOIS RECEIVED JUNE 25, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Molecular Rotation in Solid Aliphatic Alcohols

BY C. P. SMYTH AND S. A. MCNEIGHT

A previous investigation has given indications of the occurrence of dipole rotation in solid methyl alcohol.[1] This paper presents the results of measurements of the dielectric constants of methyl, tertiary butyl and *n*-octyl alcohols from liquid air temperatures to the melting points. The apparatus and technique employed were essentially the same as that described in earlier papers from this Laboratory,[2] the same bridge being used.

Purification

Methyl Alcohol.—C. P. synthetic methyl alcohol was refluxed over lime for several hours and fractionally distilled. The middle fraction was then fractionally distilled from shiny magnesium ribbon, b. p. 64.74 ± 0.05°.

Tertiary Butyl Alcohol.—An Eastman Kodak Co. product was washed with a saturated solution of sodium bisulfite, the alcoholic layer decanted and refluxed for several hours with 10% sodium hydroxide solution. The alcohol was distilled off and dried with sodium sulfate and potassium carbonate and then refluxed over lime for several hours before distilling. The lime treatment was repeated, after which the distillate stood over calcium turnings for two days before distilling. The final fractional distillation was made from tartaric acid; b. p. 82.3°. The distillate was then recrystallized from its own melt four times; m. p. 24.8°.

Octanol-1.—The material was part of a sample employed in a previous determination of dipole moment.[3]

Experimental Results

The dielectric constants ϵ and the specific conductances k (ohm^{-1} cm.^{-1}) are given in Table I, the absolute temperatures being given in the first column and the frequencies in kilocycles across the top of each group of data. Many determinations at intermediate temperatures and frequencies are omitted for the sake of brevity. Unless otherwise indicated, the values were obtained with rising temperature. The values for methyl alcohol could not be extended to higher temperatures because increasing conductance made the bridge measurements too inaccurate.

Discussion of Results

The melting point found for methyl alcohol, 175.4°K., is sharp and is in very good agreement with the value 175.3°K. given in "International Critical Tables" but indicates a less pure sample

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC CONDUCTANCES

Methyl Alcohol (m. p. 175.4°K.)

Kc.	50	5	0.5	50	5	0.5
T, °K.		ϵ			$k \times 10^9$	
108.4	3.22	3.28	3.36	0.96	0.17	0.02
126.6	3.38	3.52	3.66	2.27	.30	.04
138.0	3.54	3.76	3.92	3.61	.40	.04
154.9	3.68	3.93	5.07	3.60	1.78	1.12
156.5	3.73	4.10	5.65	5.00	2.85	1.82
157.3	3.78	4.21	6.01	6.31	3.59	2.35
158.2	3.81	4.37	6.50	7.74	4.65	3.14
159.0		4.46			5.55	
159.4		4.56			6.20	
159.9		4.66			7.01	
159.9		5.65			5.64	
160.0		5.97			5.04	
161.0		7.03			3.47	
163.2	6.46	7.50	10.82	13.0	4.23	1.48
169.0	6.88	9.00		27.7	9.16	
171.6		10.82			16.6	
173.8		15.43			50.2	
		(Falling temperature)				
166.2		8.15			6.06	
157.5		6.95			3.21	
150.8		6.46			0.88	
138.8		6.35			.19	
132.9		5.59			.28	
		Tertiary Butyl Alcohol (m. p. 297.9°K.)				
94.3	2.23	2.22	2.20	0.17	<0.01	<0.01
99.7	2.24	2.24	2.19	.17	< .01	< .01
111.5	2.24	2.24	2.20	.18	< .01	< .01
120.5	2.24	2.24	2.20	.17	< .01	< .01
131.0	2.24	2.24	2.21	.17	< .01	< .01
140.0	2.24	2.25	2.22	.17	< .01	< .01
143.2	2.25	2.25	2.22	.17	< .01	< .01
152.6	2.26	2.26	2.22	.18	< .01	< .01
162.1	2.26	2.26	2.23	.18	< .01	< .01
179.9	2.27	2.27	2.24	.18	< .01	< .01
196.4	2.28	2.28	2.25	.17	.02	< .01
213.7	2.30	2.30	2.28	.17	.02	.02
228.6	2.32	2.31	2.29	.17	.02	.02
234.8	2.32	2.32	2.29	.18	.02	.02
251.5	2.35	2.36	2.35	.18	.04	.02
257.9	2.40	2.42	2.50	.81	.15	.04
272.9	2.53	2.70	3.23	2.88	1.04	.52
287.9	2.74	3.04	3.86	4.01	1.53	.67
		(after 24 hours)				
292.2	2.53	2.66	3.03	2.23	0.72	0.32
295.3	2.69	2.96	3.68	2.83	1.52	.71
297.4	3.50	4.12	5.43	6.08	5.52	3.78
		Liquid				
299.2		12.12			26.6	
301.9		11.92			29.6	

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(1) Smyth and Hitchcock, THIS JOURNAL, **56**, 1084 (1934).

(2) Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932); **55**, 1830 (1933).

(3) Smyth and Stoops, *ibid.*, **51**, 3312 (1929).

TABLE I (*Concluded*)

Octanol-1 (m. p. 256.8°K.)

Kc. ...... T, °K.	50	5 ϵ	0.5	50	5 $k \times 10^9$	0.5
87.3	2.32	2.32	2.25	0.67	<0.03	<0.03
102.6	2.32	2.32	2.25	.70	< .03	< .03
118.8	2.33	2.32	2.26	.67	< .03	< .03
128.8	2.33	2.33	2.29	.67	< .03	< .03
159.1	2.34	2.36	2.33	.67	.03	< .03
179.1	2.35	2.38	2.42	.93	.06	< .03
208.0	2.36	2.47	2.60	1.22	.15	< .03
249.2	2.71	3.06	4.50	3.71	.97	.32
251.3	2.77	3.25	5.70	4.11	1.41	.53
253.7	3.03	4.15	9.13	6.49	3.28	1.50
254.6	3.63	5.38	11.7	10.0	6.63	4.07
255.5	5.55	7.47	12.3	17.2	14.9	13.7
256.0	6.58	8.70		21.8	19.9	
256.6	9.63	11.79		32.3	34.6	
Liquid						
258.9	12.97	13.0	13.1	48.5	48.1	51.1
260.9	12.71	12.82	13.1	54.6	53.1	57.5
262.0	12.66	12.80	13.1	58.2	56.0	56.9
269.1	11.93	12.22	12.7	78.2	76.0	77.4
272.6	11.60	11.87	12.3	92.5	89.6	90.5
287.1	10.34	10.57	11.0	127	124	125
296.3	9.47	9.58	10.1	140	139	141
Solid Cooling						
252.5	4.08	4.80	5.4	8.48	2.43	0.24
222.1	2.36	2.46	2.48	1.63	0.09	< .03
203.8	2.30	2.36	2.36	1.05	.06	< .03
Warming						
210.9	2.30	2.39	2.40	1.05	.09	< .03
217.0	2.32	2.42	2.44	1.25	.09	< .03
224.2	2.34	2.45	2.52	1.40	.12	< .03
230.5	2.36	2.50	2.62	1.63	.15	.03
237.2	2.41	2.56	2.78	1.92	.25	.06
243.6	2.46	2.66	3.17	2.30	.35	.12
249.7	2.56	2.89	4.20	3.07	.70	.18
252.5	2.68	3.18	4.33	3.78	1.05	.24

than that for which Timmermans and Hennaut-Roland[4] report 176.1°K. It is to be regretted that the difficulty of purification has prevented the removal of the last traces of impurity, which have some effect upon the results in the neighborhood of the melting point. The dielectric constant curve in Fig. 1 for a frequency of 5 kilocycles shows a transition at 159.9°K. with a sharp rise in value with rising temperature. The transition is somewhat obscured by anomalous dispersion both below and above it but for high frequencies the change in the value of the dielectric constant is quite sharp and a time–temperature curve shows a halt at 159.9°K. for a period of between thirty and forty minutes for rising temperature. The apparent conductance at 5 kc. also shows a maximum at this temperature. This is 0.8° higher than that previously reported but differs by only 0.1° from the transition temperature found for another sample and lies between the values found from specific heat measurements, 157.4°K. by Kelley[5] and 161.1°K. by Parks.[6] Falling temperature gives a very much delayed transition, for with decreasing temperature the high temperature form has been observed as far down as 133°K., whereas with rising temperature a lag of more than 0.1° has never been detected.

The solid, in spite of every effort to purify it, contains a small amount of impurity, presumably water, as shown by the slightly low melting point and the slight premelting indicated by a time–temperature curve taken over the melting range. As the eutectic point of the methyl alcohol–water system is about 134°K.,[7] a minute trace of liquid would remain down to this temperature, which is just about where the cooling dielectric constant curve dips downward toward the rising temperature curve. This apparent hysteresis loop, which, unfortunately, was not completed experimentally, is not unlike that found for phenol containing a trace of water. It may arise from the presence of a minute quantity of liquid, which would raise the dielectric constant, or it may be due merely to an unusually large lag in the transition, supercooling undoubtedly occurring. Probably, both factors contribute to the seeming discrepancies and the changes of dielectric constant and conductance with time observed here and in the earlier work. The considerable variation of the dielectric constant and the conductance with frequency is doubtless contributed to by the liquid, but the uniform rise of dielectric constant with temperature below and above the eutectic point of the methyl alcohol–water system, the difference between it and the much lower values, almost constant in this region, found for *t*-butyl and octyl alcohols, and the sharp rise at the transition followed by a further rapid increase as the temperature rises toward the melting point indicate a very small amount of rotation at low temperature, increasing with temperature and rising sharply at the transition, which loosens the structure. Even above the transition, rotation encounters a resistance which diminishes with rising temperature and causes the dielectric constant to be higher at lower frequencies. The approxi-

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(4) Timmermans and Hennaut-Roland, *J. chim. phys.*, **27**, 401 (1929).

(5) Kelley, THIS JOURNAL, **51**, 180 (1929).

(6) Parks, *ibid.*, **47**, 338 (1925).

(7) Baumé and Borowski, *J. chim. phys.*, **12**, 276 (1914).

mate value calculated for the polarization at 108.4°K. is 13.8 as compared to a molecular refraction 8.23 for the D sodium line while at 173.8° it is 27.4, values indicative of rotation, as the difference 5.6 between the polarization at the low temperature and the refraction seems too high to arise entirely from the atomic polarization of so small a molecule.

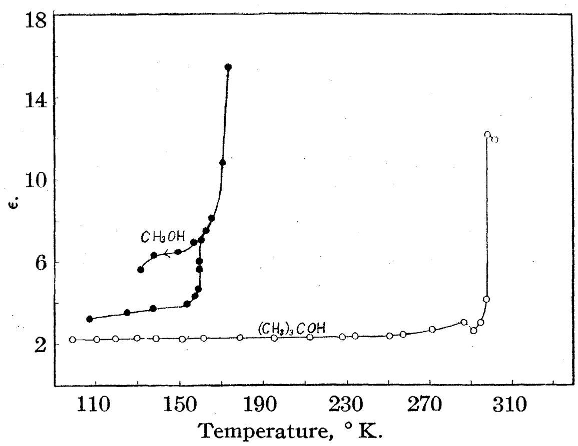

Fig. 1.—Variation with temperature of the dielectric constants (5 kc.) of methyl and *t*-butyl alcohol.

The dielectric constant of solid *t*-butyl alcohol at 5 kc. (Fig. 1) is as low as that of liquid benzene and other non-polar substances, showing the absence of any freedom of the dipole in the molecule to rotate. The small rise in the dielectric constant and the considerable rise in the conductance as the melting point is approached is the normally observed behavior, and is, presumably, due to the presence of traces of impurities which cause very small quantities of liquid to form in this region of temperature. The small break in the curve at 287.9°K. is the effect of twenty-four hours' standing between measurements, which is apt to cause a setting of the structure and reduction of molecular freedom. The increase of dielectric constant with decrease in frequency is reduced by this setting and the apparent conductance is cut in half. In the case of *n*-octyl alcohol, the resolidified sample gave a slightly lower dielectric constant depending less on frequency and a lower conductance except at the first temperature measured after solidification. The dielectric behavior of *n*-octyl alcohol (Fig. 2) is practically identical with that of *t*-butyl, the curves being hardly distinguishable at the lower temperatures. A slight rise with some dependence upon frequency develops near the melting point, probably due mainly to the presence of minute quantities of liquid, but possibly due in part to an occasional molecular rotation with loosening of the structure just below the melting point. In general, however, there is obviously no appreciable amount of rotation of the molecule as a whole or of the hydroxyl group in the molecule in either of these two alcohols in the solid state.

Dielectric constant measurements on phenol[2] and specific heat measurements on many alcohols have failed to show rotation. It is evident, therefore, that the rotation in solid methyl alcohol must be a rotation of the entire molecule rather than of the hydroxyl group within the molecule, since the latter could occur equally well in the other alcohols. As rotation of the methyl alcohol molecule around its C–O axis should involve little change in the space occupied by the molecule, such rotation would probably not be blocked by the surrounding molecules. The main hindrance would be the strong intermolecular attraction probably expressing itself in the formation of a hydrogen bond between molecules such as seems to exist in ice.[8] The opportunity for such bond formation is not as good as in ice and, even in ice, the dielectric constant gives evidence of some molecular rotation. The anomalous dispersion in ice is much stronger than in solid methyl alcohol, probably because of the stronger internal field of the crystal. Because of the presence of the methyl group in the molecule, the freezing point of methyl alcohol is much lower than that of water and molecular rotation can occur in the solid at a low temperature with higher frequencies than in ice.

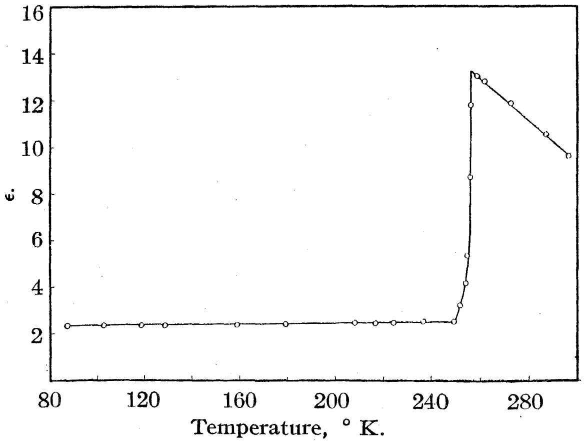

Fig. 2.—Variation with temperature of the dielectric constant (5 kc.) of octanol-1.

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(8) Pauling, THIS JOURNAL, **57**, 268 (1935).

Although the molecule of *t*-butyl alcohol is not very far from spherical in shape, reasonably close packing of the molecules, such as would naturally occur in the crystal lattice, would probably cause the rotation of a molecule to be blocked by its neighbors. In the crystal of *n*-octyl alcohol, the molecules probably lie as extended zig-zag chains parallel to one another. As many cases are known in which carbon chains parallel to one another in a solid rotate about their long axes,[9] there would seem to be a possibility of rotation of this type here, which is evidently not realized. Bernal has found by x-ray analysis[10] that *n*-dodecyl alcohol shows a transition from a monoclinic to a hexagonal crystal at 289°K. with molecular rotation setting in around the axis of the carbon-chain. It is probable that the higher temperature attainable before melting gives the energy necessary to overcome the resistance to rotation, lacking in the *n*-octyl alcohol, which melted 32° below this transition temperature.

Summary

The dielectric constants of solid methyl, *t*-butyl and *n*-octyl alcohols have been measured from liquid air temperatures up to the melting point in order to investigate the question of dipole rotation in the solid state. The high dielectric constant of methyl alcohol just below the melting point, dropping to a low value at a transition temperature 159.9°K., gives evidence of dipole rotation in this region. The absence of dipole rotation in solid *t*-butyl and *n*-octyl alcohols and the failure of specific heat measurements to show transitions in many other alcohols, indicate that the hydroxyl group does not rotate inside the molecule, but that the entire methyl alcohol molecule rotates above the transition point.

PRINCETON, N. J.

RECEIVED JUNE 22, 1936

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[9] Müller, *Nature*, **129**, 436 (1932); Southard, Milner and Hendricks, *J. Chem. Phys.*, **1**, 95 (1933).

[10] Bernal, *Nature*, **129**, 870 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

The Magnetic Rotation of Lanthanum and Neodymium Chlorides in Aqueous Solution

BY CHARLES M. MASON, ROGER D. GRAY AND GRACE L. ERNST

The magnetic rotation of the plane of polarized light is particularly interesting in the case of the rare earths. The chemical properties of these substances in aqueous solutions are so nearly identical that it is only by physical measurements of this type that any differentiation of properties can be made.

In this work the Verdet constants of aqueous solutions of lanthanum and neodymium chlorides have been measured over a temperature interval of from 10 to 50°. The concentration of the solutions was varied from zero (water) to 3.7 molal for the lanthanum chloride and 0.5 molal for the neodymium chloride. For comparison the Verdet constants were determined for aluminum chloride solutions from zero to 2.8 molal over the same temperature range.

Experimental Details

The rotations were measured with a Franz Schmidt and Haensch Model 55 "Landolt" half shade polarimeter, which could be read to hundredths of a degree.

The two light sources used were a mercury "Lab-Arc" with Corning filters G-555-Q and G-35-Y to transmit λ 5460.7 Å. and a sodium "Lab-Arc." This latter was used without filters since the accuracy attained in setting the polarimeter without any filters more than offset any error due to wave lengths other than the principal doublet λ 5893 Å.

The solution, the rotation of which was to be measured, was placed in a water-jacketed cell of Pyrex glass. This was equipped with optical windows of the same, fused on to the ends. The cell, which is shown in Fig. 1, was provided with an entrance through which a calibrated thermometer could be placed in the solution while the rotation was measured.

The magnetic field was provided by a coil of fourteen layers of No. 20 B. and S. cotton and enamel covered copper wire. The total number of turns was 2,059 and the length of the coil was 23.57 cm. The inside diameter was 2.84 cm. and the outside diameter 6.70 cm. The length of the light path through the solution was 21.74 cm. From these data the field strength, *H*, of the coil at any point along the axis is easily calculated. The product of the effective field strength times the length of the light path in the cell was determined by integration. The value of this integral was found to be 2218.2 gauss-cm. per ampere of current through the coil. This value, when used to calculate the Verdet constants for water and carbon bisulfide, checked the standard values[1] within 0.5%. This is a good check when we consider the irregularities of the coil winding as shown by an examination of Fig. 1.

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[1] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. VI, 1926, p. 425.

A current of 4.000 ± 0.001 amperes was used, supplied from storage batteries. Current regulation was obtained by the use of a manually operated potential divider similar to that described by MacInnes and Longsworth.[2]

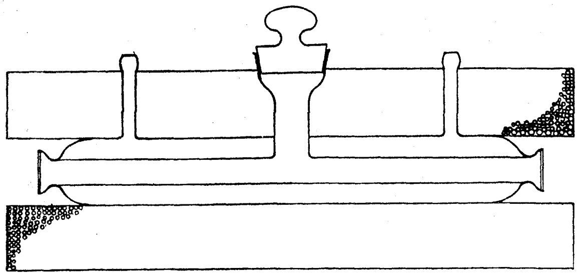

Fig. 1.—Magnetic rotation cell.

In order that the current adjustment might be made accurately, a Leeds and Northrup student type potentiometer was used to measure the potential drop across a standard 0.10 ohm resistance in series with the coil. The potential divider was operated during a reading of the rotation so that the galvanometer connected in the potentiometer circuit showed no deflection while the observation was made.

Temperature control was obtained by circulating water from a thermostat through the water jacket of the cell. The temperature could be controlled to within ±0.05° of any chosen point.

The rare earth salts had been carefully prepared by repeated recrystallization. The chlorides were prepared from the oxalates by ignition to the oxides and solution of these in redistilled hydrochloric acid. These chlorides were then twice recrystallized by concentration of the mother liquor and shaking out with hydrogen chloride gas. They were then dried at room temperature and placed for several weeks in a vacuum desiccator over potassium hydroxide. Examination of the solutions with the hand spectroscope and chemical test showed the absence of other rare earths.

The commercial c. p. grade of aluminum chloride hexahydrate was used without further purification. It was guaranteed by the manufacturer to be better than 99.85%. For the present investigation this slight percentage of impurity would not vitiate the result.

Concentrated aqueous solutions of these salts were prepared with conductivity water. These were analyzed gravimetrically for the chloride. The dilute solutions were then prepared from these by weight. The water used was of conductivity grade.

The c. p. grade of carbon bisulfide was purified by the method of McKelvey and Simpson.[3]

Results

The Verdet constant[4] is given by the expression

$$V = \Theta / \int H dl \qquad (1)$$

where Θ is the angle of rotation in minutes and $\int Hdl$ is the average field strength over the whole light path.

If we choose to calibrate our apparatus with some liquid whose Verdet constant is known, such as water or carbon bisulfide, we find that

$$V = \frac{\Theta}{\Theta_s} V_s \qquad (2)$$

where Θ_s and V_s are the rotation and Verdet constant of the standard liquid used and Θ and V are those for the solution under investigation. In the present work equation (2) was employed to calculate the Verdet constants obtained. Water was employed as the reference liquid in these calculations. This was done because the irregularity of the coil made exact calculation of the field strength impossible.

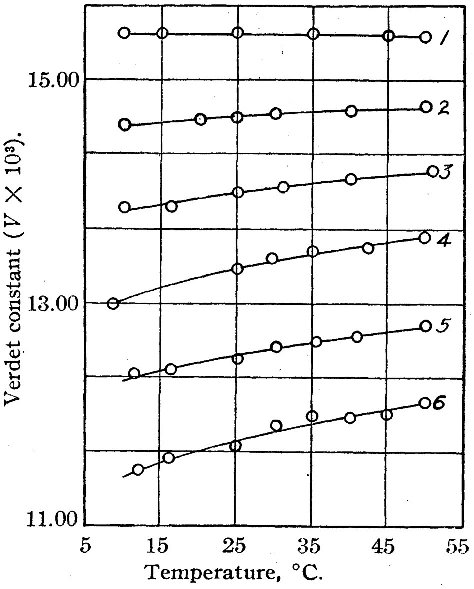

Fig. 2.—The Verdet constants of neodymium chloride solutions as a function of the temperature: 1, water; 2, 0.1 molal; 3, 0.2 molal; 4, 0.3 molal; 5, 0.4 molal; 6, 0.5 molal.

It was difficult to take readings rapidly at fixed temperature intervals due to the heating effect of the coil. The data were therefore often taken at odd temperature intervals. These data were then plotted on a large scale as shown by the plot for neodymium chloride in Fig. 2. The data taken from these plots are presented in Tables I, II and III for aluminum, lanthanum and neodymium chlorides, respectively. No data were obtained for neodymium chloride for the wave length λ 5893 Å. because of the strong absorption band in this region of the spectra.

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(2) MacInnes and Longsworth, *Chem. Rev.*, **11**, 189 (1932); Mason and Gray, *Rev. Scientific Instruments*, **7**, 289 (1936).

(3) McKelvey and Simpson, This Journal, **44**, 108 (1922).

(4) This quantity is discussed and the literature is surveyed in Bhatnagar and Mathur, "Physical Principles and Applications of Magnetochemistry," The Macmillan Co., London, 1935.

TABLE I

VERDET CONSTANTS OF ALUMINUM CHLORIDE SOLUTIONS

λ = 5893 Å.

	$V \times 10^3$ at the indicated temperature					
Molality	10°	20°	25°	30°	40°	50°
0.00	13.19	13.12	13.07[a]	13.10	13.10	13.10
.01	...	13.13	13.14	13.14	13.14	13.15
.05	13.22	13.25	13.27	13.29	13.32	13.36
.10	13.39	13.39	13.39	13.39	13.39	13.39
.50	14.66	14.66	14.66	14.66	14.66	14.66
1.00	15.94	15.94	15.94	15.94	15.94	15.94
1.50	17.21	17.21	17.21	17.21	17.21	17.21
2.00	18.41	18.41	18.35	18.31	18.28	18.28
2.78	20.15	20.02	20.02	19.95	19.95	19.90

λ = 5460.7 Å.

	$V \times 10^3$ at the indicated temperature					
Molality	10°	20°	25°	30°	40°	50°
0.00	15.40	15.40	15.40	15.40	15.40	15.33
.01	...	15.47	15.47	15.47	15.47	15.47
.05	...	15.83	15.78	15.73	15.62	15.51
.10	15.94	15.94	15.94	15.94	15.94	15.94
.50	17.14	17.14	17.14	17.14	17.14	17.14
1.0	18.61	18.61	18.61	18.61	18.61	18.61
1.50	20.09	20.09	20.09	20.09	20.09	20.09
2.00	21.49	21.49	21.56	21.56	21.63	21.63
2.78	23.77	23.77	23.70	23.64	23.50	23.50

[a] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. VI, 1926, p. 425.

TABLE II

VERDET CONSTANTS OF LANTHANUM CHLORIDE SOLUTIONS

λ = 5893 Å.

	$V \times 10^3$ at the indicated temperature					
Molality	10°	20°	25°[a]	30°	40°	50°
0.00	13.19	13.12	13.07	13.10	13.10	13.10
.10	13.46	13.46	13.47	13.53	13.53	13.53
.40	14.40	14.40	14.37	14.40	14.33	14.33
.80	15.67	15.60	15.55	15.40	15.33	15.33
.9967	16.07	16.07	16.08	16.14	16.14	16.14
1.40	17.21	17.21	17.22	17.21	17.14	17.14
1.7509	...	18.08	18.21	18.15	18.01	17.94
2.20	19.08	19.15	19.14	19.10	19.10	19.10
2.50	19.89	19.86	19.83	19.69	19.69	19.69
2.80	20.56	20.56	20.35	20.30	20.29	20.15
3.10	...	20.96	20.97	20.96	20.96	20.96
3.40	21.56	21.56	21.52	21.43	21.29	21.23
3.9640	21.96	21.96	22.03	21.96	21.76	21.69

λ = 5460.7 Å.

	$V \times 10^3$ at the indicated temperature					
Molality	10°	20°	25°[a]	30°	40°	50°
0.00	15.40	15.40	15.40	15.40	15.40	15.40
.10	15.73	15.73	15.75	15.80	15.80	15.80
.40	17.07	16.94	16.85	15.87	16.87	16.87
.80	18.35	18.35	18.17	18.40	18.41	18.41
.9967	19.15	19.08	19.03	19.02	19.02	19.02
1.40	20.42	20.35	20.35	20.29	20.22	20.22
1.7509	...	21.43	21.49	21.49	21.43	21.36
2.20	22.43	22.50	22.50	22.43	22.43	22.43
2.50	23.37	23.34	23.28	23.30	23.30	23.30
2.80	24.10	24.07	24.04	24.00	23.95	23.90
3.10	...	24.90	24.80	24.64	24.57	24.31
3.40	25.44	25.44	25.43	25.31	25.24	25.11
3.9640	26.18	25.91	25.88	25.85	25.80	25.71

[a] All values of this constant at 25° are the mean of at least five measurements.

TABLE III

VERDET CONSTANT OF NEODYMIUM CHLORIDE SOLUTIONS

λ = 5460.7 Å.

	$V \times 10^3$ at the indicated temperature					
Molality	10°	20°	25°[a]	30°	40°	50°
0.00	15.40	15.40	15.40	15.40	15.40	15.33
.05	15.40	15.40	15.40	15.40	15.40	15.40
.10	14.60	14.64	14.66	14.68	14.70	14.73
.20	13.84	13.95	13.99	14.06	14.10	14.16
.30	13.03	13.22	13.32	13.39	13.49	13.59
.40	12.30	12.40	12.47	12.60	12.70	12.81
.50	11.45	11.67	11.72	11.82	11.95	12.14

[a] All values of this constant at 25° are the mean of at least five measurements.

In order to show more clearly the relationship between the Verdet constant and the concentration, the data obtained at 25° have been plotted in Fig. 3.

Discussion

Comparison with Other Data.—The value obtained for the Verdet constant of 0.1 molal lanthanum chloride with the green line λ 5460.8 Å. at 20°, 15.73×10^{-3}, may be compared with that obtained by Roberts, Wallace and Pierce[5] for a solution of lanthanum sulfate, 0.094 molal in lanthanum ion. They obtained 15.40×10^{-3}. The maximum error of measurement in this work for the wave length λ 5460.8 Å. is about ±0.01° of arc which corresponds to a total possible error of 0.14×10^{-3} min. per gauss-cm. in the Verdet constant.

These authors do not state the error in their visual observations. If it is presumed to be of the same order of magnitude as in the present investigation the difference between the two values is within the experimental error. They do state, on the basis of one measurement of magnitude less than the probable error, that aqueous solutions of lanthanum sulfate have a negative rotation. In this investigation lanthanum chloride has consistently a positive rotation in solutions of all concentrations. This difference of sign is not significant however in view of the limits of error discussed above and the different negative ions present.

Direction of Rotation.—The theory of Serber[6] for the Faraday effect in molecules points out that the Verdet constant may be expressed by an equation of three distinct terms. Two of these terms are diamagnetic and the third is paramagnetic. For diamagnetic substances the third term drops

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[5] Roberts, Wallace and Pierce, *Phil. Mag.*, **17**, 934 (1934).

[6] Serber, *Phys. Rev.*, [2] **41**, 489 (1932).

out and the theory predicts that the Verdet constant should be positive.

Lanthanum chloride and aluminum chloride are known to be weakly paramagnetic and diamagnetic, respectively. It would be expected therefore in both cases, since the third term in the equation mentioned above would either be insignificant or vanish, that these substances would have a positive effect on the Verdet constant.

Examination of the data in Tables I and II shows the experimental verification of these conclusions, as in both cases the Verdet constant of the solutions is increased positively by the added salt.

Neodymium chloride on the other hand is strongly paramagnetic and would be expected by Serber's theory to have a negative effect on the Verdet constant. Examination of the data in Table III shows the marked negative effect of neodymium chloride as predicted by the theory.

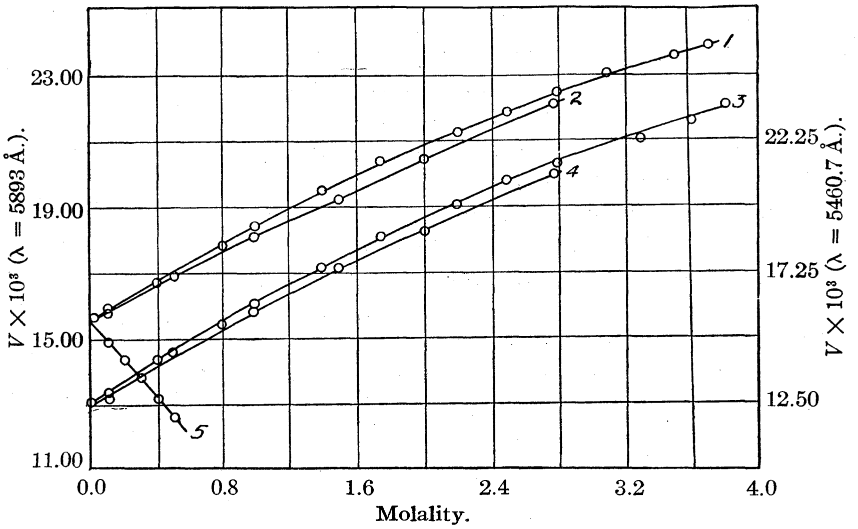

Fig. 3.—Verdet constants of the solutions as a function of concentration at 25°: 1, $LaCl_3$, λ 5460.7 Å.; 2, $AlCl_3$, λ 5460.7Å.; 3, $LaCl_3$, λ 5893 Å.; 4, $AlCl_3$, λ 5893 Å.; 5, $NdCl_3$, λ 5460.7Å.

Temperature Effect.—In the equation mentioned by Serber[6] the third or paramagnetic term contains the expression $1/T$ where T is the absolute temperature. From this the conclusion may be drawn that the Verdet constant for paramagnetic substances should vary with temperature and that diamagnetic substances should not vary with temperature. From the "International Critical Tables"[1] (p. 359) it is noted that the magnetic susceptibilities of aluminum chloride, lanthanum chloride and neodymium chloride (estimated) are in the ratios $-0.6:5.6:25$. From these the theoretical conclusions may be drawn that aqueous solutions of aluminum chloride should have no temperature coefficient, those of lanthanum chloride should have a slight temperature coefficient and neodymium chloride solutions a marked temperature coefficient. Examination of the data in Tables I, II and III shows that the conclusions are justified by the experimental results. No temperature coefficient was observed for the aluminum chloride solutions within the experimental error. A slight temperature coefficient was observed for the lanthanum chloride solutions in the higher concentrations. Neodymium chloride solutions, on the other hand, showed a marked temperature coefficient, even in dilute solutions.

It was found that the Verdet constants of the neodymium chloride solutions gave a straight line when plotted against $1/T$. From these straight lines a family of equations of the type

$$V = a/T + b \tag{3}$$

were obtained, where a and b are constants. The data for these constants for equation (3) and the maximum deviation of the calculated values from the experimental values are given in Table IV.

TABLE IV

CONSTANTS FOR THE TEMPERATURE EQUATIONS (3) FOR NEODYMIUM CHLORIDE SOLUTIONS

Molality, m	a	b	Max. dev.
0.10	− 325.0	16.94	0.04
.20	− 662.5	16.60	.04
.30	−1212.5	17.37	.03
.40	−1220.0	16.21	.03
.50	−1553.6	15.75	.02

Recently several authors[7] have shown that the Curie–Weiss law of magnetic susceptibilities may be applied to the molecular magnetic rotation. This law is usually stated

$$(T - \Delta)\chi_m = C_m \tag{4}$$

where χ_m is the gram-molecular magnetic susceptibility, T the absolute temperature, C_m a constant and Δ a constant called the Curie point.

(7) Ollivier, *Compt. rend.*, **186**, 1001 (1928); Ollivier, *ibid.*, **191**, 130 (1930); Pernet, *ibid.*, **195**, 376 (1932); Gorter, *Physik. Z.*, **34**, 238 (1933).

In order to make this application to the present data the molecular rotations for the neodymium chloride solutions have been calculated from the equation

$$D = \frac{M}{pd_s}(V - d_1 V_w/d_w) \qquad (5)$$

where D is the molecular rotation of the solution, M is the molecular weight of the neodymium chloride, d_s is its density, p is the number of grams of salt per gram of solution, d_1 is the density of the solution, d_w is the density of pure water and V and V_w are the Verdet constants of the solution and pure water, respectively. The densities of the solutions at 25° were obtained from the data of Mason and Leland.[8] The densities for the other temperatures were calculated from these on the assumption that the temperature coefficient of the density of the solutions was the same as that for pure water. The values of D obtained are listed in Table V.

TABLE V

THE MOLECULAR ROTATION OF $NdCl_3$ IN AQUEOUS SOLUTION

Molality, m	p	D at the indicated temperature 10°	20°	25°	30°	40°	50°
0.1	0.0245	3.07	2.96	2.91	2.85	2.80	2.67
.2	.0477	3.06	2.91	2.85	2.76	2.71	2.63
.3	.0699	3.15	2.97	2.87	2.81	2.72	2.62
.4	.0911	3.23	3.17	3.12	3.02	2.95	2.87
.5	.113	3.32	3.19	3.17	3.11	3.03	2.92
Ave.		3.16	3.04	2.98	2.93	2.82	2.72

There is some drift toward the higher concentrations but this may be due to slight error in the density calculation.

The average data in Table V were used to calculate the values of C and Δ in the equation

$$(T - \Delta)D = C \qquad (6)$$

which is analogous to equation (5), the Curie–Weiss law.

The value of Δ was found to be close to 32.6° which was taken as the best value. Equation (6) was tested by calculating the values of C for the several temperatures. The values of C obtained, which checked with each other within one part in a thousand, gave an average value of −790.1. This constancy of C shows that the equation

$$(T - 32.6)D = -790.1 \qquad (7)$$

is applicable to the data for neodymium chloride over the temperature range studied.

Concentration Effect.—For the wave length λ 5460.8 Å. the Verdet constants of the aluminum and neodymium chloride solutions were found to be a linear function of the concentration over the range studied. None of the other data give linear relationships, as may be seen by examination of Fig. 3.

The authors wish to express thanks to Dr. H. C. Fogg for advice regarding the purification of the rare earth salts.

Summary

The magnetic rotations of aqueous solutions of aluminum, lanthanum and neodymium chlorides have been measured from 10 to 50° at wave lengths λ 5893 and 5460.8 Å.

The Verdet constants of these solutions have been calculated and those for neodymium chloride solutions found to vary linearly with $1/T$.

The molecular rotations of the neodymium chloride solutions have been calculated and found to vary with temperature according to the equation $(T - 32.6)D = -790.1$.

The variations of the Verdet constants with temperature were found to agree qualitatively with the predictions of Serber.[6]

DURHAM, N. H. RECEIVED MAY 28, 1936

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[8] Mason and Leland, THIS JOURNAL, **57**, 1507 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Ionization Constant of Hydrazinium Hydroxide[1]

BY G. C. WARE, J. B. SPULNIK AND E. C. GILBERT

A systematic investigation of the ionization constant of hydrazinium hydroxide ("hydrazine hydrate"), its variation with temperature and with ionic strength, has never been reported. Bredig[2] measured the conductivity of aqueous solutions of hydrazine and calculated the ionization constant at 25°. He reported some difficulty due to decomposition and his values varied from 4.4 to 2.2×10^{-6} depending upon the concentration. The mean of these two, 3×10^{-6}, is the value commonly accepted and used in text and reference works, although the "International Critical Tables"[3] accepts the lower value 2.2×10^{-6}. Hughes using the glass electrode made a single measurement[4] and reported a value of 1.4–1.7×10^{-6} depending upon the interpretation of his results. Gilbert studied the equilibrium[5] between ammonia and hydrazine in aqueous solutions and obtained the ratio of the constants of the two bases at 20° and two ionic strengths. The method is not suitable for extension to a general study at various temperatures and concentrations such as made in the present investigation.

The work described in this paper was carried out by the use of the glass electrode. The highly reactive nature of hydrazine and its instability in the presence of platinum black makes it impossible to use the quinhydrone or hydrogen electrode satisfactorily. Furthermore, it is impossible for the same reason to use the ordinary reference electrodes (calomel, mercuric oxide, or silver chloride) except through the medium of a liquid junction or salt bridge. However, the recent important work of Guggenheim and Schindler[6] on cells with liquid junction justifies confidence in this type of measurement within certain limits. The method has moreover been applied recently for a similar study of hypochlorous acid.[7]

Experimental Part

The hydrogen ion activity of a series of solutions was determined, each containing exactly equivalent amounts of hydrazinium hydroxide and hydrazinium ion, the ionic strength being varied by the addition of potassium sulfate, sodium chloride or sodium perchlorate. Measurements were made at 15, 25 and 35°, using a vacuum tube potentiometer of the type devised by De Eds.[8] Considerably more shielding was found advisable than specified by De Eds. The following cell arrangement was used

$$\text{Hg, Hg}_2\text{Cl}_2\text{, KCl (0.1 }N\text{) | KCl (satd.) | unknown solution, glass, buffer | KCl (0.1 }N\text{), Hg}_2\text{Cl}_2\text{, Hg}$$

When a reading had been made with the "Unknown Solution" in the cell, this was replaced with a buffer of similar ionic strength whose hydrogen ion activity had been determined accurately by the use of a hydrogen electrode at the same temperature. From these quantities the hydrogen ion activity of the hydrazinium buffer may be calculated readily.[9] Voltage readings could be duplicated within 0.3–0.5 mv., corresponding to ±0.01 *p*H. Calculation of the liquid junction potentials by Henderson's formula[10] as recommended by Guggenheim and Schindler showed them to be less than the uncertainty in the voltage readings. The liquid junction was made with the type of salt bridge devised by Ingham and Morrison,[7] which proved to be highly reproducible if subject to careful temperature control. In measuring the *p*H of the standard buffers with the hydrogen electrode the value given by Guggenheim and Schindler,[6] 333.7 mv., was used for the 0.1 *N* calomel electrode at 25°, 334.2 at 15° and 332.9 at 35°.

The solutions were made by weight, adding the calculated amount of carbonate-free sodium hydroxide solution to hydrazinium perchlorate solutions or in one series by adding barium hydroxide to hydrazine sulfate. The barium hydroxide was standardized gravimetrically. The ionic strength was adjusted by the addition of neutral salts such as potassium sulfate, sodium chloride or perchlorate. The water was de-oxygenated and the solutions were protected from the atmosphere at all times. Readings were constant with the glass electrode and easily duplicated.

Results

In Table I are given the results of the measurements. At each temperature determinations were made at a series of salt concentrations permitting extrapolation to zero ionic strength. The measurements at 25° were repeated with different salts. In agreement with Brönsted's principle of specific ionic interaction the slopes of the curves for different salts were different but extrapolation led to the same value at zero ionic strength. The rather small salt effect observed

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[1] A portion of this paper is taken from a thesis submitted by J. B. Spulnik for the degree of Master of Science in June, 1935, at the Oregon State College.

[2] Bredig, *Z. physik. Chem.*, **13**, 289 (1894).

[3] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. VI, p. 260.

[4] Hughes, *J. Chem. Soc.*, 491 (1928).

[5] Gilbert, *J. Phys. Chem.*, **33**, 1236 (1929).

[6] Guggenheim and Schindler, *ibid.*, **38**, 533 (1934).

[7] Ingham and Morrison, *J. Chem. Soc.*, 1200 (1933).

[8] De Eds, *Science*, **78**, 556 (1933).

[9] Cobb and Gilbert, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 69 (1933).

[10] Henderson, *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908).

agrees with the predictions of Brönsted's extended theory of acids and bases, namely, that for bases of the ammonia type the dissociation constant should be little affected by salts.[11]

TABLE I

HYDROGEN ION ACTIVITY OF HYDRAZINIUM BUFFER SOLUTIONS[a]

(a) In presence of K_2SO_4

μ (total)	15°	25°	35°
0.000	8.24	7.99	7.82
.009	8.25	7.99	7.82
.029	8.24	7.99	7.82
.044	8.27	....	7.83
.095	8.30	8.02	7.87
.170	8.37	8.09	7.90

(b) In presence of NaCl

μ (total)	25°
0.000	7.99
.010	7.99
.050	8.00
.100	8.02
.150	8.04

(c) In presence of $NaClO_4$

μ (total)	25°
0.000	8.00
.010	8.00
.050	8.01
.100	8.02
.150	8.03

[a] Expressed as *p*H.

Since the experimentally determined quantity in this work is the hydrogen ion activity, the calculations follow more simply if made on the basis of treating the hydrazinium ion as an acid.

$$N_2H_5^+ \rightleftarrows N_2H_4 + H^+$$

then

$$(a_{N_2H_4}a_{H^+})/a_{N_2H_5^+} = K_A$$

and

$$pK_A = pH + \log (a_{N_2H_5^+}/a_{N_2H_4})$$

At zero ionic strength where $a_{N_2H_5^+} = m_{N_2H_5^+}$ and in an equimolal solution of N_2H_4 and $N_2H_5^+$ such as used in this work pK_A may be taken as equal to *p*H.

Values for K_A obtained in this manner are shown in Table II. Now from the ion product of water as recently accurately determined by Harned and Hamer[12] the corresponding conventional ionization constant of the hydrazinium hydroxide may be calculated since $K_B = K_w/K_A$. These values are also shown in Table II, together with the corresponding values for $\Delta F°$ for the basic ionization. The value for $\Delta H_{291\cdot1}$ calculated from these results is 3850 cal., which may be compared to the value 3950 cal. obtained calorimetrically by Bach.[13] This quantity has a very large temperature coefficient. Since different salts affect the ionization constant to a different degree, it is not possible to set up a general equation for the constant as a function of the ionic strength. The observed salt effect however is not large.

TABLE II

IONIZATION CONSTANT OF HYDRAZINIUM ION AS AN ACID, AND OF HYDRAZINIUM HYDROXIDE AS A BASE

	15°	25°	35°
$K_A \times 10^9$	5.75	10.2	15.2
$K_B \times 10^6$	0.785	0.984	1.37
$\Delta F°$, cal.	8052	8200	8270

The values which have been found are considerably lower than those commonly accepted. They are of course the extrapolated values as opposed to those which have previously been determined in the presence of salts.

Summary

The ionization constants for the hydrazinium ion as an acid and hydrazinium hydroxide as a base have been determined at 15, 25 and 35° from glass electrode measurements.

CORVALLIS, OREGON RECEIVED JUNE 22, 1936

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[11] Brönsted, *Chem. Rev.*, **5**, 281 (1928).

[12] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933).

[13] Bach, *Z. physik. Chem.*, **9**, 241 (1892).

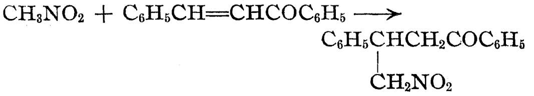
[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

Alcoholic Ammonia as a Reagent for Nitro Compounds and Unsaturated Ketones

BY DAVID E. WORRALL AND CYRIL J. BRADWAY

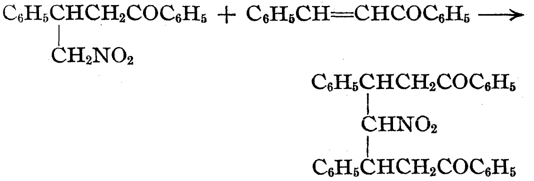
Although it has been known for some time that secondary amines[1] promote certain additions to unsaturated systems, the superior reactivity of sodium alcoholates has diverted attention from the use of such substances. Kohler[2] for example used sodium methylate to obtain a reaction between nitromethane and benzalacetophenone. Yet the organic bases possess some virtues and it has been shown recently[3] that ammonia causes the formation, through the interaction of nitrostilbene with nitro compounds, of substances otherwise inaccessible. We have now found ammonia useful with unsaturated ketones.

In the presence of sodium methylate a nitro ketone is eventually formed from benzalacetophenone and nitromethane.



$$CH_3NO_2 + C_6H_5CH{=}CHCOC_6H_5 \longrightarrow C_6H_5\underset{\begin{array}{c}|\\CH_2NO_2\end{array}}{CH}CH_2COC_6H_5 \quad \text{I}$$

It can also be obtained in the presence of ammonia, a reaction that we believe involves 1,4-addition of the ammonium salt of nitromethane followed by spontaneous decomposition into the enol of I. Since the latter still contains mobile hydrogen, it not only rearranges into I but tends to react with unchanged benzalacetophenone, repeating the cycle of changes.



$$C_6H_5\underset{\begin{array}{c}|\\CH_2NO_2\end{array}}{CH}CH_2COC_6H_5 + C_6H_5CH{=}CHCOC_6H_5 \longrightarrow \begin{array}{l}C_6H_5CHCH_2COC_6H_5 \quad \text{II}\\ \qquad\;\;|\\ \qquad CHNO_2\\ \qquad\;\;|\\ C_6H_5CHCH_2COC_6H_5\end{array}$$

Eventually I entirely disappears and a good yield of II results. Tertiary amines are effective and the presence of water promotes the reaction.

A number of trimolecular compounds have been synthesized (previously only one had been isolated),[4] using nitromethane with various unsaturated ketones. I may be used with derivatives of benzalacetophenone, thus producing nonsymmetrical combinations, but attempts to prepare trimolecular compounds from nitroethane or phenylnitromethane failed. Equally futile were attempts with unsaturated ketones prepared from *o*-substituted aldehydes.

Experimental

α,α′-Diphenyl-β,β′-dibenzoyldiethylnitromethane.—Ammonia gas, prepared by heating concd. aqueous ammonia solution, was bubbled into a mixture of 8 g. of nitromethane and 50 g. of benzalacetophenone in 250 cc. of ordinary ethyl alcohol until it was well saturated. The initial product separating out on standing overnight consisted largely of Kohler's compound. On longer standing the solution gradually acquired a dark red color due to the presence of a highly colored fluorescent substance, which after four to five days began to discolor the product. The process was interrupted at this point; yield of crude substance approximately 45 g. The substance was a mixture of two stereoisomers. It was extracted with hot toluene from which clumps of tiny needles melting at 229–230° separated on cooling.

Anal. Calcd. for $C_{31}H_{27}O_4N$: C, 78.0; H, 5.7. Found: C, 78.0; H, 5.5.

Several volumes of alcohol were added to the filtrate concentrated to a small volume. The resulting precipitate was recrystallized from hot alcohol, separating in feathery clusters of needles melting at 157–158°.

Anal. Calcd. for $C_{31}H_{27}O_4N$: C, 78.0; H, 5.7. Found: C, 78.0; H, 5.6.

The isomers are easily separated since the high melting form is insoluble in alcohol, while the other is very soluble in toluene. The low melting isomer was present in greater amount. Substitution of absolute alcohol resulted in a much poorer yield. On standing for a similar period of time excellent yields were obtained with diethylamine and piperidine, using the molar equivalent in each case. Primary amines (amylamine) were less satisfactory, while tertiary ethylamine was noticeably more sluggish in its action. It produced a substance unusually free from colored impurities. No reaction was observed with aniline.

α-Bromo-α,α′-diphenyl-β,β′-dibenzoyldiethylnitromethane was prepared in chloroform solution by the action of bromine in the presence of sunlight on the low melting isomer of II. The resulting oil after removal of solvent and all traces of hydrogen bromide by evaporation on the water-bath became crystalline on standing. It separated from alcohol solution in microscopic crystals melting rather indefinitely around 80° and easily becomes oily. We were unable further to purify the substance which was thought to represent a mixture of isomers as the analysis for bromine was satisfactory. A more tractable substance was obtained from the high melting isomer, brominating in nitrobenzene. The resulting mixture was filtered from unchanged material, steam distilled and the residue crystallized from hot alcohol. Small needles

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(1) Knoevenagel, *Ber.*, **27**, 2339 (1894).

(2) Kohler, THIS JOURNAL, **38**, 889 (1916).

(3) Worrall, *ibid.*, **57**, 2209 (1935).

(4) Kohler and Williams, *ibid.*, **41**, 1644 (1919).

TABLE I

β,β'-DIBENZOYLDIETHYLNITROMETHANE

	M. p., °C.	Formula	Analyses, % Calcd. C		Found C	
			C	H	C	H
α,α'-Dianisyl[a]	211–212	$C_{33}H_{31}O_6N$	73.8	5.8	73.5	5.8
α,α'-Dipiperonyl	192–193	$C_{33}H_{27}O_8N$	70.0	4.8	70.0	4.6
α,α'-Di-*p*-bromophenyl	239–240	$C_{31}H_{25}O_4NBr_2$	58.6	3.9	58.2	4.0
α,α'-Di-*p*-tolyl	209–210	$C_{33}H_{31}O_4N$	78.4	6.1	78.0	6.2
α,α'-Di-*m*-bromophenyl	200–201	$C_{31}H_{25}O_4NBr_2$	58.6	3.9	59.0	3.8
α,α'-Di-*m*-nitrophenyl	237–239	$C_{31}H_{25}O_8N_3$	65.6	4.4	65.8	4.5
α,α'-Dicinnamyl	216–218	$C_{35}H_{31}O_4N$	79.4	5.9	79.0	5.8
α-Phenyl-α'-anisyl	205–206	$C_{32}H_{29}O_5N$	75.7	5.7	75.5	5.8
α-Phenyl-α'-piperonyl	218–219	$C_{32}H_{27}O_6N$	73.7	5.2	73.5	5.2
α-Phenyl-α'-*m*-bromophenyl	227–228	$C_{31}H_{26}O_4NBr$	66.7	4.7	66.2	4.5
α-Phenyl-α'-*p*-tolyl	191–192	$C_{32}H_{28}O_4N$	78.4	5.7	77.9	5.9
α-Phenyl-α'-*m*-nitrophenyl	219–220	$C_{32}H_{26}O_6N_2$	71.2	5.0	70.9	5.0
α-Anisyl-α'-piperonyl	189–190	$C_{33}H_{29}O_7N$	71.9	5.4	71.5	5.5
α-Anisyl-α'-*p*-tolyl	196–197	$C_{33}H_{31}O_5N$	76.0	6.0	75.6	6.1
α-Piperonyl-α'-*m*-nitrophenyl	218–219	$C_{32}H_{26}O_8N_2$	67.8	4.6	67.9	4.5
α-Piperonyl-α'-*p*-tolyl	198–199	$C_{33}H_{30}O_6N$	73.9	5.6	73.6	5.5
α-Piperonyl-α'-*m*-bromophenyl	215–216	$C_{32}H_{26}O_6NBr$	64.0	4.3	63.6	4.4

[a] Oil separating out first discarded. After twelve days crystal formation started.

melting with decomposition and foaming at 241–242° separated.

Anal. Calcd. for $C_{31}H_{26}O_4NBr$: Br, 14.4. Found: Br, 14.2.

α,α' - Diphenyl - β,β' - dibenzoyldiethylbromonitromethane was prepared by the action of bromine on a cold methyl alcohol solution of II dissolved in sodium methylate. It was crystallized from a large volume of alcohol in the form of flat needles melting at 205–206°.

Anal. Calcd. for $C_{31}H_{26}O_4NBr$: Br, 14.4. Found: Br, 14.4.

Preparation and Properties of Trimolecular Addition Products.[5]—Unsaturated ketones obtained from anisaldehyde and other substituted aldehydes were prepared and allowed to react with nitromethane. These additions went much less readily in many cases than with benzalacetophenone and it was necessary to work with dilute solutions because of the insoluble character of the reactants. Consequently, only one substance was isolated as a rule. Non-symmetrical combinations were made by using I or similar compounds with unsaturated ketones of a different species. Thus benzalacetophenone was treated with the anisal compound corresponding to I. The reverse combination was much less suitable, hardly changing after standing for three weeks in alcohol saturated with ammonia. No evidence of reaction was obtained with the ketone prepared from *o*-chloro or *o*-nitrobenzaldehyde. This was also true using diethylamine or sodium methylate as a substitute for ammonia. The substances obtained were usually quite insoluble in alcohol, but crystallized from toluene or acetone–water mixture in small needles. When heated, these compounds melt with partial decomposition. The primary addition products of nitromethane with anisal and piperonalacetophenone, used as intermediates, have not previously been described. They were eventually obtained (Kohler's method) as needles melting respectively at 50–51° and 94–95°. The analyses agreed with the formula in each case.

The primary addition products of nitromethane with anisal and piperonalacetophenone, used as intermediates, have not previously been described. They were eventually obtained (Kohler's method) as needles melting respectively at 50–51° and 94–95°. The analyses agreed with the formula in each case.

Summary

It has been shown that nitromethane in the presence of alcoholic ammonia can be combined with two equivalents of the same or different unsaturated ketones of the benzalacetophenone type, producing nitro diketones.

MEDFORD, MASS. RECEIVED JUNE 29, 1936

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(5) The trimolecular compound from benzal-*p*-bromoacetophenone obtained by Kohler and Williams,[4] who did not give the melting point, was found to consist of a mixture of isomers, one soluble in alcohol and melting at 151–152°; the other, crystallized from toluene, melted at 218–219°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Reaction of Metal Halides with Acetylenic Grignard Reagents

BY JAMES P. DANEHY AND J. A. NIEUWLAND

That particular type of reaction between a Grignard reagent and a metal salt which involves the reduction of the salt and the coupling of the organic radicals was first observed by Bennet and Turner,[1] who treated phenylmagnesium bromide with chromic chloride in an attempt to prepare organochromium compounds of the type $RCrCl_2$. However, they obtained diphenyl and chromous chloride in almost theoretical yields.

$$2CrCl_3 + 2C_6H_5MgBr \longrightarrow C_6H_5\text{—}C_5H_6 + 2CrCl_2 + 2MgClBr$$

This reaction was extended by the original investigators and others,[2] who showed that it is general for many types of Grignard reagents as well as for most metal salts which can be reduced to lower salts or, in the case of iron and silver, to the free metal. The intermediate formation of organometallic compounds is indicated by the work of Reich and of Krause and Wendt,[3] who obtained phenyl-silver from phenylmagnesium bromide and silver halides. The phenyl-silver so formed underwent decomposition to silver and diphenyl. The ephemeral nature of such intermediates is emphasized by Job and Champetier[4] who, working with ferric chloride and phenylmagnesium bromide, attempted unsuccessfully to isolate intermediate organoiron compounds but stated that their existence is probable, particularly at low temperatures.

We have investigated the reaction between certain metal halides and acetylenic Grignard reagents in order, first, to determine whether or not the general reaction as just described is applicable to acetylenic Grignard reagents and, second, to seek corroborative evidence for the intermediate formation of organometallic compounds in reactions of this type.

Results

It was found that the general reaction is applicable to acetylenic Grignard reagents and that the action of cupric bromide on acetylenic Grignard reagents produces diacetylenes and cuprous bromide in good yields. In the case of phenylacetylenemagnesium bromide the addition of the stoichiometric amount of cupric bromide resulted in the formation of diphenyldiacetylene with a yield of 72%. A small amount of phenylacetylene was recovered from the hydrolyzed reaction mixture and the formation of no other products was observed.

When an equivalent amount of cupric bromide was added to *n*-butylacetylene magnesium bromide at 25° dibutyldiacetylene was obtained in 60% yield. In addition to the expected product a 7% yield of 1-bromo-1-hexyne was obtained. It was found that if the *n*-butylacetylene magnesium bromide was cooled to −5° by an ice–salt mixture and maintained at this temperature during the addition of the cupric bromide a 55% yield of dibutyldiacetylene was obtained and the yield of 1-bromo-1-hexyne was increased to 14%. Attempts to further increase the yield of 1-bromo-1-hexyne by maintaining the *n*-butylacetylene magnesium bromide at −33° (by immersing the reaction vessel in liquid ammonia) were unsuccessful since at this temperature no reaction takes place appreciably, even after four hours.

When cupric chloride was added to *n*-butylacetylene magnesium bromide at 25° dibutyldiacetylene was formed with a yield of 35%. No 1-chloro-1-hexyne was found but 5% of 1-bromo-1-hexyne was obtained in this case also. When cooling (−5°) was used the yield of 1-bromo-1-hexyne was increased by 2% and the yield of dibutyldiacetylene was found to be 30%. Cupric chloride, like cupric bromide, does not react appreciably with *n*-butylacetylene magnesium bromide at −33°. Cupric bromide reacts with *n*-butylacetylene magnesium chloride to yield dibutyldiacetylene (30%) and about 1% of 1-bromo-1-hexyne. Despite the variation of halogen in both Grignard reagent and salt no 1-chloro-1-hexyne was formed in any experiment. The behavior of ferric chloride toward the acetylenic Grignard reagent was similar to that of the copper halides, the yield of dibutyldiacetylene at 25° being 50%.

In no cases were higher boiling residues left; *n*-butylacetylene not accounted for as dibutyldi-

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[1] Bennet and Turner, *J. Chem. Soc.*, **105**, 1057 (1914).

[2] Krizewsky and Turner, *ibid.*, **115**, 559 (1919); Sakellarios and Kyrimis, *Ber.*, **57**, 322 (1924); Gilman and Kirby, *Rec. trav. chim.*, **48**, 155 (1929).

[3] Reich, *Compt. rend.*, **177**, 322 (1922); Krause and Wendt, *Ber.*, **56**, 2064 (1923).

[4] Job and Champetier, *Compt. rend.*, **189**, 1089 (1929).

acetylene and 1-bromo-1-hexyne was recovered as *n*-butylacetylene.

Since substituted silver acetylides are stable it was believed that the action of silver bromide on an acetylenic Grignard reagent would give a stable silver derivative. When butylacetylene magnesium bromide was treated with the calculated amount of silver bromide the reaction product was found to contain no dibutyldiacetylene whatsoever. Silver butylacetylide was obtained in 60% yield. This offers corroborative evidence that the first stage of reaction between a Grignard reagent and a metal halide in the type of reaction under consideration is the formation of an organometallic compound and, if the organometallic compound is sufficiently unstable, decomposition ensues.

Experimental

Materials.—The substituted acetylenes used in this work were prepared in liquid ammonia by the usual method. The metal halides used were of analytical reagent grade.

Preparation of Diphenyldiacetylene.—In a three-necked, one-liter flask equipped with a motor-driven, mercury-sealed stirrer, a reflux condenser and a dropping funnel, 0.4 mole of ethylmagnesium bromide was prepared. To this was added dropwise and with stirring 40 g. (0.4 mole) of phenylacetylene diluted with an equal volume of ether. The contents of the flask were refluxed on a water-bath for two hours to expel all ethane. In eight small portions 90 g. (0.4 mole) of cupric bromide was added with rapid stirring. Vigorous reaction occurred after each addition. When almost all the cupric bromide had been added the precipitation of a large amount of flocculated material occurred. It was found that the reaction was quite complete within fifteen minutes after the addition of all the cupric bromide; refluxing did not increase yields. Water was added slowly through the top of the reflux condenser until no further action occurred. The ether layer was separated from the sludge of cuprous bromide, dried over calcium chloride and the ether was evaporated under diminished pressure. The non-volatile residue consisted of 29 g. of diphenyldiacetylene and 3 g. of phenylacetylene. The diphenyldiacetylene was recrystallized from the minimum amount of boiling ethanol; m. p. 87°; 72% yield.

The technique was essentially the same for all experiments except that the dibutyldiacetylene (b. p. 104° at 8 mm.) and 1-bromo-1-hexyne (b. p. 46° at 26 mm.) were isolated by fractional distillation.

Preparation of Silver Butylacetylide.—The addition of 75 g. (0.4 mole) of silver bromide to the Grignard reagent made from 33 g. (0.4 mole) of *n*-butylacetylene resulted in the formation of 46 g. of crystalline silver butylacetylide (62% yield). The *n*-butylacetylene was regenerated from the silver butylacetylide by refluxing with twice the theoretical amount of aqueous potassium cyanide.

Summary

1. Acetylenic Grignard reagents react with cupric bromide, cupric chloride and ferric chloride to yield diacetylenes predominantly and some 1-bromo-1-alkyne.

2. Confirmatory evidence is given for the intermediate formation of organometallic compounds in all reactions of this type.

NOTRE DAME, INDIANA RECEIVED MAY 23, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Urethans as Local Anesthetics. III. Alkyl N-(8-Quinolyl) Carbamates

BY R. E. DAMSCHROEDER AND R. L. SHRINER

A study of *p*-aminophenyl urethans[1] showed that these compounds possessed high local anesthetic power, but were very irritating to the tissues. The irritation appeared to be associated with the *p*-phenylenediamine grouping and not with the urethan structure.[2] Since many different types of substituted quinolines exhibit local anesthetic action,[3] and are not especially irritating, it was thought that a combination of the quinoline nucleus with the urethan grouping would produce compounds with interesting pharmacological properties. Accordingly, a series of urethans derived from 8-aminoquinoline was prepared. These particular quinoline derivatives were chosen because the derivatives of 8-aminoquinoline, such as plasmoquin, are of value in treating malaria. Hence, these alkyl N-(8-quinolyl) carbamates would be of interest not only from a study of their local anesthetic action, but also because of the possibility of their antimalarial action.

8-Nitroquinoline was prepared by the Skraup reaction and reduced to 8-aminoquinoline. Treatment of the latter with alkyl chloroformates in the presence of saturated sodium carbonate solution produced the urethans.

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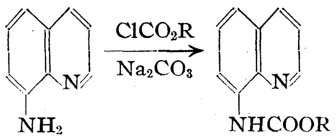
[1] Horne, Cox and Shriner, THIS JOURNAL, **55**, 3435 (1933).

[2] Ma and Shriner, *ibid.*, **56**, 1630 (1934).

[3] Hirschfelder and Bieter, *Physiol. Rev.*, **12**, 190 (1932); Miescher, *Helv. Chim. Acta* **15**, 163 (1932).



Since the bases were insoluble, they were converted to the hydrochlorides which were used for the pharmacological tests.

Experimental

8-Nitroquinoline and 8-Aminoquinoline.—The procedures described by Smith and Getz[4] were followed. The average yield on six runs was 37% of 8-aminoquinoline, (based on the *o*-nitroaniline used) melting at 64–65° and boiling at 159–161° at 16 mm.

Alkyl Chloroformates.—The series of alkyl chloroformates was prepared from phosgene and the anhydrous alcohols according to the method of Adams, Kamm and Marvel.[5]

Alkyl N-(8-Quinolyl) Carbamates.—Two methods were used in order to obtain the urethans. The first method consisted in adding a slight excess of alkyl chloroformate to an ether solution of 8-aminoquinoline. The mixture was vigorously stirred and the precipitate of 8-aminoquinoline hydrochloride was removed by filtration. The ether was distilled, and the residue recrystallized from absolute alcohol. By this method only half of the 8-aminoquinoline was used to form the urethan, and difficulty was experienced in obtaining complete reactions, even though the mixture was stirred for several days. Better yields were obtained when the reaction was carried out in the presence of sodium carbonate.

A solution of 10 g. of 8-aminoquinoline in 75 cc. of ether and 75 cc. of saturated sodium carbonate solution was placed in a flask and stirred vigorously. A very slight excess of the alkyl chloroformate was added slowly. The mixture was stirred until a test portion of the ether layer failed to give a precipitate of 8-aminoquinoline hydrochloride upon addition of hydrochloric acid. The ether layer was then separated, dried with sodium sulfate and the ether distilled. After recrystallization from absolute alcohol the pure bases were obtained. The lower alkyl chlorocarbonates gave 80–90% yields, but the yields dropped as the alkyl group increased in size, so that the yield of the *n*-hexyl derivative was only about 10%. The properties and analyses are given in Table I. The *n*-amyl, *i*-amyl and *n*-hexyl derivatives were oils which could not be crystallized. They were converted to the hydrochlorides for analysis.

TABLE I

ALKYL N-(8-QUINOLYL) CARBAMATES

Alkyl group	M. p., °C.	Mol. formula	Nitrogen analyses, % Calcd.	Found
Methyl	61.5–62.5	$C_{11}H_{10}O_2N_2$	13.84	14.05
Ethyl	66–67	$C_{12}H_{12}O_2N_2$	12.95	12.84
n-Propyl	58–59	$C_{13}H_{14}O_2N_2$	12.16	12.07
n-Butyl	40	$C_{14}H_{16}O_2N_2$	11.46	11.83
i-Butyl	69–70	$C_{14}H_{16}O_2N_2$	11.46	11.67
n-Amyl	Oil	$C_{15}H_{18}O_2N_2$	...	...
i-Amyl	Oil	$C_{15}H_{18}O_2N_2$	...	...
n-Hexyl	Oil	$C_{16}H_{20}O_2N_2$	...	...

Hydrochlorides.—The urethans were dissolved in anhydrous ether and the solution saturated with dry hydrogen chloride. The hydrochlorides precipitated at once as amorphous solids or viscous oils which solidified on stirring or standing. Recrystallization from absolute alcohol yielded the pure hydrochlorides as white or light yellow crystals. The salts hydrolyzed when dissolved in water and the free base precipitated. In order to obtain solutions for the pharmacological tests, it was necessary to add sufficient hydrochloric acid in order to prevent hydrolysis. The minimum normality of hydrochloric acid necessary to prevent separation of the free base is shown in Table II along with the analyses.

TABLE II

HYDROCHLORIDES OF ALKYL N-(8-QUINOLYL) CARBAMATES

Alkyl group	Minimum *N* of HCl for solution	M. p., °C. (dec.)	Chlorine analyses, % Calcd.	Found
Methyl	0.05	199–201	14.86	14.83
Ethyl	.09	165–166	14.04	14.02
n-Propyl	.19	156–157	13.30	12.83
n-Butyl	.35	146–149	12.63	11.98
i-Butyl	.7	155–165	12.63	12.33
n-Amyl	1.0	147–149	12.03	11.80
i-Amyl	1.0	149–152	12.03	11.72
n-Hexyl	1.0	145–147	11.50	12.21

Pharmacological Data

Through the courtesy of the Lilly Research Laboratories, the toxicity and local anesthetic action of the compounds shown in Table II were determined. The hydrochlorides were dissolved in the proper strength of hydrochloric acid, so as to obtain 1% solutions which were used for the tests. A brief summary of the essential data is given in Table III.

TABLE III

PHARMACOLOGICAL ACTION OF HYDROCHLORIDES OF ALKYL N-(8-QUINOLYL) CARBAMATES

Alkyl group	Toxicity Mice–intravenous, mg. per kg.	Anesthesia duration Rabbit eyes, min.	Guinea pig skin min.	Irritation rabbit eyes and rabbit skin
Methyl	65	None	56	
Ethyl	200	24	46	Severe
n-Propyl	100	None	None	Severe
n Butyl	70	None	None	Severe
i-Butyl	50	None	None	Severe
n-Amyl	70	None	None	Severe
i-Amyl	60	None	None	Severe
n-Hexyl	250	None	None	Severe

Examination of the data in Table III shows that these quinoline derivatives are not especially toxic as compared to other anesthetics, but that their local anesthetic effect is very low or absent. The severe irritation is undoubtedly due to the fact that the solutions tested were strongly acid,

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(4) Smith and Getz, *Chem. Rev.*, **16**, 114 (1935).

(5) Adams, Kamm and Marvel, "Organic Chem. Reagents I," *Univ. of Ill. Bull.*, **43**, 42 (1919).

the *p*H being between 1 and 2. The tests against the malarial parasite are not completed.

Summary

The hydrochlorides of a series of alkyl N-(8-quinolyl) carbamates in which the alkyl group was varied from methyl to *n*-hexyl were prepared and tested for their local anesthetic activity. The methyl and ethyl derivatives produced local anesthesia for a short time. All the compounds were irritating.

URBANA, ILLINOIS RECEIVED JUNE 15, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE OF THE COLLEGE OF THE CITY OF NEW YORK]

The Binary System Potassium Dichromate–Sodium Dichromate

BY ALEXANDER LEHRMAN, HARRY SELDITCH AND PHILIP SKELL

The literature lists no determination of the liquidus curve of the system potassium dichromate–sodium dichromate. These are two fairly stable compounds having low melting points as compared with most salts and there existed the possibility of a low temperature eutectic mixture which could be used as a bath liquid. Furthermore as potassium dichromate has a transition point at about 240° the system offered the possibility of detecting the formation of solid solution by a change in the transition point due to solid solution. Still further the melting point of sodium dichromate is recorded in the literature on the basis of a determination made in 1886.[1] The report of this early work does not state the method of purification of the salt, nor the method of determining the melting temperature. It was thought advisable to measure it with more modern instruments.

In the work being reported the points on the liquidus curve were determined by two methods. The first was that of thermal analysis using copper–constantan couples and a potentiometer. The second was that of observing the temperature on a thermometer when crystallization of a homogeneous melt started or when the last crystal of a previously melted and solidified mix disappeared. The melting point of sodium dichromate and the transition point of potassium dichromate were determined by thermal analysis using time–temperature and time–differential temperature curves.

Experimental

Materials.—The potassium dichromate was twice recrystallized from a filtered solution of the C. P. salt and then fused in an electric furnace which was kept just above the melting point of potassium dichromate. As potassium dichromate expands on passing through its transition point the tube containing the molten salt was tilted before solidification to an almost horizontal position to prevent cracking of the tube when the expansion took place. On changing crystal form and expanding, the solid mass disintegrates and was poured from the tube as a coarse powder. In separating the crystals from the mother liquid and in subsequent handling care was taken to avoid contact with organic material.

Sodium dichromate was prepared from C. P. hydrated salt by recrystallizing twice after rejecting the first crop of crystals.[2] The recrystallized hydrate was kept in a porcelain dish at 170° for eight hours in which time it was converted to the anhydrous salt. It was then fused in Pyrex tubes set in a furnace which was maintained at a temperature just above the melting point. The molten salt was poured into a porcelain dish and the resulting solid ground to a powder and kept over phosphorus pentoxide.

The mixtures were made by weighing by difference, the weights being taken to the nearest centigram. The salts were poured from the weighing tubes directly into the Pyrex test-tubes used for the determinations.

Apparatus.—The apparatus for thermal analysis consisted of a cylinder of electrolytic copper 7.6 cm. in diameter and 12.7 cm. high, having three drilled wells. Two of the wells held Pyrex test-tubes 2.5 × 20 cm., one of which contained the dichromates and the other shredded asbestos. A thin layer of asbestos paper surrounded the test-tubes and ensured a small temperature difference between the salt and the copper block when the temperature of the block was changing. The third well, much smaller in diameter, held a chromel–alumel couple which was connected with a millivoltmeter graduated to read in degrees centigrade. This was used for the convenience of knowing the temperature of the copper block. The cylinder fitted snugly into a resistance furnace which was only slightly lagged. A rheostat and ammeter in series permitted control of the rate of heating and cooling.

The temperature measuring system consisted of two copper–constantan couples (24 gage wire) combined in the well-known way to allow a reading of the temperature of the sample, and of the difference in temperature between the sample and the shredded asbestos hereafter referred to as ΔT. Leeds and Northrup potentiometer indicators

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[1] A. Stanley, *Chem. News*, **54**, 195 (1886).

[2] In connection with this see Nikitina, *Trans. Inst. Pure Reagents*, **9**, 161 (1930), and Richards and Kelley, THIS JOURNAL, **33** 847 (1911).

were used to read the e. m. f. produced. A switch made it possible to read both the temperature and ΔT on the same instrument, but generally two potentiometers were used. A second switch reversed polarity in the ΔT circuit. All leads were of the same copper wire as used in the couples and the switches were protected from radiation from the furnace. The cold junction was cracked ice in an unsilvered Dewar flask. With these potentiometers the e. m. f. could be estimated to 0.01 mv. for temperatures up to 313°. For higher temperatures the scale allowed estimation only to 0.5 mv. It is our opinion that the error in reading the potentiometer was within 0.2° on the lower scale and within 0.5° on the higher one. The same potentiometer was always used for the temperature measurement. The couples were held in a shield of small bore Pyrex tubing.

Method.—The mixed salts in a Pyrex tube were inserted in the copper cylinder and the temperature raised to above the melting point. The couple in the guard tube was inserted into the melted salt, used to stir the liquid and then held in the center of the liquid by a cork stopper at the top of the tube. The rate of cooling of the copper cylinder was set as desired and readings taken every one-half or full minute of the temperature, and on alternate half or full minutes of ΔT when desired. The time–ΔT curve proved valuable in many cases, such as determining the transition point, and the eutectic temperature where the original mixture differed greatly from the eutectic mixture and the eutectic halt was of small duration.

The couple was calibrated against the boiling point of water, the melting point of Bureau of Standards tin and of twice crystallized potassium nitrate,[3] and a curve of its deviation from the standard curve of Adams[4] was prepared. The deviation curve was found to be a straight line and the melting point of potassium dichromate determined using this curve was 397.4°, which agrees with the value 397.5° found by Roberts.[5] While the melting point of potassium dichromate is about 10° higher than the limit set for the copper–constantan couple by the standard tables, it was considered justifiable to extrapolate through this short range.

There was no stirring during the cooling of the melts and supercooling generally took place. To find the temperature at which crystallization would have started had supercooling not occurred, the cooling curve after crystallization had set in was extended back to its intersection with the cooling curve previous to crystallization. This point of intersection was taken as the initial crystallization point of the mix.

Sodium dichromate supercools much more than potassium dichromate. In one case pure sodium dichromate supercooled 40°. There was usually considerable supercooling at the eutectic point as well as at the temperature of initial crystallization, so much so in many cases that when crystallization of the second solid finally set in the temperature was so low that the heat of crystallization was insufficient to bring the temperature up to the eutectic point, and many of the runs resulted in useless curves. In the range between 15 and 45% of potassium dichromate it was impossible to get a melting point without stirring. Even inoculation by dropping in a crystal of sodium dichromate did not help as the rate of solidification was too slow. The melting point of 22.9% potassium dichromate was obtained by using the guard tube and the couple as a stirrer.

The melted dichromates form a very dark liquid, impossible to see through to more than a few millimeters. Accordingly, for visual determinations of the temperature of initial crystallization, small Pyrex test-tubes were used as the containers and of course smaller charges. With the thermometer inserted the liquid in the annular space was short in depth and with good light the appearance or disappearance of the crystals could be observed. A thin glass rod was used to stir the mixture. The test-tube was suspended in a kerosene lamp chimney and the flame of a Tirril burner kept a short distance below the lower end of the chimney.

A nitrogen-filled mercury thermometer (5 to 500°) was used. It was calibrated in the apparatus for the depth of immersion used in the dichromate mixtures against the copper–constantan couple used in the other portion of this work. The temperature of the appearance and disappearance of the crystals could be found on repeated trials within a range of 2°. Due to the stirring there was practically no supercooling.

Results.—Five determinations of the melting point of sodium dichromate using different batches of the purified compounds gave the following values: 356.4, 356.6, 356.9, 356.4 and 357.2°; average 356.7°. The error all things included is probably within ±1.0°. This value of the melting point of sodium dichromate is 36° higher than that obtained by Stanley[1] and chosen by the "I. C. T."[6] Table I contains the results of measurements on the binary system obtained by thermal analysis, Table II contains those obtained by the visual method. The values are plotted in Fig. 1.

TABLE I

M. P. OF $K_2Cr_2O_7$–$Na_2Cr_2O_7$ (BY THERMAL ANALYSIS)

% $K_2Cr_2O_7$	M. p., °C.	Eutectic temp., °C.
100.0	397.4	...
84.7	373	304
69.1	351	304.6
57.9	328	304
53.2	317	303
37.9	...	304.6
26.9	...	306
24.9	...	304
22.9	315	304.6
14.6	335	...
0.0	356.7	...

The transition point of pure potassium dichromate was sharply shown by the ΔT and cooling curves. The cooling curve itself gave only a

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(3) "I. C. T.," Vol. I, p. 155.

(4) "Pyrometric Practice," Bureau of Standards Technological Paper No. 170, p. 309.

(5) H. S. Roberts, *Phys. Rev.*, **23**, 386 (1924).

(6) "I. C. T.," Vol. I, p. 152 (referred to in error as the m. p. of $Na_2Cr_2O_7 \cdot 2H_2O$).

TABLE II

M. P. OF $K_2Cr_2O_7$–$Na_2Cr_2O_7$ (VISUAL METHOD-THERMOMETER)

% $K_2Cr_2O_7$	M. p., °C.	% $K_2Cr_2O_7$	M. p., °C.
85	372	45	311
72	351	37	303
61	333	29	310
50	316	21	320

slight inflection. This was to be expected, previous workers having shown the heat of transition to be quite small.[7,10,11] Two determinations on different batches of purified potassium dichromate gave the values 241.3 and 242.0°; average, 241.6° with an error probably within ±1.0°.

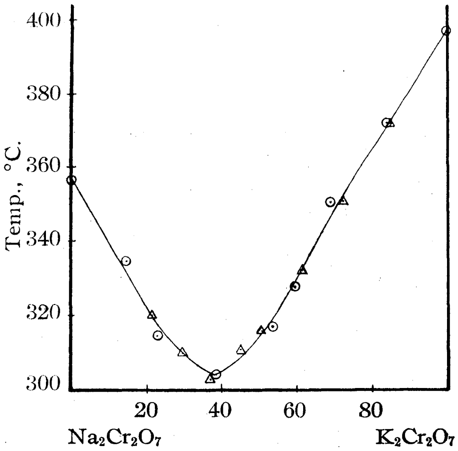

Fig. 1.—Liquidus of the $Na_2Cr_2O_7$–$K_2Cr_2O_7$ system: △, visual m. p.; ⊙, m. p. by thermal analysis.

This value is higher than any recorded in the literature and about 5° higher than the value chosen by the "I.C.T."[8] The most recent determination is that of Robinson, Stephenson and Briscoe.[9] They found the transition point to be 236.8° using a platinum resistance thermometer and 241° using a mercury thermometer. Their paper does not state the method of calibrating the resistance thermometer, nor of the purification of the potassium dichromate. Earlier determinations are those of Schemtschuschny, trans. p. 236°,[10] and Tammann, trans. p. 240°.[11]

No mixture of potassium and sodium dichromates used in determining the liquidus curve gave any indication of passing through a transition point between the eutectic temperature and room temperature. The ΔT curve showed no break and furthermore the solid masses formed around the thermocouple guard tube could be slid up and down the test-tubes after room temperature had been reached. When pure potassium dichromate was used the tube cracked due to expansion on passing through the transition. Robinson, Stephenson and Briscoe pointed out that the transition of potassium dichromate could be observed by dipping a rod into the molten salt, withdrawing the rod and letting it cool rapidly in the air.[9] At the transition point the adhering salt changes color, swells and cracks into minute pieces which drop off leaving the rod clean. This phenomenon was used to find approximately the minimum concentration of sodium dichromate needed to prevent the transition of potassium dichromate. A 10% sodium dichromate on cooling on the rod became lighter in a few spots, but the change in color did not travel through the mass, as it does in pure potassium dichromate. A 5% sodium dichromate mixture on cooling turned lighter throughout, the color change traveling slowly. The resulting mass however adhered to the rod though it crumbled off easily when touched.

Cooling and ΔT curves were determined for the 5% and a 2.3% sodium dichromate mixture. The tube containing the 5% mixture cracked when the temperature reached 202° but the curves did not indicate the position of a transition point. The 2.3% mixture in one run cracked the tube at 215° and gave a slight but inconclusive break in the ΔT curve at 221°. A second run on the same mixture did not result in a cracked tube and gave no break in the ΔT curve.

Discussion

This binary system is of the simple eutectic type. That no extensive solid solution takes place is shown by the presence of a eutectic halt for mixtures far removed in composition from the eutectic mixture.

The results of efforts to measure a change in the transition point of potassium dichromate due to possible solid solution are inconclusive. Probably a slight amount of solid solution takes place which lowers the transition temperature and also slows the rate of transition.

That the transition point of pure potassium dichromate obtained in this work is higher than the values obtained by previous investigators is

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(7) Mitscherlich, *Ann. Phys. Chem. Pogg.*, **28**, 120 (1833).

(8) "International Critical Tables," Vol. IV, p. 8.

(9) Robinson, Stephenson and Briscoe, *J. Chem. Soc.*, **127**, 547 (1925).

(10) Schemtschuschny, *Z. anorg. Chem.*, **57**, 267 (1908).

(11) Tammann, "Kristallisieren und Schmelsen," Leipzig, 1903, p. 262.

due probably to its detection by a differential temperature curve. It should be pointed out that one temperature used in standardizing the thermocouple was 231.9° (m. p. of Bureau of Standards tin) which is quite close to the temperature of the transition in question.

Résumé

The liquidus curve of the binary system potassium dichromate–sodium dichromate has been determined. It is of a simple eutectic type.

The melting point of sodium dichromate and the transition point of potassium dichromate have been redetermined.

The effect of the presence of sodium dichromate on the transition point of potassium dichromate has been noted.

NEW YORK, N. Y. RECEIVED JUNE 18, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

A Study of the Heat Capacity of Aqueous Solutions of Barium Chloride

BY CHESTER M. WHITE

Thomsen[1] measured the specific heat of barium chloride solutions at 18° while some years later Marignac[2] reported values at 24.5°. More recently Urban[3] has determined the specific heat at several temperatures for a number of solutions. Also Tippetts and Newton[4] have made e. m. f. measurements on barium amalgam cells at several temperatures from which differences in partial molal heat capacities may be calculated. By an indirect method Richards and Dole[5] have probably obtained the most precise data for barium chloride solutions, although the precision of their experiments is somewhat in doubt. Specific heats were redetermined for these solutions to provide precise results by the direct method. They will be useful as a test of recent theories of strong electrolytes for higher valence salts. The measurements were made with a twin adiabatic calorimeter.[6] While the general design of the apparatus was similar to that of Gucker,[7] the precision was of the order of 0.02%. This paper will stress the changes which were made in the construction and operation of the calorimeter to increase the precision to 0.01%.

Experimental

Modified Apparatus.—Figure 1 shows the construction of one of the calorimetric units. A threaded joint was used to secure the calorimeters in place. Internally threaded collars (A) and externally threaded rings (B) were cast of brass. These were sweated to the original annular rings (C) which were secured permanently to the studs on the calorimeter cover by four special nuts (D). Originally the calorimeters were sealed to the annular rings, but the ground joint was not water tight after being in use two years. A coating of litharge and glycerol was placed between the calorimeter cover and the ring so that the joint would be water tight. A coating of de Khotinsky cement (E) was placed around the outside of the joint as a further protection. The Dewar jars (F), which served as calorimeters, were sealed to the rings by litharge and glycerol.

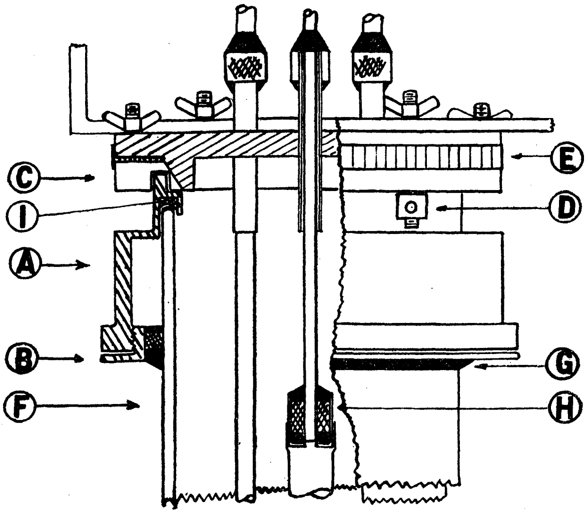

Fig. 1.—One unit of calorimeter.

After this mixture was dry, a 3.2-mm. coating of Bakelite cement (G) was applied above and below the litharge seal. After baking for a week at 60°, several coatings of Bakelite varnish were applied. The threads were lubricated with a water-proof grease, since the entire unit was submerged in water. The joint was entirely water tight during the entire series of measurements. A flat gasket (I) of soft rubber was fitted into the top of the collar so that the vapor

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[1] Thomsen, "Thermochemische Untersuchungen," Leipzig, 1882.

[2] Marignac, "Oeuvres Complètes," Eggiman, Geneva, Vol. II, 1902, p. 624.

[3] Urban, *J. Phys. Chem.*, **36**, 1108 (1932).

[4] Tippetts and Newton, THIS JOURNAL, **56**, 1575 (1934).

[5] Richards and Dole, *ibid.*, **51**, 794 (1929).

[6] Unpublished work of Hess and Gramkee; see B. E. Gramkee, Master's Thesis, University of Rochester Library, 1930.

[7] Gucker, THIS JOURNAL, **50**, 1005 (1928).

space in the calorimeters was fairly tight. Thus the method of securing the calorimeters in place was modified without dismantling the apparatus.

The calorimeter heaters were made along the same general plan as before. The heating elements were made of No. 30 bare constantan wire. At the ends of this wire 3.2-cm. pieces of No. 28 copper wire were soldered, to which the lead wires (No. 18 bell wire) were soldered.[8] The wire was wound bifilar on a slotted strip of mica. Thin protecting pieces of mica were tied with thread to the slotted strip and the whole was slipped into the case of the heater. The case was flattened and closed with a small amount of solder. The case[9] was of thin copper chromium plated. A copper sleeve (H) was soldered to the neck of the heater. There was a shoulder inside the sleeve to support the Pyrex tube through which the lead wires ran. Asbestos fibers were packed around the bottom of the tube and a layer of litharge and glycerol poured over them. When this was dry, a layer of Bakelite cement was applied. The insulation resistance of the heaters was measured by the Meggar.[10] Both heaters showed an infinite resistance between the case and either lead wire. The insulation resistances of the thermels were tested in the same way. The difference thermel (24 junctions) had an infinite resistance while the two adiabatic thermels (8 junctions each) showed resistance greater than 10 megohms.

In order to obtain an increased sensitivity without disturbing the thermels, Leeds and Northrup supplied a galvanometer with about five times the sensitivity of the original galvanometer but with the same damping resistance. The sensitivity with the difference thermel in series was 1.8 cm. μv (or 0.00006°/mm.). Since this galvanometer was more sensitive to vibrations, the simple Julius suspension was replaced by the improved type of Brevoort.[11] The entire suspension was enclosed by a double wall of shellacked paper to protect it from air currents.

It was found necessary to increase the speed of the calorimetric stirrers from 138 to 250 r. p. m. in order to establish thermal equilibrium in a relatively short time, fourteen minutes.

A large capacity Becker balance, which had a sensitivity of 3 mg. per scale division at 2000 g., was available for all but a few runs.

Materials, Constants, Molecular Weights, etc.—Baker C. P. barium chloride was used to make the solutions. The salt which was dehydrated at 120°[12] was always kept in the oven except when preparing the solutions. The usual precautions were taken in weighing the anhydrous material. A definite quantity of salt was added to a weighed amount of distilled water in the solution calorimeter. In some experiments a solution was weighed directly in the solution calorimeter. Its molality was determined by weighing the silver chloride residues and also by weighing the anhydrous salt after evaporation of the water. The results of these two methods were in good agreement.

The lithium chloride was Baker C. P. material. It was recrystallized three times from distilled water but was not analyzed for alkali chlorides.[13] The solution was made up and analyzed by weighing the silver chloride residues.

The molecular weight of barium chloride was calculated from the 1934 International Atomic Weight.[14] The heat capacities are expressed in 15° calories. The specific heat of water at 25° in 15° calories is taken as 0.9979.

Experimental Procedure.—In these experiments a 1° temperature interval was employed. The Beckmann thermometer was used to measure the rise in temperature. As a result of a careful comparison with a thermometer standardized by the Bureau of Standards, suitable corrections were applied to the total rise in each determination. The fore and after drifts, which were followed for forty minutes, were plotted in the usual way and a straight line was fitted to the linear portion of each drift by the method of averages.[15] The equations were used to extrapolate the drifts to the middle of the heating period. Equilibrium was usually established in 14 ± 4 min. for the after drifts following the cessation of the input of electrical energy. The atmospheric conditions were recorded for the purpose of reducing the weight of water in the solution calorimeter to the vacuum basis.

Water standardization and heat capacity runs were made at 24.5 and 25.5°. The specific heat in 25° calories was obtained by averaging the specific heat at 24.5 and 25.5° (in 24.5 and 25.5° calories). The averaged value was translated to 15° calories. Thus in each run the specific heat at 25° depends on two separate determinations (24.5 and 25.5°) and more confidence may be placed on the extrapolation of the drifts.

The tare always contained 700 g. of water (uncorr.). It would be better theoretically to correct the weight of water in the tare, but since the correction factor presented some difficulty, no account was taken of the change in the weight with atmospheric conditions. The maximum effect on the specific heat amounted to less than 0.003% in one experiment. The results at 24.5 and 25.5° are plotted in Fig. 2. The radius of the circle for each point represents a deviation of 0.005%. The weight of water in the solution calorimeter varied from 704 to 706 g. (uncorr.). The data at each temperature were fitted to a linear equation by the method of least squares. The equation was of the form

$$W = A + B\Delta G$$

where W is the weight of water and ΔG is the deflection of the galvanometer in cm. No runs were omitted at 24.5° while one run was cast out at 25.5° since its deviation was greater than four times the average deviation. The constants and the probable error at each temperature are given in Table I. The curves shown in Fig. 2 were determined by least squares.

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(8) This procedure, which has been used previously by (a) Randall and Rossini, THIS JOURNAL, **51**, 326 (1929), and (b) Gucker and Schminke, *ibid.*, **54**, 1358 (1932), simplifies the construction of these heaters.

(9) The cases were those used in the construction of the Cenco Lagless Knife Heaters and were supplied by the Central Scientific Company. Their length was cut to about 12.7 cm.

(10) The author is indebted to the Physics Department of the University of Rochester for the loan of this instrument.

(11) Brevoort, U. S. Bureau of Mines, Report of Investigations No. 3086.

(12) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928.

(13) Gucker and Schminke stated that this procedure diminishes the quantity of sodium and potassium chlorides to such amounts that they have a negligible effect on the specific heat.

(14) THIS JOURNAL, **56**, 753 (1934).

(15) Daniels, "Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Co., Inc., New York, 1928.

TABLE I

WATER STANDARDIZATION SUMMARY

Temperature, °C.	24.5	25.5
No. of runs	32	33
Water equivalent (A), g.	705.901	705.933
Sensitivity (B/10), g./mm.	0.048	0.049
Probable error, %	.007	.006

During the salt measurements a standardization run was made occasionally to test the integrity of the apparatus.

The apparatus in its original form had checked some of Randall and Rossini's data to 0.01%. Since several changes had been made in the construction and the operation of the calorimeter, it seemed advisable to compare the results of the modified apparatus with the recent precise results of Gucker and Schminke on lithium chloride solutions. The results in 25° calories are recorded in Table II.

TABLE II

SUMMARY OF RESULTS FOR LiCl SOLUTIONS AT 25°, MOLALITY 0.0492

Expt.	Soln., g.	ΔG(24.5) cm.	ΔG(25.5) cm.	Sp. heat, cal.$_{25}$ deg.$^{-1}$ g.$^{-1}$	Φ	Φ (calcd.)
R 2	707.735	−0.36	−0.39	0.99717	−14.8	−14.5
R 3	707.735	− .06	− .70	.99717	−14.8	
R 4	707.735	− .40	− .20	.99722	−13.8	
R 5	707.742	− .40	− .14	.99724	−13.3	

The average deviation for these runs is 0.003% and they check the curve of Gucker and Schminke to 0.003%, which is about half of his precision. Thus the results are in good agreement with Gucker's precise measurements. These determinations were performed after the work on barium chloride was completed so that they constitute an added check on their reliability.

Experimental Results

The specific heats for barium chloride solutions are summarized in Table III. The experiments are numbered in chronological order. All weights are *in vacuo*. The averaged value of ΔG_{25} is recorded in Table III for a one degree rise. The average difference between $\Delta G_{24.5}$ and $\Delta G_{25.5}$ is 1.5 mm. The maximum difference amounts to 6.9 mm. in one run. The empirical equations were used to calculate the equivalent weight from ΔG. The apparent molal heat capacity as well as the specific heat is tabulated. The maximum deviations from the nominal temperature of 25.00° change the specific heat by ±0.001% in three runs. One run was discarded from each of the series *D* (out of 3), K (out of 4) and M (out of 4), while three were discarded from series N (out of 6). In each case the average deviation was greater than four times the average with the questionable run omitted. As far as was known, nothing went wrong during these determinations but it was felt that they should be discarded for the above reason. The concentration of all these runs except D was below 0.01 molal.

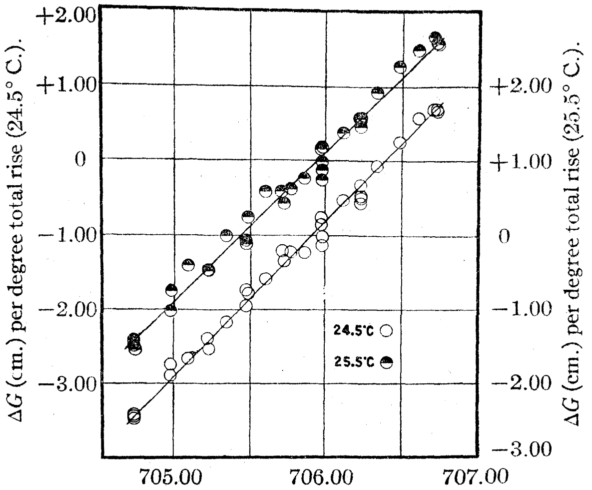

Fig. 2.—Calibration curves.

The so-called "evaporation error," which results from the substitution of a salt solution for the water in the solution calorimeter, depends on the lower vapor pressure and greater density of the salt solution. Because of the lack of vapor pressure measurements over a temperature range, it is difficult to correct for this effect in the case of barium chloride solutions. For an approximate calculation the vapor pressure lowering and density data in the "International Critical Tables" were used. The volume of the air space above the liquid level in the calorimeter was estimated at 265 cc. This error influenced the specific heats by about 0.003% at 0.5 molal. Thus, the above heat capacities need not be corrected for this effect.

The temperature difference for the two calorimeters was noted just before the heating current was stopped. It was usually about 0.007°, which compares favorably with Gucker's value of 0.005°.[7]

Two series of measurements were made at 0.12 molal (P and Q). The Q series was made by direct weighing of the salt in the usual manner, while in the P series an analyzed solution was weighed out directly in the solution calorimeter. While the Φ values differ by slightly more than 0.01% the average deviations are about large enough to account for this difference. Thus, it makes no difference by which method the solution is prepared.

TABLE III

SUMMARY OF RESULTS FOR BARIUM CHLORIDE SOLUTIONS

Expt.	Molality	Soln., g.	Av. ΔG_{25}, cm.	Sp. heat, cal.$_{15}$ deg.$^{-1}$ g.$^{-1}$	Φ
N3	0.0030	706.668	+0.49	0.99717	−35.8
N4	.0030	706.668	+ .37	.99709	−62.5
N5	.0030	706.675	+ .46	.99714	−45.8
M1	.0050	706.965	+ .06	.99646	−76.8
M2	.0050	706.986	+ .11	.99649	−70.8
M3	.0050	706.979	+ .18	.99652	−65.0
L1	.0072	707.272	− .07	.99593	−60.0
L2	.0072	707.272	+ .01	.99599	−57.9
L3	.0072	707.272	− .06	.99594	−64.8
K1	.0080	707.403	+ .02	.99581	−54.0
K2	.0080	707.403	− .19	.99571	−66.5
K3	.0080	707.410	− .02	.99572	−65.3
K4	.0080	707.410	− .07	.99579	−57.8
J1	.0090	707.556	− .12	.99552	−57.4
J2	.0090	707.557	− .10	.99552	−57.4
J3	.0090	707.550	− .25	.99543	−67.4
J4	.0090	707.543	− .10	.99554	−55.2
I1	.0100	708.184	+ .56	.99509	−73.9
I2	.0100	708.198	+ .60	.99510	−72.9
I3	.0100	708.198	+ .50	.99503	−79.9
I4	.0100	708.205	+ .77	.99521	−61.7
H1	.0200	708.670	−2.40	.99237	−70.1
H2	.0200	708.677	−2.22	.99250	−63.5
H3	.0200	708.677	−2.27	.99246	−65.6
H4	.0200	708.670	−2.10	.99258	−59.5
O1	.0200	708.670	−2.49	.99232	−72.6
O2	.0200	708.670	−2.53	.99229	−74.1
A1	.0300	711.143	−1.25	.98971	−67.3
A2	.0300	711.122	−1.19	.98979	−64.6
A3	.0300	711.115	−1.22	.98979	−64.6
B1	.0500	715.087	−0.92	.98449	−63.3
B2	.0500	715.087	−1.07	.99438	−63.5
C1	.0700	719.056	−0.65	.97923	−62.9
C2	.0700	719.049	− .79	.97914	−64.2
D1	.1000	725.524	+ .85	.97150	−61.8
D3	.1000	725.524	+ .81	.97148	−62.0
P1	.1200	729.520	− .92	.96630	−62.1
P2	.1200	729.521	−1.09	.96634	−61.7
P3	.1200	729.528	−0.96	.96625	−62.5
P4	.1200	729.506	−1.18	.96642	−61.1
Q1	.1196	729.512	+1.24	.96645	−61.6
Q2	.1199	729.505	+1.19	.96643	−61.2
Q3	.1199	729.512	+1.28	.96648	−60.8
Q4	.1199	729.512	+1.43	.96658	−59.9
E1	.1499	734.987	+0.81	.95896	−60.0
E2	.1499	734.980	+ .91	.95904	−59.5
F1	.1999	744.498	+1.32	.94705	−57.2
F2	.1999	744.483	+1.40	.94712	−56.8
G1	.2998	762.558	+0.47	.92585	−53.8
G2	.2998	762.565	+ .59	.92559	−53.5

Discussion

An equation was fitted to the heat capacities by the method of least squares. In dilute solution a given error in the specific heat produces a large percentage error in Φ, but the error rapidly diminishes as the concentration increases. It was felt that this difficulty would be largely eliminated if the curve was fitted to the ΔC_p values, since ΔC_p is defined as $m\ \Phi$.[16] The following equation was obtained

$$\Phi = -73.46 + 36.1\, m^{1/2}$$

with a probable error of 0.007%. An inspection of Fig. 3 will show the magnitude of the deviations of the experimental points from the empirical equation. The average value at each concentration and the empirical equation are plotted in Fig. 3. The dotted lines indicate an error of 0.01% from the straight line. The apparent molal heat capacities are adequately represented by the linear equation. The dotted lines indicate that large percentage errors in Φ occur below 0.01 molal. Several determinations were made at the same concentration for these very dilute solutions in the hope that the average value would yield some information as to the shape of the curve in this region. Since the results fall within the 0.01% band in a fairly random manner, they are in agreement with the linear equation.

It is a simple matter to calculate the partial molal heat capacity of the solvent and the solute from the empirical equation for Φ. The necessary thermodynamic equations which connect with $\overline{C}_{p_2}$ and $\overline{C}_{p_1}$ are given by Randall and Rossini. $\overline{C}_{p_2}$ curve is also plotted in Fig. 3.

The results of Richards and Dole (recalculated to cal.$_{15}$) are plotted in Fig. 3. This calculation was unnecessary for comparison with the present data, since the correction amounts to 0.003% at 0.3 molal. It reaches 0.007% at 1.0 molal. Their heat capacities were calculated from heats of dilution and specific heat measurements at two temperatures by the Person–Kirchoff relation. The curve for these results as drawn by Rossini[17] has a definite curvature at the higher concentrations. Richards and Dole pointed out in their paper that the specific heats of the $BaCl_2 \cdot 100H_2O$ might be in error by 0.05 to 0.1%. An error of 0.1% in the heat capacity of this solution would cause an error of 0.05% in the calculated specific heat at $BaCl_2 \cdot 200H_2O$. Therefore as the solutions become more dilute the original error decreases. If the procedure is reversed, an error of

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(16) This method of treatment was developed several years ago in connection with an unpublished research on the specific heat of sodium chloride solutions.

(17) Rossini, *Bur. Standards J. Research*, **4**, 313 (1930).

0.1% in $BaCl_2 \cdot 100H_2O$ will cause an error of 0.2% in $BaCl_2 \cdot 50H_2O$. This is their most concentrated solution. The curvature is established by the results at $BaCl_2 \cdot 50H_2O$ and $BaCl_2 \cdot 100H_2O$, which are the least precise. Therefore their data were fitted to a linear instead of a parabolic equation by the same procedure as mentioned above. The following equation was obtained

$$\Phi = -74.36 + 35.5m^{1/2}$$

with a probable error of 0.013%. This equation as well as the individual runs of Richards and Dole in dilute solution are in good agreement with the present data. The results of Marignac check the equations to about 0.1%, while the data of Urban show differences of the order of 0.5%.

Recently Tippetts and Newton reported relative partial molal heat contents which compared favorably with the values of Richards and Dole. Their $\bar{C}_{p_2} - \bar{C}^0_{p_2}$ values, however, did not agree with those calculated from Richards and Dole's or the present empirical equation. In Table IV values at several concentrations are compared for the three methods. It is evident that the e. m. f. measurements merely indicate the order of magnitude of the results—a fact which Tippetts and Newton recognized.

TABLE IV

A COMPARISON OF $\bar{C}_{p_2} - \bar{C}^0_{p_2}$ VALUES FROM THREE SOURCES

Molality	Heat capacities	Heat capacities and heats of dilution	E. m. f.
0.1	17.1	16.8	74
.3	29.7	29.2	96
.5	..	37.7	100
1.0	..	53.3	91

The e. m. f. measurements usually agree more closely with the calorimetric values than in this case.[18] The extrapolation of the e. m. f.'s to infinite dilution is eliminated when the results are expressed as $(\bar{C}_{p_2} - \bar{C}_{p_2})_{m = 0.05}$. While somewhat better agreement is obtained by this procedure, the e. m. f. values still differ by a factor of 2.

In Table V the slope of $\bar{C}_{p_2}$ curve for barium chloride is compared with the limiting value as predicted by the Debye–Hückel theory[8a] and the modified form which was put forth by La Mer and Cowperthwaite.[19] It is also interesting to compare the slopes of biunivalent and unibivalent salts. Present theories predict the same slope for both valence types. The values of sodium and potassium sulfate in the table were determined by Randall and Rossini.

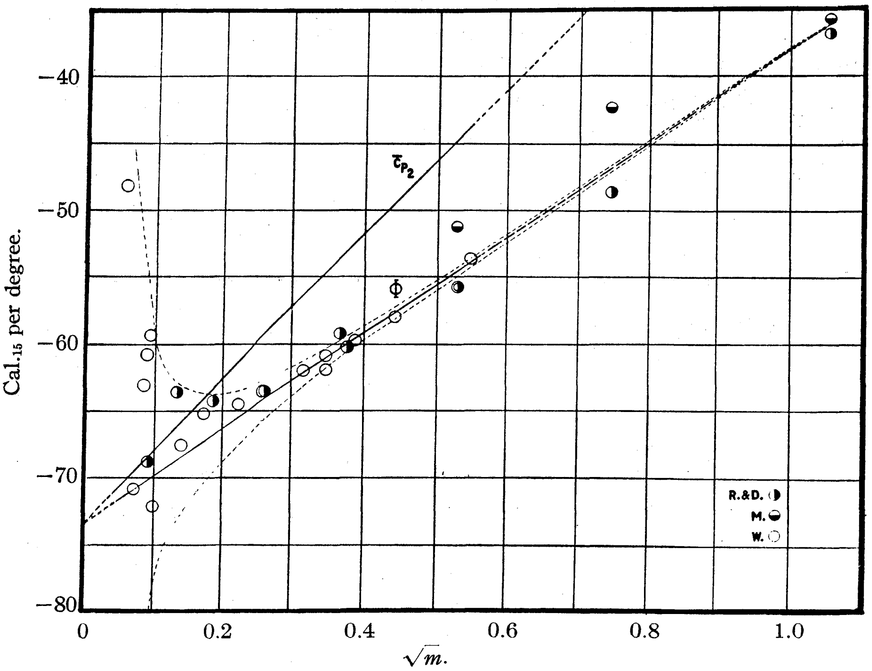

Fig. 3.—Apparent molal heat capacity (Φ) and partial molal heat capacity ($\bar{C}_{p_2}$) of barium chloride solutions.

TABLE V

COMPARISON OF THE SLOPE OF THE PARTIAL MOLAL HEAT CAPACITY CURVES WITH THE LIMITING VALUES

$BaCl_2$	Na_2SO_4	K_2SO_4	Debye–Hückel	La Mer and Cowperthwaite
54	76	62	31	69

The slopes of the three salts merely show the same order of magnitude, since the differences greatly exceed the precision of measurement. The barium chloride slope seems to agree with limiting value somewhat closer than the 1-2 salts and other uniunivalent electrolytes where the slopes are about three times the limiting value. Gulbransen and Robinson[20] have suggested that the

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(18) Harned and Hecker, THIS JOURNAL, **55**, 4838 (1933).

(19) La Mer and Cowperthwaite, *ibid.*, **55**, 1004 (1933).

(20) Gulbransen and Robinson, *ibid.*, **56**, 2637 (1934). The dilution measurements of these authors for sodium chloride have been recalculated recently by Young and Groenier, *ibid.*, **58**, 187 (1936). Their values of the slope differ from the theory by 5%.

rather good agreement for sodium chloride solutions with the La Mer and Cowperthwaite modification is "largely fortuitous." Because of the uncertainty in $f(DT)$ there is probably an error of 15 calories or more in the limiting value for a 2-1 salt. Although the present results were extended to 0.003 molar, the slope as given by the least squares is determined by runs in relatively concentrated solutions, where the theory is not applicable. As far as these theories are concerned specific heat measurements apparently cannot be used to verify the limiting law. When a theory is proposed for relatively concentrated solutions, the heat capacity data should be of value.

The author wishes to express his appreciation to Dr. A. A. Sunier for many helpful suggestions during the course of this work.

Summary

1. A twin adiabatic calorimeter was used to measure the heat capacity of barium chloride solutions from 0.003 to 0.3 molal at 25° with a precision of better than 0.01%.

2. The apparent molal heat capacity of the salt plotted against the square root of the molality follows the usual linear relationship. An empirical equation is given from which the apparent heat capacity and partial molal heat capacity of the solute, and the partial molal heat capacity of the solvent may be computed.

3. The present data have been shown to be in satisfactory agreement with the results of indirect determinations.

ROCHESTER, N. Y. RECEIVED MAY 18, 1936

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

A Study of the Heat Capacity of Aqueous Solutions of Urea and Mannite

BY CHESTER M. WHITE

Several investigators have studied the specific heat of solutions of electrolytes in a precise manner. Richards and his co-workers[1,2] have presented precise values for some weak electrolytes, but substances which are strictly non-electrolytic have been largely neglected in recent years. Some semi-precision results on amino acids were reported recently by Zittle and Schmidt.[3] The determinations reported in this paper were made with a view to supplying specific heats for such solutions with a precision of ±0.01%. The present work will be concerned with aqueous solutions of urea and mannite from 0.01 to 1.0 molal. Many years ago Magie[4,5] determined specific heats for both of these solutions at several concentrations. The precision of his experiments was believed to be about 0.05%. Recently Funzel, Burian and Haas[6] reported heat capacities at several temperatures for urea solutions from heats of dilution. Their precision was placed at ±0.1%. Apparently no other workers have reported measurements for urea or mannite solutions.

The experiments were performed with a previously described twin calorimeter.[7,8] No changes were made in the construction or method of operation of the calorimeter. The reader is referred to the previous paper for a complete description of the apparatus and the experimental technique.

Materials

Merck and E. K. Co. urea was used. It was twice recrystallized from methanol. After pulverizing, it was dried for two weeks at a temperature which was always maintained below 55° so that ammonium cyanate would not be formed. Shnidman and Sunier,[9] who had highly purified some urea for solubility determinations, kindly supplied the author with some of this material. The runs at 0.125 molal were made with this urea. Since these experiments were in satisfactory agreement with the other determinations, the above method of purification was sufficient for specific heat work.

The mannite, which was Pfanstiehl product, was thoroughly dried for all the runs. For some of the experiments it was recrystallized from distilled water and dried to constant weight at 130°. The experiments in which the purified mannite was used showed no substantial deviations from the other runs. The urea solutions were prepared by adding a known amount of solute to the solution calorimeter, which contained a weighed quantity of distilled water. Since a noticeable cooling effect takes place on the solution of mannite above 0.2 molal, the concentrated

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[1] Richards and Gucker, THIS JOURNAL, **51**, 712 (1929).

[2] Richards and Mair, *ibid.*, **51**, 740 (1929).

[3] Zittle and Schmidt, *J. Biol. Chem.*, **108**, 161 (1935).

[4] Magie, *Phys. Rev.*, **9**, 65 (1899).

[5] Magie, *ibid.*, **13**, 91 (1901).

[6] Funzel, Burian and Haas, *Z. Elektrochem.*, **41**, 419 (1935).

[7] White, THIS JOURNAL, **58**, 1615 (1936).

[8] Unpublished work of Hess and Gramkee.

[9] Shnidman and Sunier, *J. Phys. Chem.*, **36**, 1232 (1932).

solutions had to be prepared in a flask and a portion of this solution was weighed in the solution calorimeter.

Experimental Results

In Tables I and II the results are summarized for the urea and mannite solutions. The deviations from 25.00° were such that no corrections to the specific heat were necessary. The experiments are numbered in chronological order. All weights are on the vacuum basis. The 1935 atomic weights were used. The molality is expressed in moles per 1000.0 g. of water. ΔG is the galvanometer deflection which corresponds to a 1° rise. The average of $\Delta G_{24.5}$ and $\Delta G_{25.5}$ is given in the table. These two values differed by 1.4 mm. on the average. The maximum difference amounted to 6.6 mm. in one run. The equivalent weights of water were calculated from the empirical equations given in the previous paper.[7] Water standardizations were made frequently during the course of the experiments. These runs did not show deviations greater than ±0.01% from the linear equations. The specific heats are given in 15° calories. The specific heat of water was taken as 0.9979 at 25°. The apparent molal heat capacity Φ was calculated in the manner described by Randall and Rossini.[10] The magnitude of the "evaporation error" is less than 0.001% at 1.0 molal with a vapor space of 265 cc. Thus, no correction is necessary for this effect.

TABLE I

SUMMARY OF RESULTS FOR UREA SOLUTIONS

Expt. no.	Molality	Solution, g.	Av. ΔG_{25}, cm.	Sp. heat, cal.$_{15}$ deg.$^{-1}$ g.$^{-1}$	Φ
6A	0.0100	705.635	−1.24	0.99745	+14.8
B	.0100	705.635	−1.38	.99735	+ 4.8
5A	.0300	706.186	−0.90	.99691	+26.8
B	.0300	706.186	− .93	.99688	+25.8
1A	.0500	706.819	− .85	.99604	+22.6
B	.0500	706.819	− .78	.99609	+23.6
2A	.1000	707.928	−1.26	.99420	+21.2
B	.1000	707.928	−1.29	.99420	+21.2
11A	.1250	708.990	−0.90	.99296	+20.0
B	.1250	708.997	− .82	.99301	+20.4
3A	.1522	709.626	− .80	.99214	+21.7
B	.1522	709.640	− .68	.99221	+22.2
4A	.1998	711.147	− .40	.99029	+21.3
B	.1998	711.140	− .31	.99037	+21.7
7A	.2997	714.333	+ .81	.98669	+21.8
B	.2997	714.340	+ .61	.98654	+21.3
8B	.5000	719.659	+ .57	.97923	+21.4
B	.4995	719.652	+ .69	.97933	+21.6
9A	.6993	724.885	+1.07	.97250	+22.0
B	.6993	724.899	+1.06	.97248	+22.0
10A	.9990	731.573	−0.64	.96248	+22.25
B	.9990	731.573	− .69	.96245	+22.26

TABLE II

SUMMARY OF RESULTS FOR MANNITE SOLUTIONS AT 25°

Expt. no.	Molality	Solution, g.	Av. ΔG_{25}, cm.	Sp. heat, cal.$_{15}$ deg.$^{-1}$ g.$^{-1}$	Φ
9A	0.0100	706.014	−1.13	0.99699	+90.5
B	.0100	706.014	−1.13	.99699	+90.5
10A	.0200	706.794	−0.53	.99630	+101.4
B	.0200	706.794	− .60	.99625	+98.9
1A	.0300	707.558	− .05	.99555	+102.9
B	.0300	707.558	− .06	.99555	+102.9
2A	.0500	709.101	+ .96	.99408	+104.6
B	.0500	709.101	+1.16	.99422	+105.4
3A	.0699	709.630	+0.16	.99273	+106.9
B	.0699	709.630	+ .19	.99281	+108.0
4A	.1000	710.900	− .52	.99056	+106.9
B	.1000	710.906	− .77	.99044	+105.7
C	.1000	710.957	− .51	.99049	+106.2
5A	.1500	713.662	− .32	.98685	+106.0
B	.1500	713.683	− .34	.98681	+105.7
6A	.1998	716.360	+ .22	.98350	+107.0
B	.1998	716.367	+ .21	.98354	+107.2
7A	.2997	721.553	+ .57	.97665	+107.0
B	.2997	721.553	+ .46	.97658	+106.7
8A	.5002	730.946	− .16	.96362	+107.2
B	.5002	730.946	− .19	.96357	+107.1
11A	.6997	740.355	+1.05	.95218	+108.1
B	.6997	740.343	+1.05	.95219	+108.1
12A	.9995	753.107	+0.78	.93588	+108.4
B	.9995	753.107	+ .67	.93581	+108.3

The heat capacities, expressed as ΔC_p, were fitted to an empirical equation by least squares. The constants and the probable error of an individual run from the equation are given in Table III for the two non-electrolytes.

TABLE III

CONSTANTS AND PROBABLE ERRORS FOR LINEAR EQUATIONS

Solute	Urea	Mannite
Intercept (A)	20.52	105.16
Slope (B)	1.72	3.23
Probable error (cal.)	±0.065	±0.069

The individual determinations of Φ are plotted against the $\sqrt{m}$ for urea and mannite solutions in Figs. 1 and 2, respectively. The least square curves are also plotted and the dotted lines indicate an error of ±0.01% from the linear equation. An inspection of Figs. 1 and 2 will indicate the magnitude of the deviations of the experimental points from the empirical equations.

The relation between the partial molal heat

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[10] Randall and Rossini, THIS JOURNAL, **51**, 326 (1929).

capacity of the solute (or the solvent) and the apparent molal heat capacity has been derived by Randall and Rossini. It is only necessary to differentiate the empirical equation for Φ and substitute in their equation to obtain an expression for the variations of $\bar{C}_{p_2}$ (or $\bar{C}_{p_1}$) with m. The following empirical expressions were obtained for the partial molal quantities.

UREA

$$\bar{C}_{p2} = 20.52 + 2.58\, m^{1/2}$$
$$\bar{C}_{p1} - \bar{C}^0_{p1} = -0.0154\, m^{3/2}$$

MANNITE

$$\bar{C}_{p2} = 105.16 + 4.85\, m^{1/2}$$
$$\bar{C}_{p1} - \bar{C}^0_{p1} = -0.0291\, m^{3/2}$$

The $\bar{C}_{p_2}$ curves for urea and mannite are also plotted in Figs. 1 and 2, respectively.

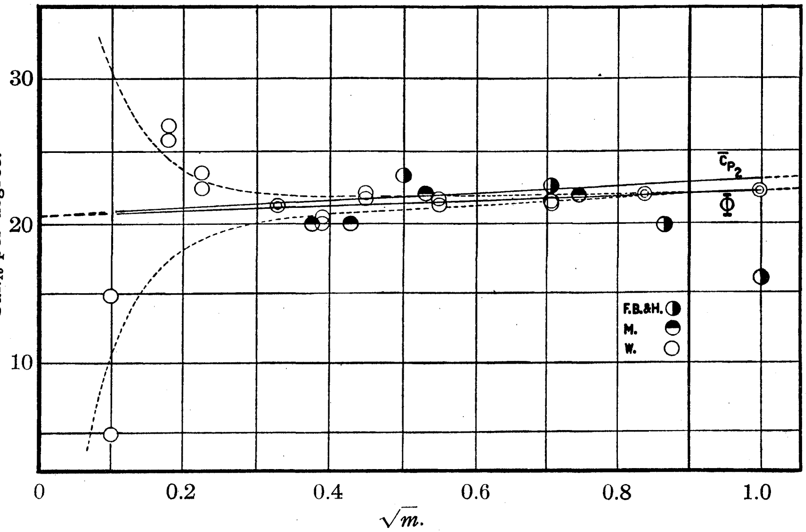

Fig. 1.—Apparent molal heat capacity (Φ) and partial molal heat capacity ($\bar{C}_{p2}$) of urea solutions.

The data of Magie[4] for urea solutions are also plotted in Fig. 1. These values are in excellent agreement with the present results since the average deviation of the points from the empirical equation is about 0.02%. The recent results of Funzel, Burian and Haas, which were determined with a precision of ±0.01%, are shown in Fig. 1. The plotted values of Φ were calculated from the specific heats at 24° (without converting to 25°) and the specific heat of water which they used. The average deviation of the Φ values from the empirical equation is 0.2%. In view of their precision of measurement the agreement with the present data is satisfactory.

Magie[4,5] is apparently the only worker who has studied mannite solutions. His results are plotted in Fig. 2. They appear to be in good agreement with the present data except for three points which differ from the empirical equation by 0.1 to 0.3%. Magie pointed out in the first paper that these three determinations were probably in error. The points, which show deviations of only 0.05% from the equation, were published in the second paper. While Magie does not record the temperature of his experiments he gives a quantity which is equivalent to Φ. This uncertainty in the temperature introduces an insignificant error in the Φ values.

It is apparent from the plots that the Φ values for urea are equally distributed about the linear equations in dilute solution. The mannite solutions show a break at 0.06 m below which the apparent molal heat capacities decrease. However, it is evident that the deviations are equal to the probable experimental error so that no importance may be attached to them. If the lowest points had been discarded in the least square calculation, the slope of the equation would not be substantially altered.

It is interesting to compare the extrapolated intercept of the $\bar{C}_{p_2}$ (or Φ) curve with the molal heat capacity of the solute in the pure state (c_p). c_p for crystalline urea and mannite at 25° are 19.2 and 58.3 cal., respectively. $\bar{C}^0_{p_2}$ for urea is in very close agreement with c_p. In the case of mannite there is an appreciable difference. It is interesting to note that this deviation is positive while all electrolytes show negative deviations from c_p. Presumably the intercepts for the two types of compounds are equally uncertain because of the extrapolation from 0.01 m to zero concentration which has been shown for electrolytes, at least, to be a questionable procedure. Edsall[11] has suggested that non-electrolytes which possess polar groups have Φ values which approximate rather closely the heat capacity of the pure solid while a single polar group attached to a long hydrocarbon chain yields Φ values which show positive deviations from c_p.

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(11) Edsall, THIS JOURNAL, **57**, 1506 (1935).

Because of the lack of data for these solutions, his conclusions were based on results at various concentrations. Since these rules are expected to apply in concentrated solution, it is suggested that the apparent value of $\overline{C}^0_{p_2}$ be used. On this basis the present results for urea follow his rule while those for mannite do not. Edsall found that the available data for glycerol, which is also a polyhydric alcohol, are in satisfactory agreement with the theory at 1 m. Obviously more data must be obtained before the validity of these rules may be tested.[12]

In the derivation of the theoretical slope of the C_{p_2} curves for electrolytes from the Debye–Hückel theory, Randall and Rossini considered that the free energy change, on passing from a definite concentration to the infinitely dilute solution, was composed of the part due to the ions taken as ideal solutes and the part due to the effect of the charged ions. For non-electrolytes the second term is zero and the total free energy is given by $RL \ln c$. The second derivative of this expression with respect to the temperature is zero. Thus Φ or $\overline{C}_{p_2}$ would be independent of the concentration. Zwicky[13] is led to the same conclusion on the basis of his theory. The present results for urea and mannite show small but appreciable slopes. Gucker[14] has shown that the apparent molal volume and compressibility for urea solutions also have small slopes when plotted against the $\sqrt{c}$. Apparently these properties have not been studied for mannite solutions. It should not be implied that all non-electrolytes have small slopes because Gucker has shown that Φ (V) and Φ (K) for sucrose solutions have slopes equal to a 2-1 electrolyte. These properties have been studied over a wide range of concentration and very definitely follow a linear equation when plotted against $\sqrt{c}$. Since the apparent molal heat capacities in the present paper cover a relatively limited range of concentration and change only slightly with m, it is difficult to determine whether the Φ values for urea and mannite are strictly proportional to $\sqrt{m}$ or to m itself. On the basis of these results it may be said that they seem to cluster more closely about a straight line when plotted against $\sqrt{m}$.

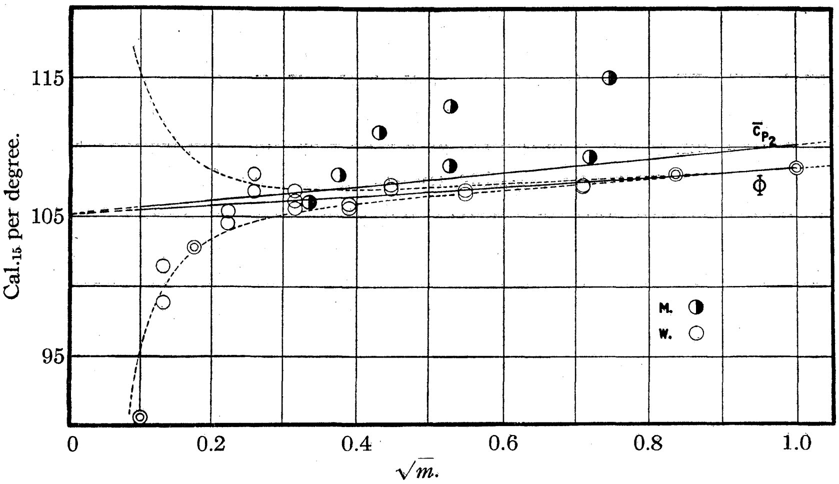

Fig. 2.—Apparent molal heat capacity (Φ) and partial molal heat capacity ($\overline{C}_{p_2}$) of mannite solutions.

The author wishes to thank Professor A. A. Sunier for suggesting the problem and for his helpful suggestions in the preparation of the manuscript.

Summary

1. The twin adiabatic calorimeter method was used to determine the specific heats of aqueous solutions of urea and mannite at 25° from 0.01 to 1.0 m with a precision of ±0.01%.

2. The apparent molal heat capacities were calculated and they seem to follow a linear equation when plotted against the $\sqrt{m}$. The intercepts are positive and the slopes are small for these solutes. Empirical equations are given for the apparent and the partial molal heat capacities of the solutes and the relative partial molal heat capacity of the solvent.

ROCHESTER, N. Y. RECEIVED MAY 18, 1936

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[12] The reviewer of the paper suggested that $\overline{C}^0_{p_2}$ for an ideal solution would be more nearly equal to the heat capacity of the pure liquid.

[13] Zwicky, *Physik. Z.*, **27**, 271 (1926).

[14] Gucker, *Chem. Rev.*, **13**, 111 (1933).

[Contribution from the Chemical Laboratory of Harvard University]

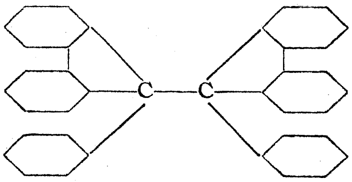
Single Bond Energies. III. The C–C Bond in Diphenyl Di-biphenylene Ethane

By H. E. Bent and J. E. Cline

The first two papers of this series give an answer to a question regarding the strength of the C–C bond in hexaphenylethane.[1] Until the approach to the problem with the aid of wave mechanics it had been assumed that the C–C bond is weak in those ethanes which dissociate to give free radicals. Quite the opposite point of view has been suggested by Pauling and Wheland[2a] and by Hückel.[2b] These authors assume that the C–C bond is normal and that dissociation is caused by a stabilization of the free radical as a result of the resonance energy made possible by the presence of an odd electron and the unsaturated structures in the benzene rings. The evidence presented from a study of the heat of oxidation and the heat of hydrogenation of hexaphenylethane leads to the conclusion that neither point of view is entirely correct but that about half of the "*apparent*" weakening of the C–C bond is due to a weakening of the bond in the ethane. We have assumed that this bond is weaker than normal on account of steric hindrance.

Many problems are suggested by these experiments. The one with which we wish to deal in this paper is the question as to what extent variation in the degree of dissociation of various ethanes is due to differences in steric hindrance in the ethane and to what extent due to different amounts of resonance energy in the various free radicals.

Diphenyl di-biphenylene ethane is chosen for this study on account of its remarkable properties.



Although very closely related to hexaphenylethane it exhibits a very different behavior. The loss of four hydrogens and tying together of the benzene rings produces an ethane which dissociates much less than hexaphenylethane. Pauling and Wheland have accounted for this decreased dissociation by a smaller amount of resonance energy in the free radical. Conant[3] has pointed out the striking difference between the properties of phenyl xanthyl and phenyl fluoryl. In one case the benzene rings are tied together by means of oxygen and in the other case are tied together directly. Yet phenyl xanthyl is less associated than triphenylmethyl and phenyl fluoryl is more associated. If one constructs models for these free radicals it becomes apparent that steric hindrance might be much less in the case of phenyl fluoryl. We therefore wished to compare experimentally the strength of the C–C bond in diphenyl di-biphenylene ethane with the bond in hexaphenylethane. In the first two papers of this series we evaluated the strength of the C–C bond by making use of Pauling's single bond energies. For the purpose of the comparison which we now propose to make it is not necessary to know any values for single bond energies. We may interpret our experimental results with the aid of the assumption that the strength of the C–O and O–O bonds in the various peroxides formed is the same.

Another reason for studying the heat of oxygenation of this particular compound arose in connection with the determination of the free energy of addition of sodium to diphenyl di-biphenylene ethane. These experiments indicated that the free energy of addition of sodium to phenyl fluoryl is more negative than in the case of triphenylmethyl by about 12 kcal.[4] This was a very unexpected result since Wheland has suggested from theoretical considerations that the electron affinity as a first approximation should be a constant for organic free radicals. His conclusion is quite in accord with experimental investigations of these compounds.[5] If the resonance energy of phenyl fluoryl is large, then steric hindrance must be very small in order to give a compound which is only very slightly dissociated. A small steric effect should lead to a stronger C–C bond and hence a much lower heat of oxidation.

Experimental

The apparatus has been considerably improved and changed in a number of important respects since the work

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[1] Bent, Cuthbertson, Dorfman and Leary, This Journal, **58**, 165 (1936); Bent and Cuthbertson, *ibid.*, **58**, 170 (1936).

[2] (a) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933); (b) Hückel, *Z. Physik*, **83**, 632 (1933).

[3] Conant, *J. Chem. Phys.*, **1**, 427 (1933).

[4] Bent and Keevil, This Journal, **58**, 1367 (1936).

[5] Dorfman, *ibid.*, **57**, 1455 (1935).

reported in the first papers of this series. The purpose of these modifications is to increase the ruggedness and permanence of the apparatus and reduce the number of materials in contact with the liquid or vapor in the reaction vessel. In the earlier apparatus cement was used at various points and thermocouple wires and heater leads were not only exposed to the vapor of the solvent but also subjected to mechanical motion when the capsule was broken. In the present apparatus all wires are enclosed in glass with the exception of the platinum heater wire and a silver lead which may be changed to platinum if desired. No cement is used to hold the heater wire in place or at other points in the apparatus. We are now quite free from any possible solvent action and can use the apparatus for chlorination if desired.

In order to save space only the changes in the apparatus will be mentioned and the figure given in the first paper of this series will be used for reference. The chief alteration consisted in sealing the tube which carries the thermocouple and the heater to the stationary tube above the ground joint "D." Two ring seals are used for this purpose, one just below the tube marked "C" in the original figure and the other just above this side tube. The thermocouple leads then pass through this side tube and down through an annular space to the bottom. The annular space is necessary in order that the magnet may now move a glass rod which passes through the whole length of the apparatus and pushes the capsule "J" out at the bottom and breaks it on the Dewar. The lower side tube, at the left in the original figure, is now used for the heater leads which are sealed through the glass by the method of Cox, Kraus and Fuoss.[6] We have used No. 22 silver wire for part of the lead. The heater has a resistance of 17.845 ohms and is made by winding No. 40 platinum wire on glass supports which hold it out about 1 mm. from the glass tube. This is accomplished by first sealing eight pieces of glass rod 1.8 cm. long and 1 mm. in diameter to the bottom of the tube. Tiny dots of glass are then fused to these rods and the wire wound between the glass dots. By using alternate spaces in winding the wire down from the top the two ends can be anchored at the top and crossing of the wire avoided.

The electrical measurements have also been considerably improved since the report of earlier work. All measurements of temperature and current are made with the aid of a type K potentiometer. By means of appropriate switches the potentiometer can be connected to the thermocouple for the measurement of temperature or to the heater, with the aid of a potential divider, to determine the potential drop across the latter. Another switch connects the potentiometer to a standard resistance in series with the heater, this potential drop giving a measure of the current.

The use of platinum as a heater made necessary an automatic control of the energy input on account of the change in resistance of the platinum with temperature. This is accomplished by putting in series with the heater an external resistance of the same size. The latter coil is made from 13.7 meters (45 ft.) of No. 22 Advance wire which has a very small temperature coefficient and is wound without a core in order to dissipate heat rapidly. This arrangement maintains the energy input constant with a fluctuating resistance provided the voltage supply is constant. This can easily be shown to be true as a first approximation and is due to the fact that as the resistance of the heater increases the current decreases but this is appropriately compensated by an increase in the potential drop across the heater. By measuring the resistance of the heater we were able to calculate its rise in temperature above that of the solvent. Using a current of 0.2 amp. we find the rise in temperature to be about one degree, and the increase in resistance to be about 0.3%. An increase in resistance of 1.0% would have caused a decrease in the power input of only 0.002%. Appropriate calculations of heat loss by thermal conduction in the lead wires indicate that this factor introduces less than 0.2% error. The method of calibrating the apparatus electrically at the end of each run takes care of all constant heat losses.

Materials

Diphenyl Di-biphenylene Ethane.—Phenylbiphenylene carbinol was first prepared according to the directions of Ullmann and von Wurstemberger.[7] This was converted to the chloride according to the method of Gomberg and Cone[8] and the chloride converted to the ethane using the procedure of Dorfman.[5] Since the ethane is much less soluble than the chloride or carbinol, which might be present as impurity, crystallization of the ethane from benzene and washing with solvent gave material of satisfactory purity.

Tetraphenyl Di-α-naphthyl Ethane.—Diphenyl α-naphthyl chloromethane was prepared according to the directions of Halford for preparing triphenyl chloromethane.[9] The chloride was converted to the free radical with lead amalgam using the procedure of Dorfman as for the previous compound.

Experimental Results

Table I gives the experimental data on the heat of oxidation of diphenyl di-biphenylene ethane in benzene as a solvent. The first column gives the weight of the sample and the second the purity of the compound as indicated by the amount of oxygen absorbed. The chief uncertainty in the figure for the impurity arises from the fact that the reaction flask contains a vapor phase which is a mixture of benzene and oxygen and the connecting tube contains pure oxygen. It is impossible to estimate with high precision the volume which is to be considered saturated with benzene when making a correction for the change in vapor pressure of benzene during the course of a run. The value for the purity of the compound is probably good to about 0.5%. The third column gives the heat of oxidation per mole based on the amount of oxygen actually absorbed. This value refers to

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[6] Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 750 (1935).

[7] Ullmann and von Wurstemberger, *Ber.*, **37**, 73 (1904).

[8] Gomberg and Cone, *ibid.*, **39**, 2967 (1906).

[9] Halford, THIS JOURNAL, **53**, 105 (1931).

the solid ethane as the reactant and peroxide in solution in benzene as the product of the reaction. The next column gives a small correction which it seemed proper to add for the heat of solution of unreacting material. The heat of solution of the ethane is found to be 4.6 ± 0.3 kcal. per mole. If we assume that the material which did not add oxygen has the same heat of solution and make the correction we obtain the values given in the last column of the table. The average given in the last column of the table is obtained by weighting those runs which gave the smoothest curves and thereby permitted the best corrections for heat loss to the surroundings.

Table I

Heat of Oxidation of Diphenyl Di-biphenylene Ethane

Sample, g.	O_2 abs., %	$-\Delta H$ per mole	Correction	$-\Delta H$ corrected
0.4352	96.4	24.05	0.17	24.2
.6600	92.0	22.3	.4	22.7
.5086	97.2	20.25	.13	20.4
.9945	99.5	20.8	.0	20.8
.9905	98.9	22.5	.05	22.55

The heats of solution of the ethane and peroxide have also been determined in order to calculate the value for ΔH when the reaction is carried out either entirely in solution or referred to the solid state. The value for the ethane is 4.6 ± 0.3 kcal. per mole and for the peroxide is 5.4 ± 0.4 kcal. From these figures we obtain the value -26.6 kcal. for the addition of oxygen to the ethane dissolved in benzene to give the peroxide in solution. Similarly if solid ethane is converted to the peroxide the value of ΔH is -27.4 kcal.

The solution of peroxide at the completion of a run was invariably red in color, apparently due to some highly colored substance. As much as 80% of the theoretical amount of white peroxide was obtained from the reaction but all attempts to isolate another compound from the remaining material were unsuccessful. Undoubtedly the yield of peroxide was considerably more than 80% but this was all we were able to isolate, apparently due to the presence of the red colored material which formed an oil when attempts were made to crystallize it.

Tetraphenyl di-α-naphthyl ethane gave results which are less satisfactory. The amount of oxygen absorbed was about 86% of the theoretical amount and the insolubility of the peroxide made it impossible to determine its heat of solution. The results of two representative runs are as follows

Wt. of ethane	O_2 absorbed	ΔH exp.	ΔH corr.
0.3788	85.3	-34.3	-35.3
.8318	87.8	-34.1	-35.1

The values given in the next to the last column are calculated on the basis of the amount of oxygen absorbed and are for the addition of oxygen to solid ethane to give chiefly solid peroxide. A small correction should be made for the heat of solution of the peroxide which remained in solution, about 17 mg. in 150 cc. of benzene. This correction cannot be of much significance, however, due to the very small amount of material involved. A correction should also be applied for the heat of solution of the material which did not react with oxygen. The heat of solution of the ethane is found to be 11 ± 3 kcal. Since this includes the heat of dissociation of part of the material, we have taken a somewhat smaller value for the heat of solution of the material which did not react with oxygen and used this to correct our experimental values and give the values in the last column of the table.

An attempt was made to improve the technique of these oxidation reactions by using pyrogallol as suggested by Ziegler, Ewald and Seib.[10] The results of these experiments were not satisfactory as the amount of oxygen absorbed was less than expected. This may be due to the fact that in our experiments solid ethane is introduced into a solution which contains oxygen. It may be that some of the normal peroxide and some $(C_6H_5)_3$-COOH is formed under these conditions.

Attempts to hydrogenate diphenyl di-biphenylene ethane were unsuccessful. Either the ethane was too insoluble, the rate of hydrogenation was too slow or else the amount of hydrogen absorbed was greater than that expected.

Discussion

The value previously reported for the oxidation of hexaphenylethane is -45.5 ± 0.5 kcal. when the reaction is from solid to solid and -39.3 ± 2.0 kcal. when the reaction is in solution. The values here reported for diphenyl di-biphenylene ethane of -26.6 and -27.4 for the corresponding reactions are so much smaller as to be very striking. The conclusion suggested by these data is that the C–C bond is stronger in diphenyl di-biphenylene ethane than it is in hexaphenylethane by about 20 kcal. This is quite in harmony with the conclusions of our previous papers which indi-

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(10) Ziegler, Ewald and Seib, *Ann.*, **504**, 182 (1933).

cated that the C–C bond in hexaphenylethane is weaker than a normal bond by about 35 kcal., which we attributed to steric hindrance. If one assumes that the C–C bond in hexaphenylethane is a normal bond then there is no way of explaining a bond in diphenyl di-biphenylene ethane which is 20 kcal. stronger. The inference from these data is that steric hindrance is much less when the benzene rings are tied together as they are in this compound, in agreement with the appearance of the model of the molecule.

The surprising result from these experiments is that the decrease in steric hindrance is so large in this compound. If this were the only factor involved in the dissociation of the ethane it would be impossible to explain the fact that the difference in the free energy of dissociation of this compound and hexaphenylethane is only three or four kcal. A solution to the problem is possible if one assumes that phenyl fluoryl has a much larger resonance energy than triphenylmethyl, thereby canceling to some extent the increased strength of the bond in diphenyl di-biphenylene ethane. This is just the opposite of the conclusion reached by Pauling and Wheland in their discussion of this compound.

The above conclusions are based on data involving materials in solution or in the solid state. A much more satisfactory treatment would be based on reactions in the vapor phase. We hope to have some such data to report in the near future but since this work is being interrupted for the present it seems desirable to report the progress which has been made to this time.

In comparing tetraphenyl di-α-naphthyl ethane with hexaphenylethane we are dealing with a difference in heats of oxidation which is not as large as in the case just discussed and therefore the interpretation is more in doubt. Since we have no data on the heat of solution of the peroxide it will not be possible to study this reaction in the vapor phase by the method which we are using with hexaphenylethane.

Summary

1. The heat of oxidation of diphenyl di-biphenylene ethane is found to be about 20 kcal. less than that of hexaphenylethane.

2. This datum indicates that steric hindrance is less than in the case of hexaphenylethane and that the free radical formed by dissociation, phenyl fluoryl, has more resonance energy than triphenylmethyl.

CAMBRIDGE, MASS. RECEIVED JUNE 26, 1936

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, STATE UNIVERSITY OF IOWA]

Antioxidants and the Autoxidation of Fats. VI. Inhibitols[1]

BY H. S. OLCOTT AND H. A. MATTILL

Previous work from this Laboratory[2,3,4] has demonstrated that the unsaponifiable lipid fractions of vegetables and vegetable oils contain compounds which are active antioxidants toward lard. It is proposed to call these compounds as a class "inhibitols," a name which indicates their function as inhibitors and also the invariable occurrence of hydroxyl groups, upon which their inhibiting action depends. Although concentrates have been prepared from various sources,[5] only the lettuce inhibitol has been crystallized.[3] The present paper contains a description of the preparation and properties of the inhibitol concentrates from wheat germ, cottonseed and palm oils.

The method used for obtaining the most active concentrates from wheat germ or cottonseed oil is exactly the same as that described for obtaining vitamin E concentrates.[6] Indeed, the physical and chemical properties of vitamin E

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[1] Presented at the Kansas City meeting of the American Chemical Society, April, 1936.

[2] H. A. Mattill and B. Crawford, *Ind. Eng. Chem.*, **22**, 341 (1930).

[3] H. S. Olcott and H. A. Mattill, *J. Biol. Chem.*, **93**, 59, 65 (1931).

[4] E. M. Bradway and H. A. Mattill, THIS JOURNAL, **56**, 2405 (1934).

[5] Inhibitols are present in lettuce, tomatoes, carrots, alfalfa, spinach; in wheat germ, cottonseed, corn, sesame, palm, soy bean and peanut oils; and probably in many other vegetable substances. No demonstrable amounts of inhibitols are present in yeast, lard; or in olive (trace), cod-liver, palm kernel or castor oils.

[6] H. S. Olcott and H. A. Mattill, *J. Biol. Chem.*, **104**, 423 (1934).

and the inhibitol from these oils are so similar that it has thus far been impossible to separate the two. The demonstration that the vitamin E and inhibitols of lettuce and tomatoes could be separated by preferential solubilities,[3,4] thus providing a vitamin E concentrate free of antioxygenic activity, has been the principal basis for the assumption that the two properties are not inherent in the same molecule.

Experimental

Preparation.—Wheat germ or cottonseed oil is saponified with alcoholic potash,[7] and extracted with ether (previously shaken with 10–20% aqueous sodium hydroxide to remove peroxides). The ether extracts are evaporated to dryness and the residue dissolved in petroleum ether, from which most of the sterols separate on cooling. The sterols are removed by filtration, and the residue obtained after removal of the solvent is extracted several times with hot methanol. The methanol-soluble fractions are combined and cooled. If more sterols crystallize they are removed. The solvent is evaporated under reduced pressure and the residue is then carefully distilled in a high vacuum. The inhibitol distils at 190–210° (0.1 mm.).

The palm oil inhibitol was concentrated as follows. The unsaponifiable fraction was dissolved in petroleum ether, diluted with an equal volume of methyl alcohol and allowed to stand cold for several weeks. Some of the carotene crystallized and was removed. The petroleum ether was then evaporated from the filtrate and an insoluble oil separated; the methanol solution was poured off, the oil was washed twice with methanol and the extracts combined and hydrogenated with platinum as the catalyst. The purpose of this step was to destroy the remaining pro-oxygenic carotenoids.[8] The catalyst was removed by filtration and the filtrate evaporated to dryness. A white inactive powder separated from a petroleum ether solution of the residue and was filtered off. The limpid oil remaining after evaporation of the filtrate amounted to 0.1% by weight of the original oil. It was carefully fractionated in high vacuum (0.03 to 0.04 mm.) and the antioxidant obtained most highly concentrated in the fraction distilling within the 165–180° range. Several of a number of runs with palm oils have yielded concentrates of high vitamin E potency. With palm oil as with wheat germ and cottonseed oils, it was not possible to separate the inhibitol from vitamin E.

Attempts further to concentrate the inhibitol from these sources or to obtain a crystalline product have not been promising. Physical methods have included crystallization from solvents at low temperatures (−80°), careful fractional distillation in high vacuum (0.002 mm.), and adsorption on silica, alumina and magnesia. No notable concentration has been effected by any of these methods. In each case all of the fractions were antioxygenic to lard. Separation of the material into soluble and insoluble fractions from methanol at 0° consistently yielded somewhat more active fractions in the soluble portion. Diphasic separation between 92% methanol and petroleum ether removed a small amount of an inactive oil in the 92% methanol layer. The inhibitol was preferentially soluble in petroleum ether.

Physical and Chemical Properties.—Inhibitol concentrates are light yellow transparent oils of medium viscosity, which do not crystallize on long standing. They are stable under ordinary laboratory conditions for years. Some physical constants and chemical analyses are given in Table I. The concentrates are soluble in the following organic solvents: ether, petroleum ether, methyl and ethyl alcohols, pyridine, glacial acetic acid, chloroform, benzene, dioxane, etc.

TABLE I

COMPOSITION OF INHIBITOL CONCENTRATES

Source	Wheat germ oil		Cottonseed oil	Palm oil
Concentrate no.	W5-10	W4-12-2	C44	P17-8-1
C[a]	82.3	82.5	81.6	81.6
H[a]	11.7	11.4	11.5	11.1
M. w.[a]	317	379	......	279
I no.	106[b,c]	120[c]	90[b]	170[c]
Refr. index (20°)	1.5161	1.5254	1.5090	1.5193

[a] Dr. Ing. A. Schoeller. [b] Ralls' method.[11] [c] Rosenmund–Kuhnhenn method.[10] We have found it difficult to obtain consistent iodine numbers of unsaponifiable lipid fractions.

The effects of various reagents on the activity of inhibitol concentrates have been used to characterize the structure of the inhibitols. Table II includes representative results of such experiments. The inhibitols are always inactivated by reagents which combine with a free hydroxyl group, including acetyl chloride, acetic anhydride in pyridine, benzoyl chloride, methyl iodide with silver oxide, dimethyl sulfate, diethyl sulfate, phenyl isocyanate, *p*-nitrophenyl isocyanate and many others. None of these derivatives yielded crystalline products. Those which contained ester linkages, including the substituted ure-

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[7] For the complete saponification of large or small amounts of fat with a minimum of time, effort and opportunity for oxidation, the following proportions of reagents have been used in this Laboratory: 26 g. of potassium hydroxide is dissolved with stirring in 22 cc. of water and poured while hot into 89 cc. of 95% ethanol. This mixture is poured directly into a flask containing 100 g. of the oil or melted fat. The flask is swirled vigorously until the mixture becomes homogeneous; usually less than a minute is required. For the extraction of unsaponifiable constituents, the soaps are allowed to cool to 40–50° and poured into 450 cc. of water; 450 cc. of ethyl ether is added and the mixture is shaken. The ether layer separates immediately. The water–alcohol solution of the soaps may be extracted repeatedly with ether without emulsification. This procedure was developed by Dr. R. B. French, who also devised a method for large scale saponification and extraction which will be described in another place.

[8] Newton [*J. Oil and Soap*, **9**, 247 (1932)] found that fats containing carotene were more stable than colorless ones, and, further, that lards could be protected from oxidation by the addition of palm oil which contains carotene. However, we had previously demonstrated that purified crystalline carotene acted as a prooxidant in lard–cod-liver oil mixtures [H. S. Olcovich and H. A. Mattill, *J. Biol. Chem.*, **91**, 105 (1931); H. S. Olcott, THIS JOURNAL, **56**, 2492 (1934)]. It now seems clear that the fats containing carotene also contained inhibitols, which, in fact, ensured the presence of carotene by protecting it from oxidation. The palm oil inhibitol was responsible for the protection afforded by the addition of palm oil to lard. The method of incorporation described was such as to destroy the pro-oxygenic carotene by heat treatment and thus stabilize the fat still further.

thans, were hydrolyzed with alcoholic sodium hydroxide. The recovered material was again antioxygenic although in most cases some of the activity was lost. Diazomethane did not affect the antioxygenic action.

TABLE II

EFFECT OF REAGENTS ON INHIBITOL ACTIVITY

Concentrate[a]	Fat	Treatment	Induction period (75°C.)	
			With inhibitor (0.02%) hrs.	Without inhibitor, hrs.
C5-9	Lard	None	34	8
		Chlorine	7	8
		Chlorine + Zn + HCl	34	8
C65	Lard–cod-liver oil	None	158	16
		Ozone	11	11
W5-10	Lard	None	62	15
		Methyl iodide	13	12
		Dimethyl sulfate	13	12
		Ethyl iodide	17	15
W5-1572	Lard	None	53	4
		Acetic anhydride	4	4
		Phenyl isocyanate	4	4
		Phenyl isocyanate + NaOH	50	6
W3-18	Lard–cod-liver oil	None	23	7
		Acetic anhydride	5	5
		Acetic anhydride + NaOH	12	4

[a] C indicates cottonseed oil inhibitol, W that from wheat germ oil.

The inhibitols are destroyed by direct bromination or chlorination, presumably by addition to a double bond. The activity can be regenerated by boiling with zinc and hydrochloric acid in methanol. Hydrogenation has uniformly failed to inactivate the inhibitols. One sample was subjected to hydrogen at 250° and 230–280 atmospheres for two hours without loss of activity.[9] The recovered material was still unsaturated, although the iodine number[10,11] had been reduced from 105 to 70. Perbenzoic acid in the cold destroyed the inhibitols. Ozone was also destructive. These facts have been interpreted to mean that inhibitol contains a difficultly hydrogenated double bond which is essential to its activity.

The inhibitols are not destroyed by dry hydrogen bromide in methanol, nor by phosphorous tribromide, at room temperature. Potassium permanganate in pyridine, chromic acid in glacial acetic acid, potassium amide in liquid ammonia, potassium ethylate in ethyl alcohol and lead tetraacetate in glacial acetic acid destroyed the activity.

The methods used for determining the effect of some of these reagents upon concentrates have been described briefly elsewhere.[12,13]

The ultraviolet absorption spectra of inhibitol concentrates show a distinct broad band with maximum at 2940 Å., the height of which is roughly proportional to the antioxygenic activity. Acetylation causes a loss in height and migration of the peak to 2810 Å. Several authors have suggested that this band is a property of vitamin E.[14,15] In our experience, the height of the band has been more nearly proportional to the antioxygenic than to the physiological activity. Most striking of such experiments is a comparison of the properties of concentrate, P16-9, from palm oil with those of concentrates from wheat germ or cottonseed oil. Although P16-9 contained less than one-fifth as much vitamin E as did the others, the band in the ultraviolet was equally strong (Table III). Concentrates W5-156 and W5-157 were consecutive fractions from a fractional vacuum distillation, equally effective as antioxidants, but not containing equal amounts of vitamin E.

TABLE III

THE RELATION OF THE INHIBITOL CONCENTRATION AND THE VITAMIN E CONTENT TO THE ABSORPTION BAND AT 2940 Å.

Concentrate	Antioxidant index[a]	$E^{1\%}_{1\ \mathrm{cm.}}$ at 2940 Å.	Minimum dose,[b] mg.
C65	4–7	70	4
P16-9	5–8	90	>30
W5-10	5–8	100	3
W5-156	5–8	65	>10
W5-157	5–8	70	2

[a] Antioxidant index is the ratio of the induction period of the protected sample to that of the control. The figures are approximations because of the natural variability in duplicate assays (Table VI). [b] The minimum amount required to ensure the birth of a litter in a vitamin E-deficient animal.

Assay.—All fractions obtained during these studies were assayed for antioxygenic activity by the procedure

TABLE IV

COMPARISON OF THE ANTIOXYGENIC ACTIVITY OF SEVERAL TYPES OF INHIBITORS ON LARD

Inhibitor	Concentration %	Antioxidant index
Hydroquinone[17]	0.01	29
a-Naphthol	.01	6–10
Inhibitol concentrate W5-10	.02	5–8
Inhibitol concentrate C65	.02	5–8
Inhibitol concentrate P17-8-1	.02	5–8
Commercial lecithin[a]	.10	1.2–1.5
Maleic acid[b]	.10	1.2–1.5
Phosphoric acid[c]	.02	1.2–1.5
Carotene[d]	.02	0.5

[a] H. Bollman, U. S. Patent 1,464,557; *C. A.* **17**, 3234 (1923). [b] G. R. Greenbank and G. D. Holm, *Ind. Eng. Chem.*, **26**, 243 (1934). [c] E. W. Eckey, U. S. Patents 1,982,907; 1,993,152; A. S. Richardson, F. C. Vibrans and J. T. R. Andrews, U. S. Patent 1,993,181, *C. A.*, **29**, 518, 2770 (1935). [d] See Newton, reference 8.

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(9) We are indebted to Professor Adkins of the University of Wisconsin for several hydrogenation experiments.

(10) K. W. Rosenmund and W. Z. Kuhnhenn, *Untersuch. Nahrungs-u. Genussmittal*, **46**, 154 (1923); M. Yasuda, *J. Biol. Chem.* **94**, 401 (1931).

(11) J. O. Ralls, THIS JOURNAL, **56**, 121 (1934).

(12) H. S. Olcott, *J. Biol. Chem.*, **107**, 471 (1934).

(13) H. S. Olcott, *ibid.*, **110**, 695 (1935).

(14) J. C. Drummond, E. Singer and R. J. MacWalter, *Biochem. J.*, **29**, 456, 2510 (1935).

(15) H. M. Evans, O. H. Emerson and G. A. Emerson, *J. Biol. Chem.*, **113**, 319 (1936).

previously described,[16,17] which measures the induction period of lard or lard–cod-liver mixtures by the oxygen absorption method. The flasks containing the samples were placed in constant temperature baths at 75°, and the time of the beginning of active oxygen absorption was recorded automatically. The most active inhibitol concentrates protected lard to a degree approaching that afforded by the phenolic inhibitors (Table IV) and were much more effective than other compounds which have been suggested for use in edible fats.

Inhibitol concentrates are effective antioxidants for purified fatty acids and esters (Table V). Preliminary observations suggest that they also protect other easily oxidized organic compounds. They are, however, ineffective as antioxidants for the vegetable fats and oils from which they are prepared.

TABLE V

EFFECT OF AN INHIBITOL CONCENTRATE ON VARIOUS SUBSTRATES

Substrate fat	Inhibitol concentrate W5–10 %	Induction period at 75° With inhibitor, hrs.	Without inhibitor hrs.
Ethyl ricinoleate	0.10	56	16
Ethyl linolate (58°)	.10	8	0.5
Methyl oleate	.03	10	4
	.10	40	4
Oleic acid	.02	30	4
β-Ionone	.10	4	0.5
9,10-Octadecene	.13	84	13

The assays are subject to interference by many factors, some unknown. Attention has been called elsewhere[17] to the variability in fats and among samples of the same fat, not only in keeping quality, but in their reactions to added inhibitors. Table VI indicates the results which may be expected in assays of inhibitol concentrates on different lots of the same kind of fat.

TABLE VI

EFFECT OF INHIBITOL CONCENTRATES ON DIFFERENT SAMPLES OF LARD

+0.02% C65, hrs.	Blank hrs.	A. I.[a]	+0.02% P17–8–1, hrs.	Blank hrs.	A. I.[a]	+0.02% W5–10, hrs.	Blank hrs.	A. I.[a]
82	13	6.3	84	13	6.5	47	13	3.6
59	6	10.0	67	15	4.5	77	15	5.1
46	15	3.1	84	12	7.0	84	12	7.0
55	12	4.6	53	10	5.3	34	10	3.4
65	13	5.0	49	5	9.8	50	5	10.0
52	10	5.2	50	10	5.0	40	10	4.0
2	5	6.4						
51	9	5.3						

[a] Antioxidant index.

Furthermore, the mere fact that an inhibitor is effective in one fat at an elevated temperature does not mean that it will be effective in other fats or at other temperatures. Preliminary experiments do show, however, that inhibitols protect lard at room temperature.

The authors are indebted to Lever Brothers Company for a grant in support of this research and to Dr. R. B. French and Dr. Lyle A. Hamilton for their help in the preparation and assay of inhibitol concentrates.

Summary

The unsaponifiable lipid fractions of many vegetables and vegetable oils contain compounds which are active antioxidants to lard and which are here named inhibitols. The inhibitols from wheat germ and cottonseed oils may be concentrated by processes of crystallization and distillation similar to those used for obtaining vitamin E concentrates from which the inhibitols have not been separated. The preparation of inhibitol concentrates from palm oil is aided by the destruction by hydrogenation of the accompanying pro-oxygenic carotenoids.

Inhibitol concentrates are transparent oils which have resisted crystallization. Some chemical and physical properties are outlined. The inhibitols are destroyed by reagents which attack a hydroxyl group or saturate a double bond. Inactive esters may be hydrolyzed to regenerate the activity. They are resistant to hydrogenation. Chlorine or bromine addition products can be reactivated with zinc and hydrochloric acid. The concentrates have a strong absorption band at 2940 Å. roughly proportional to their activity.

The inhibitol concentrates have been assayed by an oxygen absorption method. They are shown to be much more effective antioxidants in lard than any edible compounds which have been suggested for use as commercial antioxidants. The inhibitols protect purified fatty acids and esters but do not protect the vegetable oils from which they are obtained.

IOWA CITY, IOWA RECEIVED MAY 12, 1936

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(16) H. A. Mattill, *J. Biol. Chem.*, **90**, 141 (1931).

(17) R. B. French, H. S. Olcott and H. A. Mattill, *Ind. Eng. Chem.*, **27**, 724 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Hydrolysis of 1,2-Dichloro-2-methylpropane Producing Isobutyraldehyde[1,2]

BY J. M. HERSH AND R. E. NELSON

Moderate quantities of 1,2-dichloro-2-methylpropane have been available from the thermal chlorination of isobutane.[3] The ready production of this material has made it desirable to study the possibility of its conversion into more desirable derivatives, such as isobutyraldehyde. The first study of this subject was that of Newlin,[4] who succeeded in showing that the hydrolysis of 1,2-dichloro-2-methylpropane resulted in the formation of a considerable amount of hydrochloric acid and an aldehyde accepted as isobutyraldehyde. This work was carried out in the liquid phase at temperatures below 100° using the 1,2-dichloride from the thermal chlorination of isobutane. In it there were several anomalies that called for further study and clarification. The present study of this reaction had as its objectives, (1) the preparation of pure 1,2-dichloro-2-methylpropane from some source other than isobutane, (2) the comparison of dichlorides from several sources in typical hydrolysis reactions, (3) the study of the hydrolysis reaction in the liquid phase and in the vapor phase in the presence of substances which might have a catalytic effect on the reaction, and (4) the separation and identification of isobutyraldehyde. Purified 1,2-dichloro-2-methylpropane prepared from *t*-butyl alcohol was hydrolyzed, mainly in the vapor phase in the presence of contact catalysts, to produce isobutyraldehyde.

Experimental

Preparation of 1,2-Dichloro-2-methylpropane.—The desired synthesis from some source other than isobutane led to the use of tertiary and isobutyl alcohols. The procedures followed in this preparation were: (a) dehydration to isobutene with subsequent chlorination,[5] (b) direct chlorination of *t*-butyl alcohol,[6] and (c) the low temperature chlorination of 2-chloro-2-methylpropane prepared from the alcohol by treatment with hydrochloric acid.[7] Of these methods, the last was markedly successful in producing 1,2-dichloro-2-methylpropane of desirable purity. This dichloride has a clean, mild, sweetish odor; even after six months' standing it is free of hydrogen chloride. No product of thermal chlorination has yet been prepared which compares with this synthesized material in stability, freedom from hydrogen chloride and mildness. The above preparation of 1,2-dichloro-2-methylpropane allowed a reasonable assumption that it was not contaminated with 1,1-dichloro-2-methylpropane, the only other dichloride which would be difficult to remove by distillation. Pure 1,2-dichloro-2-methylpropane has the following physical constants: b. p. 38.6–39.2° (70 mm.), 59–60° (150 mm.) and 106.5° (760 mm.) (corr.); $n^{20}\text{D}$ 1.4370 (Abbe); d_{20} 1.093 g./cc.

Aldehyde Analysis.—The titration of isobutyraldehyde by the hydroxylamine hydrochloride method was found to give unreliable results. The more reliable method of Seyervetz and Bardin[8] using a sodium sulfite solution was standardized against known isobutyraldehyde–water solutions. An analytical factor was established for use in the analysis of the products of hydrolysis of subsequent reactions, and the method was found to give concordant results.

Hydrolysis in Liquid Phase.—The first hydrolysis studies followed the simpler liquid phase procedure used by Newlin. The results of these studies indicated moderate hydrolysis with the formation of appreciable quantities of aldehyde, with yields obtainable as high as 33–35%. The effective conversion to aldehyde was improved with higher water to dichloride ratios, a ratio of 20:1 giving satisfactory yields.

Throughout these hydrolysis studies it was generally apparent that the hydrochloric acid capable of titration was far in excess of the aldehyde found by analysis. This condition was especially true in liquid phase hydrolysis where the tendency toward pyrolysis was at a minimum. It was evident then, that hydrochloric acid was evolved as several intermediate products were formed; these were then incompletely converted to isobutyraldehyde. Thus the acidity of the reaction products was bound to be high without the formation of an equivalent amount of isobutyraldehyde.

Catalytic Hydrolysis in Vapor Phase.—A hydrolysis unit was set up to operate at 300–450°. The apparatus designed for this purpose is shown diagrammatically in Fig. 1. Following the diagram, the apparatus was operated in the following manner: air under pressure (A) from an adjustable hydrostatic head, varied by the mercury pressure regulators (C), forced water from a graduated cylinder (G) and a constant flow (E) of dichloride from a reservoir (F) into the preheater (H). A line (B) to a vacuum pump permitted the dichloride reservoir to be filled readily. The preheater had concentric Pyrex coils so that the water

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[1] Abstracted from a thesis by J. M. Hersh, presented to the Faculty of Purdue University, in partial fulfilment of the requirements for the Ph.D. degree, June, 1935.

[2] Presented before the Division of Organic Chemistry at the 91st meeting of the American Chemical Society, Kansas City, Mo., April, 1936.

[3] Hass, McBee and Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935); **28**, 333 (1936).

[4] Newlin, M. S. Thesis, Purdue University, 1932.

[5] Senderens, *Compt. rend.*, **154**, 778 (1912).

[6] Whitmore, THIS JOURNAL, **55**, 1136 (1933).

[7] Adams and Adkins, "Organic Syntheses," Vol. VIII, John Wiley and Sons, Inc., New York, 1928, p. 50.

[8] Seyervetz and Bardin, *J. Soc. Chem. Ind.*, **25**, 202 (1906); Adams and Adkins, THIS JOURNAL, **47**, 1358 (1925).

and dichloride were vaporized individually in the desired ratio, preheated to 200°, and sent into the adjoining reaction tube (I), which was a 22-mm. Pyrex tube 60 cm. long packed with a contact mass and held at a fixed temperature by a Hoskins electric heating unit (K). A thermocouple (J) extending into the reaction zone permitted temperature recording and regulation by a recording pyrometer and thermal regulator. The products of the reaction were condensed (L) and collected in flasks (M).

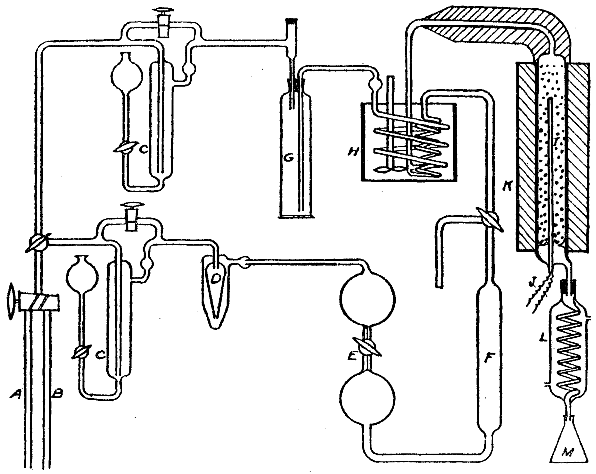

Fig. 1.

The procedure in each reaction carried out was to maintain a ratio of approximately 20:1 of water to dichloride, and to use generally 10 cc. of dichloride in each run. All the hydrolysis products were measured in volume, and the aqueous fraction containing aldehyde and hydrochloric acid was separated from the oily fraction consisting largely of unconverted dichloride. From each run two 10-cc. samples were taken from the aqueous portion and titrated for total acidity to determine the degree of conversion. The resulting neutral solution was analyzed for isobutyraldehyde by the method described. A 3-cc. sample from the aqueous portion was treated with fuchsin-aldehyde reagent for a color test of the aldehyde.

The first group of vapor phase hydrolysis studies made use of a series of fifteen catalyst filled reaction tubes. Subsequent studies made use of a series of sixteen reaction tubes in which a unit weight (10 g.) of a catalyst was mixed with a large amount of granular pumice filler. While the first reaction tubes required replacement before any large number of runs were completed, the reactors beginning with number six held up well, and ten or more runs were completed on each tube. Though fifteen catalyst filled reaction tubes were studied, at temperatures between 350 and 450°, a summary is presented in Table I of only typical catalysts, with a comparison based on the first ten hydrolysis runs completed on the reactor at 350°. The series of reaction tubes in which unit weights of catalyst were mixed with pumice is similarly summarized and presented in Table I. The average yields are given for

Table I

Comparison of Typical Catalysts[a]

No.	Catalyst Description	% Conversion	% Aldehyde	% DiCl Consumed	Criterion value
	A. Reaction tubes filled with catalyst (Approx. 50 cc.)				
1	Alumina, Weston, 4–16 mesh	66.4	29.2	51.9	44.2
2	Alumina, ALCOA, 8–16 mesh	56.6	35.3	41.4	42.2
3	Alumina, ALCOA, 4–8 mesh	52.5	21.9	49.0	36.3
4	Silica gel, granular, 8–16 mesh	31.2	20.9	33.6	26.7
5	Act. carbon, granular, finer than 10 mesh	39.9	13.4	37.7	26.1
6	Act. carbon, granular, 8–10 mesh	32.7	11.7	36.9	24.2
7	Silica gel + copper shreds	22.7	17.2	19.4	18.9
8	Pumice, granular	1.9	4.6	6.7	4.5
	B. Reaction tubes using 10.0 g. of catalyst				
1	Activated alumina, 8–16 mesh	38.1	24.0	24.1	27.6
2	Activated alumina, powdered	33.5	19.0	23.4	23.8
3	Titanium oxide, hydrated, pwd. and reduced	23.4	15.4	21.0	18.8
4	Zinc hydroxide, pptd., dried and powdered	20.0	15.0	23.0	18.3
5	Zinc chloride, deliquescent powder	16.3	16.8	21.5	17.9
6	Silica gel, granular, 8–16 mesh	18.7	16.3	20.0	17.9
7	Activated carbon, finer than 10 mesh	12.2	13.8	24.8	16.2
8	Vanadium pentoxide, powdered	16.4	15.7	17.0	16.2
9	Titanium oxide, hydrate, powdered	12.1	14.6	21.0	15.6
10	Tungstic oxide, yellow, powdered	7.2	19.3	15.0	15.2
11	Ceric oxide, yellow, powdered and reduced	12.0	15.6	13.7	14.2
12	Thorium oxide, from sintered nitrate	5.1	11.1	20.0	14.0
13	Ceric oxide, yellow, powdered	13.2	13.9	18.4	13.4
14	Thorium oxide, pptd. hydrate dried, powdered	13.3	11.2	15.4	12.9
15	Tungstic oxide, yellow powder reduced to blue	5.9	14.3	13.8	12.1
16	Thorium oxide, nitrate sintered and reduced	5.1	11.1	20.0	11.9

[a] Based upon first ten hydrolysis runs completed, using approximately 10 cc. of dichloride and 20 volumes of water.

each type of catalyst in order to give a measure of the degree of conversion, and the completeness of reaction.

Deterioration of Catalysts.—On reviewing any series of hydrolysis runs it was apparent that the catalyst was generally rapidly deactivated. This effect was first apparent with reactor number six using silica gel. The same effect was observed with each subsequent reactor and was apparent in the maximal to minimal change in conversion shown between the first and subsequent runs. This deterioration of catalysts was more pronounced at elevated temperatures where pyrolysis and carbonization were more evident, and varied also with the specific catalyst studied.

Separation of Hydrolysis Products.—The major part of the dichloride fed into the system was returned with the products of reaction as an oily, insoluble material, which was separated, filtered, dried and distilled. From 66–68% of this fraction appeared as crude dichloride which distilled over at 102–110°. It was further purified and fractionated to produce an additional quantity of 1,2-dichloro-2-methylpropane. Each batch of aqueous hydrolysis product containing isobutyraldehyde was distilled to remove an aldehyde-rich aqueous fraction. These aldehyde–water concentrates were further fractionated through a small column of the type described by Weston,[9] and the isobutyraldehyde was stripped from the large amount of water accompanying it. The crude aldehyde was purified and compared with Eastman isobutyraldehyde and with its known physical constants. Thus it was shown that the aldehyde isolated was the aldehyde expected in the reaction.

On reviewing the comparison of catalysts it was apparent that there was a pronounced difference in the catalytic influence of the several substances tested. The high value shown was that of activated alumina, and the lowest value that of granular pumice. Calculating the criterion value of these catalysts as dependent mainly (50%) on the percentage of aldehyde found by analysis, with additional consideration (25%) given to each the percentage of conversion and the percentage of dichloride consumed, the two series of catalysts were evaluated and arranged in the order of decreasing activity in Table I.

Summary

1. Pure 1,2-dichloro-2-methylpropane was prepared by the low temperature chlorination of 2-chloro-2-methylpropane. This compound was compared in hydrolysis with the dichloride from other sources; in each case isobutyraldehyde was produced in comparable yields.

2. The hydrolysis of 1,2-dichloro-2-methylpropane was quite effective in the vapor phase at 350°, with a ratio of 20:1 of water to dichloride, especially in the presence of catalysts. Yields of isobutyraldehyde were obtained as high as 33–35% per pass, or 90–100% based upon the dichloride consumed in the reaction.

3. Of the catalysts investigated, activated alumina showed a marked superiority, being especially resistant to deactivation at 350° as contrasted with catalysts such as silica gel.

4. The products of the hydrolysis of 1,2-dichloro-2-methylpropane were separated and the aldehyde produced was identified as isobutyraldehyde.

LAFAYETTE, INDIANA RECEIVED MAY 20, 1936

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[9] Weston, *Ind. Eng. Chem., Anal. Ed.*, **5**, 179 (1933).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PARKE, DAVIS AND COMPANY]

Tetraalkyl Barbituric Acids

BY ARTHUR W. DOX

For the preparation of 1,5,5-trialkylbarbituric acids two methods are available: (1) condensation of the dialkylmalonic ester with an alkylurea, and (2) direct alkylation of the 5,5-dialkylbarbituric acid. The first of these procedures was used by Fischer and Dilthey[1] and subsequently extended by Dox and Hjort.[2] The second method was studied by Dox and Jones[3] in the case of the more reactive halides such as benzyl chloride and allyl bromide, and by Lyons and Dox[4] with the still more reactive *p*-nitrobenzyl chloride.

Although the 5,5-dialkylbarbituric acids exist theoretically in two tautomeric forms, so that both N-alkyl and O-alkyl derivatives might be expected to result from direct alkylation of the sodium salt, only the former have actually been obtained and identified. The 1-benzyl-5,5-diethylbarbituric acid obtained by Dox and Jones[3] by direct alkylation of sodium barbital was identical with that prepared by them from ethyl diethylmalonate and benzylurea.

Marotta and Rosanova[5] recently claim to have obtained both tautomeric forms in the methylation of barbital by diazomethane. Their N-methyl derivative melted at 154° and was obviously identical with that which Fischer and

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[1] Fischer and Dilthey, *Ann.*, **335**, 334 (1904).
[2] Dox and Hjort, *J. Pharmacol.*, **31**, 455 (1927).
[3] Dox and Jones, THIS JOURNAL, **51**, 316 (1929).
[4] Lyons and Dox, *ibid.*, **51**, 288 (1929).
[5] Marotta and Rosanova, *Atti accad. Lincei*, **15**, 753 (1932).

Barbituric acid	Formula	M. p., °C.	Nitrogen, % Found	Calcd.
1,3,5-Triethyl-5-phenyl	$C_{16}H_{20}O_3N_2$	129	9.73	9.72
1-Methyl-3-phenyl-5-ethyl-5-propyl	$C_{16}H_{20}O_3N_2$	78	9.35	9.72
1-Methyl-3-benzyl-5,5-diethyl	$C_{16}H_{20}O_3N_2$	73	9.34	9.72
1,5,5-Triethyl-3-benzyl	$C_{17}H_{22}O_3N_2$	[a]	9.02	9.27
1,3-Dimethyl-5-ethyl-5-hexyl	$C_{14}H_{24}O_3N_2$	[b]	10.40	10.45
1,3-Dimethyl-5-ethyl-5-isoamyl	$C_{13}H_{22}O_3N_2$	[a]	10.75	11.02
1,3-Dimethyl-5-ethyl-5-(1-methylbutyl)	$C_{13}H_{22}O_3N_2$	[a]	10.72	11.02

[a] Liquid. [b] B. p. 165–170° at 12 mm.

Dilthey[1] had obtained from ethyl diethylmalonate and methylurea. In addition to this crystalline product Marotta and Rosanova obtained a non-crystallizing sirup which they assume to be the tautomeric O-methyl barbital having the isourea structure. Mention is made of methoxyl determinations but no analytical data are given. They make no mention whatever of the possibility that *both* nitrogens may have been methylated. As will be shown presently this is undoubtedly what occurred, and the non-crystallizing sirup which they assume to be the tautomeric monomethylbarbital was in reality an impure preparation of the low-melting dimethylbarbital.[6]

Experimental

Methylation was performed by dissolving the di- or trialkylbarbituric acid in a dry ether solution of diazomethane prepared by distilling ethyl N-nitroso-N-methylcarbamate with alcoholic potassium hydroxide in ether. Except in one instance where it was desired to obtain the monomethyl barbital, an excess of diazomethane was used. At room temperature the evolution of nitrogen began almost immediately and the reaction was complete in about an hour. Evaporation of the ether left a sirup which in a few instances crystallized readily, but more often required cooling or seeding, and occasionally did not crystallize at all. In two instances diazoethane, prepared similarly from the nitrosoethylurethan, was used for ethylation.

In the first experiment barbital was methylated with one equivalent of diazomethane. Evaporation of the solvent gave a crystalline product which on recrystallization from alcohol formed large prisms melting at 154°. Mixed with authentic methylbarbital the melting point showed no depression. A sirupy mother liquor failed to crystallize. This corresponds to the supposed O-methylbarbital of Marotta and Rosanova.

1,3-Dimethyl-5,5-diethylbarbituric Acid. (Dimethylbarbital.)—When barbital was treated with an excess of diazomethane, as shown by persistence of the yellow color after the evolution of nitrogen had ceased, evaporation gave only the sirup. This did not crystallize on cooling and stirring, but when seeded with a small crystal that had formed on the stem of the funnel through which the ether solution had been filtered, the sirup crystallized promptly and completely. The crystals melted at 32–34°, and recrystallization from ether raised the melting point to 37°. A peculiar property of the substance is its tendency to form a super-cooled sirup which immediately crystallizes when seeded with a crystal of the same substance. The yield was practically quantitative. The substance is readily volatile with steam, and is soluble in the usual organic solvents including petroleum ether, but insoluble in sodium hydroxide. It separates as an oil when the alcohol or acetone solution is diluted with water.

Anal. Calcd. for $C_{10}H_{16}O_3N_2$: C, 56.60; H, 7.55; N, 13.21. Found: C, 56.29; H, 7.37; N, 13.41.

The identity of the substance was corroborated by another method of synthesis. Diethylmalonyl chloride was condensed with symmetrical dimethylurea[7] by heating the mixture in an oil-bath for twelve hours at 135–140°, finally raising the temperature to 150°. The reaction product was dissolved in ether and shaken successively with water, *N* sodium hydroxide, *N* sulfuric acid, water, and finally dried with calcium sulfate. Evaporation of the ether left a sirup which immediately crystallized when seeded with a crystal of the product described above. The melting point was 37°, and mixed melting point showed no depression.

1,3-Dimethyl-5-ethyl-5-phenylbarbituric Acid. (Dimethyl-phenobarbital.)—Phenobarbital was methylated in the same manner. In contrast to the corresponding barbital derivative it crystallized spontaneously, possibly because of its higher melting point, 88–89°.

Anal. Calcd. for $C_{14}H_{16}O_3N_2$: C, 64.61; H, 6.15; N, 10.77. Found: C, 64.27; H, 6.57; N, 10.67.

These tetraalkyl barbituric acids, like the following homologs prepared from other 5,5-dialkylbarbituric acids and diazomethane or diazoethane, contain no replaceable hydrogen and hence are insoluble in sodium hydroxide. The yields were practically quantitative. Several of these products have failed to crystallize, but from the peculiar behavior of the dimethyl-barbital it may be assumed that crystallization will readily occur when once a crystal for seeding has been obtained. In three instances a 1,5,5-trialkylbarbituric acid was alkylated on the second nitrogen by the diazoalkane method.

Several of these substances possess asymmetric structure and should be separable into optical isomers. This was not attempted because the substances have neither acidic nor basic properties and cannot form salts with optically active bases or acids.

The action of diazomethane on barbituric acids containing only one alkyl in the 5-position has been studied

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(6) Marotta and Rosanova state that their work will be more fully described in the *Gazzetta chimica Italiana*. The proposed paper has not appeared after the lapse of four years.

(7) The dimethylurea was kindly supplied by Dr. Henry Gilman of Iowa State College.

by Biltz and Wittek.[8] They obtained the same trimethylbarbituric acid by diazomethane treatment of barbituric, 1-methylbarbituric and 1,3-dimethylbarbituric acids. Both nitrogens are thus amenable to methylation by diazomethane, but only one of the methylene hydrogens. To obtain a tetraalkylbarbituric acid with this reagent both of the methylene hydrogens must be previously substituted. The other method in which a symmetrical dialkylurea is used requires a condensation with the acid chloride instead of the ester of the dialkylmalonic acid. Fischer and Dilthey thus prepared the tetraethylbarbituric acid but failed to crystallize it, possibly because of its low melting point. Otherwise its properties were similar to those of the 1,3-dimethyl-5,5-diethylbarbituric acid prepared by both methods and described above.

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(8) Biltz and Wittek, *Ber.*, **54**, 1035 (1921).

Summary

Treatment of 5,5-dialkyl- or 1,5,5-trialkylbarbituric acid with diazomethane in ether solution gives practically quantitative yields of tetraalkylbarbituric acids in which both nitrogens have been methylated. A similar reaction occurs with diazoethane.

The statement of Marotta and Rosanova that the two tautomeric monomethyldialkylbarbituric acids are thus formed is erroneous. The supposed O-methylbarbital which they obtained as a sirup is in reality the low melting di-N-methyl derivative.

DETROIT, MICH. RECEIVED JUNE 17, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Absorption Edges in the X-Ray Patterns of Native and Mercerized Cellulose

BY WAYNE A. SISSON,[1] GEORGE L. CLARK AND EDWARD A. PARKER[2]

In addition to the spacings of the currently accepted unit cell of cellulose,[3] numerous reports of other long spacings have appeared from time to time in the literature. Spacings of 16.0 and 35.3 Å.;[4] 7.9 or 8.3 Å.;[5] 50.0 Å.;[6,7] 274, 168, 156 and 85 Å.;[8,9] 42.2, 44.9, 66.5 and 83.5 Å.;[10] and 40 to 50 Å.,[11] have been interpreted as being due either to micellar dimensions, or to periodicities larger than the usual diffracting planes of the cellulose unit cell.

The authors[12] recently reported three new "interferences:" two (10.1 and 13.4 Å.) in native cellulose and one (14.2 Å.) in mercerized cellulose, which appear most intense in the pattern when the x-ray beam (Cu K) is parallel to the fiber axis. Regardless of the fibers used, these "spacings" were found to be constant, which indicated that they were not due to non-cellulosic constituents.

With other radiations (Mo, Fe and Cr), the "spacings" were found to vary, while the usual cellulose diffraction lines remained constant, as can be seen by comparing the original negatives of Figs. 1 and 2. The "spacings" were parallel to the 101 and 002 planes in native and the $10\bar{1}$ plane in mercerized cellulose. They were very weak with molybdenum radiation, but increased in intensity with larger values of λ, until with chromium radiation they are almost as intense as the usual diffraction lines. It is the purpose of the present paper to show that these new "spacings" are absorption edges.

It is well known that any element placed in an x-ray beam will absorb to a greater extent those wave lengths just shorter than that element's absorption edges, and on the long wave length side of this edge the x-ray beam will be less affected. If the planes in cellulose diffract general as well as characteristic radiation, definite bromine and silver absorption edges for each plane will appear on the x-ray film which would be similar to and might be mistaken for true diffraction lines.

Since the 002 (3.98 Å.) and 101 (6.10 Å.) planes in native and the $10\bar{1}$ (4.40 Å.) plane in mercerized cellulose diffract characteristic radiation to the greatest degree, they should behave likewise

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(1) Present address, Boyce Thompson Institute, Yonkers, New York.

(2) Textile Foundation Fellow.

(3) K. R. Andress, *Z. physik. Chem.*, **B2**, 380 (1929); **B4**, 190 (1929).

(4) R. O. Herzog and W. Jancke, *Naturwissenschaften*, **16**, 618 (1928).

(5) U. Yoshida and C. Park, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **A17**, 443 (1934).

(6) H. Mark, *Trans. Faraday Soc.*, **25**, 387 (1929).

(7) G. L. Clark, *Ind. Eng. Chem.*, **22**, 474 (1930).

(8) G. L. Clark and K. E. Corrigan, *Radiology*, **15**, 117 (1930).

(9) G. L. Clark and K. E. Corrigan, *Ind. Eng. Chem.*, **23**, 815 (1931).

(10) K. E. Corrigan, Thesis, University of Illinois, 1932.

(11) W. A. Sisson, *Textile Research*, **5**, 119 (1935).

(12) G. L. Clark and W. A. Sisson, Cellulose Symposium, Am. Chem. Soc., Div. Cellulose Chem., N. Y., 1935.

with general radiation. The $\sin\Theta$ values ($\lambda = 2d\sin\Theta$) of possible absorption edges corresponding to these planes are given in column 4 of Table I. If, instead of absorption edges, these lines

TABLE I

NATIVE CELLULOSE

Absorption edge		Diffracting planes		Calculated spacings			Observed spacings		
Element	λ	d, Å.	Sin Θ	Anticathode	λ	d, Å.	D, cm.	d, Å.	Intensity
Ag	0.484	3.98	0.0608	Mo	0.708	5.82	[a]	[a]	s
Ag	.484	5.40	.0448	Mo	.708	7.90	..	..	
Ag	.484	6.10	.0397	Mo	.708	8.92	0.79	8.88	vw
Br	.918	3.98	.1150	Mo	.708	3.08	2.34	3.11	vw
Br	.918	5.40	.0850	Mo	.708	4.16	..	..	
Br	.918	6.10	.0753	Mo	.708	4.70	[a]	[a]	s
Ag	.484	3.98	.0608	Cu	1.54	12.7	1.20	13.1	w
Ag	.484	5.40	.0448	Cu	1.54	17.2	..	..	
Ag	.484	6.10	.0397	Cu	1.54	19.5	0.80	19.4	vw
Br	.918	3.98	.1150	Cu	1.54	6.7	2.34	6.7	s
Br	.918	5.40	.0850	Cu	1.54	9.1	..	..	
Br	.918	6.10	.0753	Cu	1.54	10.2	1.51	10.3	w
Ag	.484	3.98	.0608	Fe	1.935	15.9	1.22	15.7	vw
Ag	.484	5.40	.0448	Fe	1.935	21.6	..	..	
Ag	.484	6.10	.0397	Fe	1.935	24.3	0.83	23.5	vw
Br	.918	3.98	.1150	Fe	1.935	8.4	2.32	8.5	s
Br	.918	5.40	.0850	Fe	1.935	11.4	..	..	
Br	.918	6.10	.0753	Fe	1.935	12.85	1.51	13.0	w
Ag	.484	3.98	.0608	Cr	2.29	18.85	1.21	19.0	mw
Ag	.484	5.40	.0448	Cr	2.29	25.5	..	..	
Ag	.484	6.10	.0397	Cr	2.29	28.8	0.79	29.1	vw
Br	.918	3.98	.1150	Cr	2.29	9.95	2.33	10.0	s
Br	.918	5.40	.0850	Cr	2.29	13.45	..	..	
Br	.918	6.10	.0753	Cr	2.29	15.2	1.50	15.3	w

[a] Absorption edge superimposed on diffraction line.

TABLE II

MERCERIZED CELLULOSE

Absorption edge		Diffracting spacings		Calculated spacings			Observed spacings		
Element	λ	d, Å.	Sin Θ	Anticathode	λ	d, Å.	D, cm.	d, Å.	Intensity
Ag	0.484	4.0	0.0605	Mo	0.708	5.85	..	..	
Ag	.484	4.4	.0550	Mo	.708	6.44	1.14	6.24	s
Ag	.484	7.3	.0331	Mo	.708	10.70	..	..	
Br	.918	4.0	.1145	Mo	.708	3.09	..	..	
Br	.918	4.4	.1043	Mo	.708	3.39	2.12	3.41	s
Br	.918	7.3	.0628	Mo	.708	5.64	..	..	
Ag	.484	4.0	.0605	Cu	1.54	12.75	..	..	
Ag	.484	4.4	.0550	Cu	1.54	14.0	1.14	13.6	w
Ag	.484	7.3	.0331	Cu	1.54	23.25	..	..	
Br	.918	4.0	.1145	Cu	1.54	6.7	..	..	
Br	.918	4.4	.1043	Cu	1.54	7.35	[a]	[a]	s
Br	.918	7.3	.0628	Cu	1.54	12.25	..	..	
Ag	.484	4.0	.0605	Fe	1.935	15.9	..	..	
Ag	.484	4.4	.0550	Fe	1.935	17.5	1.14	17.1	mw
Ag	.484	7.3	.0331	Fe	1.935	29.1	..	..	
Br	.918	4.0	.1145	Fe	1.935	8.4	..	..	
Br	.918	4.4	.1043	Fe	1.935	9.3	2.10	9.3	s
Br	.918	7.3	.0629	Fe	1.935	15.3	..	..	
Ag	.484	4.0	.0605	Cr	2.29	18.9	..	..	
Ag	.484	4.4	.0550	Cr	2.29	20.8	1.14	20.2	vw
Ag	.484	7.3	.0331	Cr	2.29	34.6	..	..	
Br	.918	4.0	.1145	Cr	2.29	10.0	..	..	
Br	.918	4.4	.1043	Cr	2.29	11.1	2.13	10.9	ms
Br	.918	7.3	.0628	Cr	2.29	18.2	..	..	

[a] Absorption edge superimposed on diffraction line.

are interpreted as being due to diffracted monochromatic radiation from the anticathodes listed in column 5, then the spacings to which they would correspond are given in column 7. In column 9 the experimentally observed spacings (assuming monochromatic diffraction) are listed opposite the nearest calculated spacing in column 7. It is readily seen that the observed spacings correspond to calculated absorption edges for the 002 and 101 planes. Similar data for mercerized cellulose appear in Table II.

There are four criteria for testing the validity of the assumption that the "spacings" listed in column 9 of Tables I and II are absorption edges:

(a) That these edges, for a specified specimen to film distance, will remain at exactly the same place on the film regardless of the radiation.

(b) If a "Flurazure" intensifying screen is used there should be no sharp discontinuities at the bromine and silver absorption edges, but a general fogging throughout the whole region.

(c) It will be necessary to have a peak voltage on the x-ray tube of at least 25 k.v. to produce the silver absorption edge and a peak voltage of 13.5 k. v. to produce the bromine edge.

(d) If a strictly monochromatic beam (*i. e.*, the x-ray beam diffracted from the 101 face of a crystal of calcite) is used, absorption edges will not appear.

Experimental

The x-ray tubes used for the various radiations were: copper—Philips Metalix, line focus, electron tube and a Leiss–Siegbahn, self-rectifying, gas tube; iron—Leiss–Siegbahn, self-rectifying, gas tube; chromium—Leiss–Siegbahn, self-rectifying, gas tube and a modified Langsdin–Wyckoff gas tube; molybdenum—Philips Metalix, line focus, electron tube.

For the fiber patterns, the samples consisted of parallel fibers held firmly and compactly together. For the patterns with the x-ray beam parallel to the fiber axis, the fibers were tied in a parallel bundle and then a small cross section—two millimeters in length giving the best results—was cut and fastened to a mount.

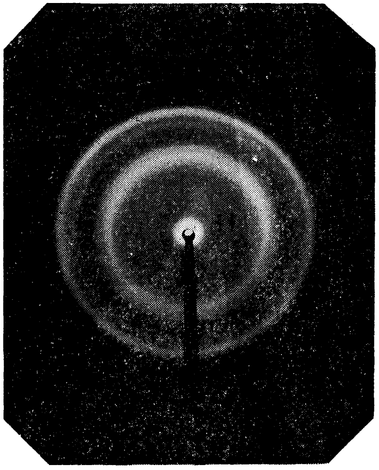

Fig. 1.

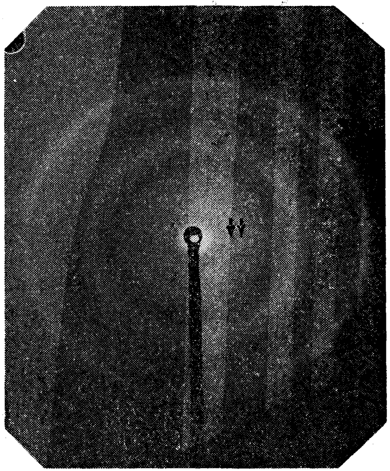

Fig. 2.

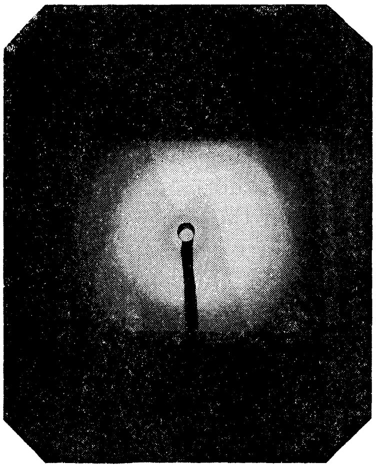

Fig. 3.

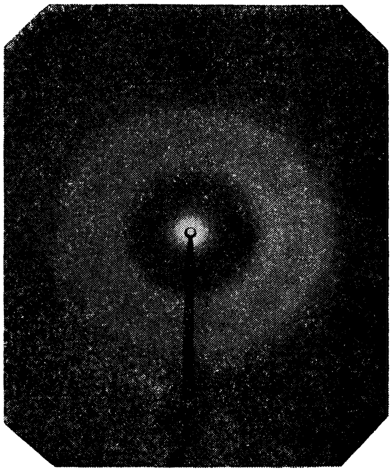

Fig. 4.

1 and 2 show x-ray diagrams of ramie fibers (beam parallel to fiber axis) taken with Cu and Fe radiation, respectively.
3. Same as Figure 2 but with intensifying screen.
4. Same as Figure 1 but with peak 13 k. v. instead of 40 k. v.

With the exception of chromium radiation, where a vacuum camera was used and a specimen to film distance of 4 to 7 cm., all patterns were taken in air and at 5 cm. specimen to film distance.

With iron and copper radiation patterns were taken at peak voltages of 13, 15–24 and 40–60 k. v. At the lowest voltage approximately fifty hours were necessary for the Leiss–Siegbahn tube operating at 2 milliamperes. The Philips copper tube at 25 milliamperes and 13 kilovolts produced patterns in twelve to fifteen hours.

Results

Figures 1 and 2, and column 8 of Tables I and II show how point (a) was fulfilled. All values for column 8 are in centimeters, corresponding to the outer diameter (*D*) of the absorption edges, and are for a specimen to film distance of 5 cm.

For point (b), a study of two diffraction patterns, shown in Figs. 2 and 3, made under exactly the same experimental conditions with the exception that an intensifying screen was used for Fig. 3, shows that with an intensifying screen the absorption edges are missing, and that the fogging due to the shorter wave lengths is quite noticeable.

For point (c), the silver edge was absent for voltages below 25 k. v., and both bromine and silver below 13.5 k. v. This is illustrated in Figs. 1 and 4.

As for point (d), owing to the experimental difficulties involved, the effect of a strictly monochromatic beam reflected from a calcite crystal was not tried, but when a nickel filter was used with copper radiation the intensity of the absorption edges diminished.

The presence of these absorption edges apparently explains some of the large interferences and micellar dimensions which have appeared in the literature. For example, Yoshida and Park's 100 spacing with iron radiation[5] may be explained as a bromine absorption edge. Likewise, if magnesium and aluminum anticathodes are used, the absorption edges for native cellulose would correspond to 36.2, 55.2, 68.4 and 104.8 Å. for aluminum radiation and 42.9, 65.5, 81.2 and 124.3 Å. for magnesium radiation, and these edges approximate some of the spacings found by Corrigan.[10] They also may explain why Sisson[11] was unable to obtain check results with aluminum and magnesium radiation and also why 15 k. v. was necessary to produce interferences. On the other hand, the micellar spacings of 150 to 280 Å. reported by Clark and Corrigan;[8,9] the 50 Å. spacing found in wood by Mark,[6] which he believed to be the cross-sectional size of the micelle; and the 35.3 and 16.0 Å. reported by Herzog and Jancke,[4] do not correspond to absorption edges.

A small strictly parallel pencil of copper radiation, at a sample to film distance of 15 to 20 cm., has been used successfully to identify spacings up to 200 Å. in protein fibers,[13] but no evidence of correspondingly large spacings was found when the method was applied to cellulose.

Summary

1. Diffracted general radiation from the 002 and 101 planes in native and the $10\bar{1}$ plane in mercerized cellulose produces, on the x-ray negative, well-defined bromine and silver absorption edges which are similar in appearance to diffraction lines.

2. Criteria for distinguishing absorption edges from diffraction lines are discussed.

3. Absorption edges correspond to some, but not all, of the large interferences or micellar dimensions for cellulose reported in the literature.

4. No spacings larger than the cellulose unit cell were found.

URBANA, ILLINOIS

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[13] G. L. Clark, E. A. Parker, J. A. Schaad and W. J. Warren THIS JOURNAL, **57**, 1509 (1935).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Interdiffusion of Acid and Base in Aqueous Solution

BY CECIL V. KING AND WILLIAM H. CATHCART

The interdiffusion of hydrochloric acid and glycine has been studied in some detail by McBain and Dawson.[1] An interesting feature of this double diffusion is the greatly increased rate of passage of material (notably the chloride ion) through the porous partition of the diffusion cell due to the chemical reaction. McBain and Dawson have interpreted the increased diffusion rates in terms of increased over-all diffusion coefficients. In view of the fact that the hydrogen-ion concentration falls to a low value at the point within the porous disk where it meets the glycine, the increased diffusion rates should be interpreted in terms of sharpened concentration gradients rather than enhanced diffusion coefficients. Analysis of the data from this viewpoint is impossible since sufficient details are not given by the authors. The presence of the glycinium ion is a complicating factor and also, as shown below, the experimental method used was probably inadequate for obtaining correct diffusion rates in this type of system.

The present paper reports measurements of the interdiffusion rates of hydrochloric acid and sodium hydroxide in the porous disk cell.[1] It is assumed that the diffusion coefficients are unaffected by the neutralization (the heat of reaction is unimportant with the dilute solutions used), and this assumption is confirmed by the results. The diffusion coefficients are affected, however, by the sodium and chloride ions accumulating in the disk, and this factor must be taken into account.

The interdiffusion of hydrochloric acid and sodium hydroxide has been studied previously by Barry and Smith,[2] by a method of superposing one solution upon the other and following the movement of the boundary and the heat evolved by the neutralization. For our purpose experiments in the porous disk cell are much easier to interpret since under suitable conditions the diffusion gradients are confined to the porous partition.

If A and δ are the effective (not the measured) area and thickness, respectively, of the porous disk, we may assume that the neutralization of acid and base occurs in a plane at a distance y from the surface in contact with base, $\delta - y$ from the surface in contact with acid. The rates are then given, assuming Fick's law to be valid for the experimental arrangement, by

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{AD_A}{\delta - y}\,\frac{a - x}{V_A} = \frac{AD_B}{y}\,\frac{b - x}{V_B} \qquad (1a)$$

where a, b = initial moles acid and base in cell compartments of volumes V_A, V_B; x = moles neutralized at time t; D_A, D_B = diffusion coefficients of the acid and base.

Solving for y and substituting,

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{A}{\delta}\left[\frac{V_BD_A(a - x) + V_AD_B(b - x)}{V_AV_B}\right]$$

If D_A and D_B are constants under the conditions of the experiment, this expression can be integrated as follows

$$kt = \frac{V_AV_B}{V_BD_A + V_AD_B}\ln\frac{V_BD_Aa + V_AD_Bb}{V_BD_A(a - x) + V_AD_B(b - x)}$$

where $k = A/\delta$, a "cell constant" dependent on the characteristics of the porous disk only and not on the volumes of the cell compartments. This equation may be rewritten

$$kt = \frac{V_AV_B}{V_BD_A + V_AD_B}\ln\frac{D_AC_A + D_BC_B}{D_AC'_A + D_BC'_B} \qquad (1)$$

where C_A, C_B are initial concentrations of acid and base, C'_A, C'_B are concentrations at the time t.

The corresponding equation for a single diffusion is, in a form convenient for use

$$kt = \frac{V_AV_B}{(V_A + V_B)D}\ln\frac{C_A}{C_A - (1 + V_B/V_A)C''_A}$$

where C''_A is the concentration of diffusing solute in the cell compartment which initially contained pure solvent. This equation was used in establishing cell constants and for the other single diffusions reported.

Experimental

Several cells were used in the course of this work, but all the final experiments were run in one rotating cell of the type described by Mouquin and Cathcart.[3] McBain and Dawson have given 2.71 sq. cm./day as the diffusion coefficient of 0.1 molar hydrochloric acid into pure water at 25°,

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(1) McBain and Dawson, THIS JOURNAL, **56**, 52 (1934).

(2) Barry and Smith, *ibid.*, **55**, 2215 (1933).

(3) Mouquin and Cathcart, *ibid.*, **57**, 1791 (1935).

and this value was used in determining all cell constants.

Rotating Cell Constant.—The volumes of the cell compartments were V_A = 69.6 cc., V_B = 71.2 cc. The cell was rotated approximately forty times per hour, both in determining the cell constant and in the double diffusion experiments. Data are given in Table I.

TABLE I

ROTATING CELL CONSTANT DETERMINATION (25 ± 0.02°)

C_{HCl}, *M*	Time, hours	C'_{HCl}, *M*	*k*
0.1002	17.75	0.00962	3.78
.0995	18.25	.00996	3.85
.0983	26.67	.01377	3.87
.0982	26.83	.01380	3.88

Salt Effect on the Diffusion Coefficients.—The diffusion coefficient of an electrolyte varies somewhat with its own concentration, but, in general, this variation amounts to only a few per cent. up to 0.1 *N* solution. The variation has been explained quantitatively for very dilute solutions in terms of the interionic attraction theory. The effect of salts on the diffusion coefficients of dilute acids and bases is much greater and has not yet been accounted for quantitatively. Since in the interdiffusion experiments acid and base diffuse into the disk, sodium and chloride ions outward in both directions, the diffusion coefficients will vary continuously with the concentration gradients unless the experiments are carried out in such a medium that the salt formed will not have this effect.

For this reason, the diffusion coefficients of acid and base were determined in solutions containing added sodium chloride. This was first done in stationary cells but, as shown below, it was found necessary to establish the curves with the rotating cell also. The coefficients of both acid and base reach maxima between 0.2 and 0.4 molar salt and apparently decrease again at higher concentrations. Measurements in the rotating and stationary cells check well with sodium hydroxide, but this is not true with hydrochloric acid. Presumably the coefficients of both should continue to rise with increasing salt concentration, the hydrogen ion reaching a value near 8 sq. cm./day when freed of all retarding effects of the negative ion.[1] This value assumes, however, no effect due to the increased viscosity of the concentrated salt solution, and ionic mobilities of the same value as at infinite dilution. In practice, 6 sq. cm./day is about the highest value reached in sodium chloride (Table II); the decrease at higher salt concentration may be real or may be due to inadequacy of the experimental method. Since the rotating cell gives higher values than the stationary cell and results below show that these higher values are substantially correct, it is possible that inadequate stirring in the cell compartments of even the rotating cell is responsible for the decreasing values obtained at high salt concentrations.

TABLE II

THE DIFFUSION COEFFICIENTS OF HYDROCHLORIC ACID (0.0492 *M*) AND SODIUM HYDROXIDE (0.0530 *M*) IN SODIUM CHLORIDE SOLUTIONS (BOTH SIDES OF CELL) AT 25°

HCl			NaOH		
C_{NaCl}, *M*	Cell	*D* (sq. cm./day)	C_{NaCl}, *M*	Cell	*D* (sq. cm./day)
0	..	(2.71)[a]	0	S	1.73 1.735
0.01	S	3.34	0.04	S	2.41
.02	S	3.26	.08	S	3.18
.04	S	3.85 4.17	.12	S	3.34
.06	S	3.98	.16	S	3.39
.10	S	4.65	.20	S	3.50
.20	S	5.36	.40	S	3.54
.30	S	5.60	.72	S	3.43
.40	S	5.46	.30	R	3.55
.50	S	5.69	.40	R	3.58
1.0	S	5.53	.50	R	3.56
1.5	S	5.08			
2.0	S	4.65 4.68			
3.0	S	3.65 3.50			
0.24	R	5.82			
.40	R	5.90 6.10			
.56	R	6.09			
1.0	R	5.94 6.09			
2.0	R	5.18			
3.0	R	4.34 4.32			

[a] Approximately the same as 0.1 *M* HCl. S = stationary, R = rotating cell.

Interdiffusion Experiments.—All these experiments were run with 0.4 molar sodium chloride in both compartments of the rotating cell, since the diffusion coefficients have their maximum value at this concentration and the higher concentration accumulating within the disk cannot affect the coefficients much. Three experiments were run, in duplicate, with acid and base concentrations between 0.04 and 0.06 molar, since the single diffusions were run at approximately 0.05 molar. The values do not change much with acid or base concentration, however, and one pair of experiments was run with 0.1 molar acid, 0.05 molar base. The values D_A = 6.05, D_B = 3.55 were selected as the approximate maxima from Table II and Fig. 1 and used in equation (1) in calculating the cell constant *k* as shown in Table III.

TABLE III

CELL CONSTANTS FROM INTERDIFFUSION EXPERIMENTS IN ROTATING CELL (25°). 0.4 *M* NaCl IN BOTH CELL COMPARTMENTS

Expt.	C_A	C_B	Time, hours	C'_A	C'_B	k
6	0.0498	0.0497	22.33	0.0301	0.0304	3.915
7	.0498	.0497	41.5	.01915	.0200	3.955
8	.0598	.0397	18.5	.04225	.0220	3.89
9	.0598	.0397	25.0	.0378	.0172	3.86
10	.04025	.0595	25.17	.0195	.0383	4.06
11	.04025	.0595	24.6	.0199	.0388	4.03
4	.0997	.0537	23.0	.0679	.02185	3.685
5	.0997	.0537	26.75	.0641	.0183	3.67

Samples of both acid and base were titrated before and after the diffusion, and a comparison of the values in Table III shows that the method is not very precise unless more precautions are taken than were thought necessary for the present purpose. The greatest discrepancy in moles of acid and base disappearing is 4.4% in experiment 9. The error in k caused by an error of 1% in any one term of equation 1 (*i. e.*, in D, V, C, C', etc.) is approximately 1%.

In Table IV are given the results of two interdiffusion experiments carried out in the same cell without rotating, the first with the acid in compartment A above, the second with base in compartment B above. The density of the sodium hydroxide solution was found by measurement to be greater than that of the acid. More moles are neutralized in less time with the base above the acid; in neither case does the diffusion proceed with the theoretical speed as shown by the very low values of k. The constant of this cell was not determined (with 0.1 molar hydrochloric acid diffusing into water) with the cell stationary, but it should be approximately 3.65.[3]

TABLE IV

INTERDIFFUSION WITH CELL STATIONARY, 25°C., 0.4 *M* NaCl

Expt.	C_A	C_B	Time, hours	C'_A	C'_B	k
20[a]	0.04925	0.0484	27.33	0.0367	0.0360	1.89
21[b]	.04925	.0484	24.17	.0348	.03405	2.53

[a] HCl above. [b] NaOH above.

Discussion.—While the greatest variation of k in Table III is 5.6% from the mean value of Table I, the average of all results is only 1.0% different. The variations are evidently due largely to the difficulty of choosing correct values of D_A, D_B and the change of the latter with acid and base concentration. The picture of the interdiffusion represented by equation (1) is fully substantiated.

The fact that the maximum coefficient for hydrochloric acid obtained with the rotating cell must be used to obtain the agreement of cell constants, as well as the fact that interdiffusion experiments in the stationary cell give abnormal results, indicates that the rotating cell has a wider range of applicability. The latter experiments especially indicate that the diffusion gradients are not confined to the porous disk unless the density relations allow adequate stirring to be maintained by convection currents, or mechanical stirring is introduced.

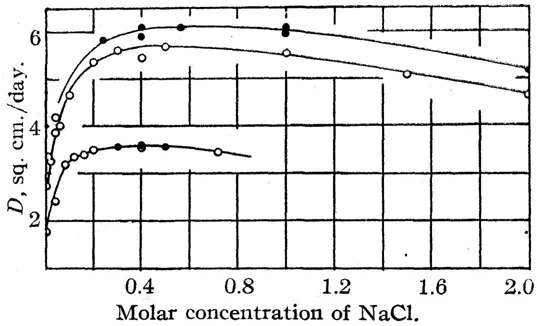

Fig. 1.—Diffusion coefficients in sodium chloride solutions: lower curve, NaOH; upper curves, HCl; ○, stationary cell; ●, rotating cell.

The point within the disk at which the neutralization occurs varies with the diffusion coefficients and concentrations of the reagents, and can be calculated from equation (1a). In the present case with equal acid and base concentrations in the presence of 0.4 molar sodium chloride, it occurs at a distance 0.37 δ from the surface in contact with the base.

Since this paper was written, an interesting and useful "multimembrane" method of studying diffusion processes has been published by Teorell.[4] In one interdiffusion experiment, the "diffusion layer" between equimolar hydrochloric acid and sodium hydroxide solutions was separated into seven portions by cellophane membranes; samples from the several compartments were analyzed after twenty-four hours, and the concentration gradients of the various ions thus recorded. The solutions contained no added salt; the neutralization occurred 0.375 of the total distance from the base compartment.

Summary

The diffusion coefficients of hydrochloric acid and sodium hydroxide have been measured in the presence of added sodium chloride over a wide concentration range.

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(4) Teorell, *J. Biol. Chem.*, **113**, 735 (1936).

The rate of interdiffusion of the same acid and base in sodium chloride solution has been studied. It is shown that the diffusion coefficients are unchanged if sufficient sodium chloride is present initially; in the porous disk cell, the diffusion *rates* are, however, greatly increased since the concentration gradients become much sharper because of the neutralization within the disk.

Some limitations of the porous disk diffusion cell are demonstrated. Adequate mixing must be maintained in the cell solutions either by natural convection or by auxiliary stirring.

NEW YORK, N. Y. RECEIVED FEBRUARY 12, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Conductance of Salts (Potassium Acetate) and the Dissociation Constant of Acetic Acid in Deuterium Oxide

BY VICTOR K. LA MER AND JAMES P. CHITTUM

The accurate calculation of the dissociation constant of a weak acid, like acetic acid, in deuterium oxide requires values of comparable accuracy of the limiting conductances Λ_0, of deuterochloric acid, potassium chloride and potassium acetate. In ordinary water the problem is solved by measuring a series of conductance values at increasing dilutions and controlling the extrapolation to infinite dilution by the Onsager[1] equation.

The limited quantities of heavy water available do not permit execution of this tedious and experimentally difficult problem at this time. We are accordingly interested in establishing the validity of two approximate rules, which will permit the calculation of Λ_0 for the deuteronium ion and for the anion of the weak acid with sufficient precision for present purposes from a single measurement at an experimentally convenient concentration ($C = 0.01$) in heavy water which is not necessarily 100% D_2O.

These rules are

$$[\Lambda_c/\Lambda_0]_{H_2O} = [\Lambda_c/\Lambda_0]_{D_2O} \qquad (1)$$

valid for acids and salts in pure D_2O, but presumably accurate only for salts in intermediate mixtures of D_2O–H_2O, owing to the complication of the exchange reactions which acids suffer in the mixed waters.[2]

$$\Lambda\eta = \text{Constant};\ \eta = \text{Viscosity}, \qquad (2)$$

valid for interpolation and for extrapolation to pure D_2O of the data obtained for the salts in H_2O–D_2O mixtures.

The justification of (1) follows from the Onsager equation[3]

$$\Lambda_c = \Lambda_0 - [\alpha\Lambda_0 + 2\beta]\sqrt{C} \qquad (3)$$

where

$$\alpha = \frac{8.173 \times 10^5}{(DT)^{3/2}} \text{ and } \beta = \frac{41.7}{(DT)^{1/2}} \times \frac{1}{\eta} \qquad (4)$$

Let $\beta' = 2\beta\eta$, then α and β' differ in H_2O and D_2O only by the ratio of the dielectric constants of H_2O and D_2O which ratio appears to be almost unity.[4,5]

$$\Lambda_c/\Lambda_0 = 1 - [\alpha + \beta'/\Lambda_0\eta]\sqrt{C} \qquad (5)$$

and

$$\frac{[\Lambda_c/\Lambda_0]_{H_2O}}{[\Lambda_c/\Lambda_0]_{D_2O}} = 1 + \frac{\beta'\sqrt{C}\,[1/(\Lambda_0\eta)_{H_2O} - 1/(\Lambda_0\eta)_{D_2O}]}{1 - [\alpha + \beta'/(\Lambda_0\eta)_{D_2O}]} \qquad (6)$$

The experimental data on potassium chloride and on potassium acetate presented below show that $(\Lambda_0\eta)_{H_2O}$ differs from $(\Lambda_0\eta)_{D_2O}$ by only 1.93%. Hence equation (6) reduces without appreciable error to equation (1).[6]

The error in $\Lambda_0(D_2O)$ calculated through equations (1) and (6) is thus less than 0.1% and less than our present experimental errors. The Λ_c *vs.* $\sqrt{C}$ curves in D_2O are, therefore, sensibly parallel to those in H_2O, and the D_2O curve can be constructed from a measurement of Λ at a single low concentration.

Since the only difference in the limiting conductance of non-acid ions in D_2O and in H_2O appears to be resident in the change in β, the electrophoretic part of the Onsager equation, we expect

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[1] Onsager, *Physik. Z.*, **27**, 288–292 (1926); **28**, 277–298 (1927).

[2] Baker and La Mer, *J. Chem. Phys.*, **3**, 406 (1935).

[3] MacInnes, Shedlovsky and Longsworth, *Chem. Rev.*, **13**, 29 (1933), eq. (7).

[4] Horst Müller, *Physik. Z.*, **35**, 1009–1011 (1935).

[5] P. Abadie and G. Champetier, *Compt. rend.*, **200**, 1387 (1935).

[6] η does not change significantly on passing from $C = 0.01$ to $C = 0$.

TABLE I

$\frac{\Delta S}{0.1079} = N_{D_2O}$	0.0	27.4	77.0	93.0	97.0	100.0
$10^5 K'$ acetic	1.84	1.352	0.741	0.608	0.575	(0.555)
Λ_{0KAc}	114.4	108.1	98.2	96.0	95.5	(94.7)
$(\Lambda_0\eta)$ KAc	114.4	115.0	115.8	116.4	116.5	(116.6)
$\Lambda_0\eta^{0.913}$ KAc	114.4	114.4	114.1	114.5	114.5	
Λ_0 (HAc-DAc)	390.6	345.6	297.5	285.9	285.2	
A (Eq. 8)	148.6	134.8	117.2	114.2	113.7	

that $\Lambda_0(H_2O)/\Lambda_0(D_2O)$ is practically constant for all completely dissociated salts of the same valence type and equal to approximately η_{D_2O}/η_{H_2O}.

Experimental.—The measurements on potassium acetate have been made at 25°, using a Jones bridge and the semi-micro method described previously,[2] at approximately 0.015 N at different mixtures of H_2O–D_2O. Λ_0 obtained by linear extrapolation from 93 and 97% D_2O is 94.8 Kohlrausch units (K. U.), a decrease of 17.1% from the H_2O value. The corresponding decrease for potassium chloride is 17.2%. Table I shows that the empirical equation

$$\Lambda_0\eta^{0.913} = \text{Constant} \qquad (7)$$

shown in the previous paper to be valid for potassium chloride, applies equally well to potassium acetate. The value of Λ_0(KAc) at 100% D_2O calculated either from equation (1) or (7) is 94.7 K. U.

Dissociation Constant of Acetic Acid.—The stoichiometric constant for approximately 0.02 N acetic acid, has been calculated using the MacInnes–Shedlovsky[7] method for each H_2O–D_2O mixture (Table I), by omitting the last (empirical) term in the equation

$$\Lambda_\epsilon(\text{HAc}) = \Lambda_0 - A\sqrt{C_i} + Bc\,(1 - \alpha\sqrt{C}) \qquad (8)$$

Λ_0 (HCl) and Λ_0 (KCl) were calculated by means of equation (1). A short series of approximations gives Λ_ϵ and hence C_i from $(1000\,\bar{L})/\Lambda_\epsilon$. ($\bar{L}$ = specific conductance of solution.)

The stoichiometric constant K' is defined as $C_i^2/(C - C_i)$, where C is the stoichiometric concentration of the acid. Linear extrapolation from 93 to 97% D_2O (Fig. 1, curve 1), gives $K' = 0.555 \times 10^{-5}$ for deutoacetic acid, which compares favorably with Lewis and Schutz' estimate of 0.59×10^{-5} obtained on less than one cc. of solution. Our value proves to be in excellent agreement with the value of 0.55×10^{-5} obtained by Korman and La Mer[8] from the e. m. f. of quinhydrone–silver chloride, Ag cells without transference and a formula defined by them for extrapolating K to 100% D_2O.

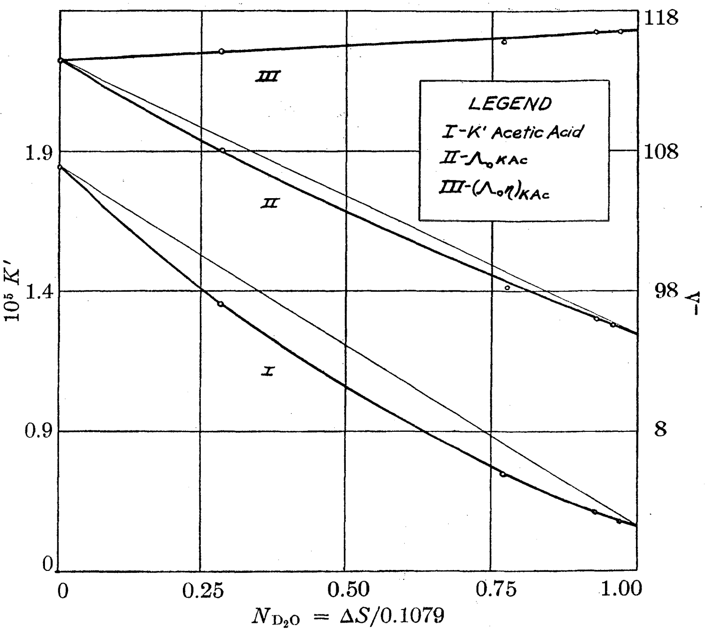

Fig. 1.

As was found previously for potassium chloride Λ_0 for potassium acetate exhibits a small negative deviation of approximately 2% at $N_{D_2O} = 0.5$. On the other hand, the dissociation constant of hydrogen acetate exhibits a much larger negative deviation from linearity amounting to 10% at $N_{D_2O} = 0.5$. The nonlinear behavior of the dissociation constant when plotted against the deuterium content of the solvent $N_{D_2O} = \Delta S/0.1079$ arises from the complications of the proto- and deuterotropic exchanges in the mixtures as was suggested for the Λ hydrogen chloride curve, which exhibits a negative deviation of 6.5% at the midpoint. Similar deviations from linearity are uniformly

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(7) MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932). We did not attempt the precautions taken by these authors, namely, of adding traces of HAc to KAc solutions because of the small volumes of D_2O available.

(8) Korman and La Mer, THIS JOURNAL, **58**, 1396 (1936); *Science*, N. S., **83**, 624 (1936).

exhibited in the kinetic processes of acid–base catalysis.[9,10]

Summary

The Walden constant = $\Lambda_0\eta$ increases (linearly) by 1.93% on passing from H_2O to D_2O for both potassium acetate and potassium chloride. With this equation and the rule

$$[\Lambda_c/\Lambda_0]_{H_2O} = [\Lambda_c/\Lambda_0]_{D_2O}$$

which follows from the Onsager equation and the Walden rule, it is shown how the dissociation constants of weak acids in D_2O may be calculated with satisfactory accuracy from a limited amount of conductance data. K' (acetic acid) equals 0.55×10^{-5} in pure D_2O, and exhibits a marked negative deviation (10%) from linearity on passing from H_2O to D_2O.

NEW YORK, N. Y. RECEIVED JULY 1, 1936

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(9) Hamill and La Mer, *J. Chem. Phys.*, **2**, 891 (1934); **4**, 395 (1936).

(10) La Mer and Greenspan, not yet published.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Ternary Systems. XXI. Lead Nitrate, Ammonium Nitrate and Water at 25°

BY ARTHUR E. HILL AND NATHAN KAPLAN

The effect of potassium nitrate in increasing the solubility of lead nitrate inwater led Le Blanc and Noyes[1] to the explanation of double salt or complex ion formation in the liquid phase. Solubility determinations by Glasstone and Saunders[2] at temperatures between 25 and 100° gave no evidence of double salts as solid phase, and similar experiments by Ehret[3] at 0° gave likewise a negative result. The work of Glasstone and Saunders[2] with sodium nitrate as added salt showed a decrease in solubility of lead nitrate, also without formation of double salt in the solid phase. The effect of ammonium nitrate, which has a much higher solubility than the corresponding sodium and potassium salts, permitting the investigation to cover a wider range of concentrations, is here reported.

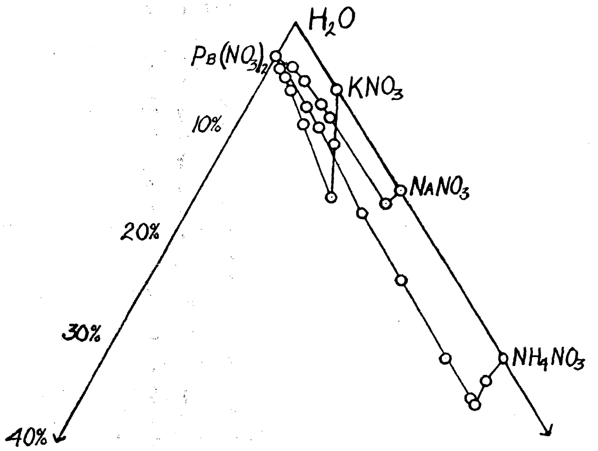

Fig. 1.—25° Isotherm, $Pb(NO_3)_2$–NH_4NO_3–H_2O, in mole per cent.

Pure recrystallized lead nitrate and ammonium nitrate were used in making up the complexes, which were rotated in closed tubes for several days at 25 ± 0.03°. The solutions at equilibrium were analyzed by evaporation of a weighed sample to give total solids, and the determination of lead as lead sulfate by the standard method. The results are given in Table I.

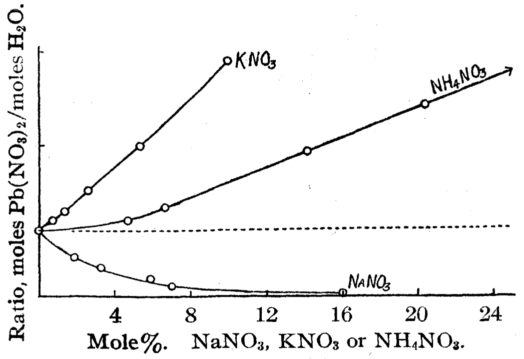

Fig. 2.—Effect of added nitrate on solubility of $Pb(NO_3)_2$ at 25°.

The solubility curves, plotted in molar percentages, are shown in Fig. 1. On the same diagram are shown the results of Glasstone and Saunders[2] for potassium nitrate and sodium nitrate. It is apparent that the effect of ammonium nitrate upon the solubility of lead nitrate is intermediate between the effects of the potassium and sodium salts, at similar molar concentrations. There is no indication of double salt formation as solid phase; tie lines drawn through the compositions

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(1) Le Blanc and Noyes, *Z. physik. Chem.*, **6**, 385 (1890).

(2) Glasstone and Saunders, *J. Chem. Soc.*, **123**, 2134 (1923).

(3) Ehret, THIS JOURNAL, **54**, 3126 (1932).

TABLE I

SYSTEM: $Pb(NO_3)_2$–NH_4NO_3–H_2O AT 25°

Original complex Wt., % $Pb(NO_3)_2$	Original complex Wt., % NH_4NO_3	Saturated solution Wt., % $Pb(NO_3)_2$	Saturated solution Wt., % NH_4NO_3	Moles $Pb(NO_3)_2$ per mole H_2O	Solid phase
...	...	37.17[2]	0.00	0.0322	$Pb(NO_3)_2$
48.03	9.72	33.99	12.35	.0344	$Pb(NO_3)_2$
59.64	10.04	34.02	16.28	.0372	$Pb(NO_3)_2$
38.39	26.74	33.65	28.75	.0487	$Pb(NO_2)_2$
41.87	31.90	32.61	36.92	.0581	$Pb(NO_3)_2$
35.91	41.39	30.79	44.58	.0680	$Pb(NO_3)_2$
39.06	42.03	29.63	48.47	.0735	$Pb(NO_3)_2$
32.36	54.54	29.44	49.00	.0743	$Pb(NO_3)_2$ + NH_4NO_3
27.84	55.22				
15.37	62.65	18.04	56.15		NH_4NO_3
...	...	0.00	68.17		NH_4NO_3

of saturated solution and original complex pass through the compositions of the two simple salts with average deviation of 1.1%.

From the molar ratio of lead nitrate to water, shown in column 5, it is apparent that addition of ammonium nitrate increases the solubility of the salt markedly. A plot of the change in solubility, as thus defined, is shown in Fig. 2, in which are shown also curves for potassium nitrate and sodium nitrate calculated from the work of Glasstone and Saunders.

Summary

The solubilities in the system $Pb(NO_2)_2$–NH_4NO_3–H_2O at 25° have been determined. The solubility of lead nitrate is increased by ammonium nitrate, but to a smaller degree than by potassium nitrate. No double salts have been found as solid phases.

NEW YORK, N. Y. RECEIVED JULY 1, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Studies in the Mechanism of Decomposition. I. The Vapor Phase Photolysis of Acetic Acid

BY MILTON BURTON

In order to explain certain observations on the pyrolysis of acetic acid, Hurd[1] suggested the formation of ketene as an intermediate reaction product. F. O. Rice[2a] showed that such formation might be considered a logical consequence of a free radical chain mechanism. However, Franck and Rabinowitsch,[3] in discussing the photolysis of organic molecules by the intermediary of free radicals and atoms, pointed out that certain polyatomic molecules might decompose directly into stable molecules and that the work of L. Farkas and Wansbrough-Jones[4] indicated that acetic acid is an example of such a compound. That conclusion was based primarily upon an analysis of the ultimate products of the decomposition, which showed such a clear correspondence of yields among the products that the two reactions following appeared to be the only tenable ones in the gaseous state

$$CH_3COOH + h\nu \longrightarrow CH_4 + CO_2 \qquad (1)$$

$$(CH_3COOH)_2 + h\nu \longrightarrow C_2H_6 + CO + CO_2 + H_2O \qquad (2)$$

Although they reported a yield of approximately 1% by volume of hydrogen, Farkas and Wansbrough-Jones favored the idea that that substance, as well as traces of acetylene found, might be a product of some subsequent reaction of the resultant molecules.

This appears to be a clear-cut case in which to test whether decomposition takes place by rupture into free radicals or by rearrangement of a stable constellation of groups into stable constellations of ultimate molecules. The mirror methods developed by Paneth[5] and by F. O. Rice and his co-workers[6] and used by Pearson[7] in the study of the photochemical decomposition of aldehydes and ketones are well suited to the test. In a previous communication[8] the writer described a procedure for the detection of hydrogen atoms in the presence of free radicals and indicated evidence for the reactions

$$CH_3COOH + h\nu \longrightarrow CH_3 + COOH \qquad (3)$$

$$COOH \longrightarrow CO_2 + H \qquad (4)$$

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[1] Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, p. 334.

[2] Rice and Rice, "The Aliphatic Free Radicals," Johns Hopkins University Press, Baltimore, 1935, (a) p. 135, (b) p. 14, (c) p. 187.

[3] Franck and Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[4] L. Farkas and Wansbrough-Jones, *Z. physik. Chem.*, **18**, 124 (1932).

[5] Paneth and co-workers, *Ber.*, **62**, 1335 (1929); *Z. physik. Chem.*, **B7**, 155 (1930); *Nature*, **125**, 564 (1930); *Ber.*, **64**, 2702 (1931); **64**, 2708 (1931); *et seq.*

[6] Ref. 2 reviews this work thoroughly.

[7] Pearson, *J. Chem. Soc.*, 1718 (1934); Pearson and Purcell, *ibid.*, 1151 (1935).

[8] Burton, THIS JOURNAL, **58**, 692 (1936).

to account for at least part of the photolysis of acetic acid.

In this report, evidence will be presented which will show that the photolysis of acetic acid can be explained entirely by a free radical mechanism but that the above indicated mechanism is incorrect.

Experimental

Light Sources.—In the work reported in the previous communication and referred to briefly in Part I following, a quartz Hanovia mercury vapor lamp operating in series with a rheostat on a 110-volt storage battery line was used. At that time no special precautions were employed to maintain constancy of current, which was held at about 4–5 amperes.

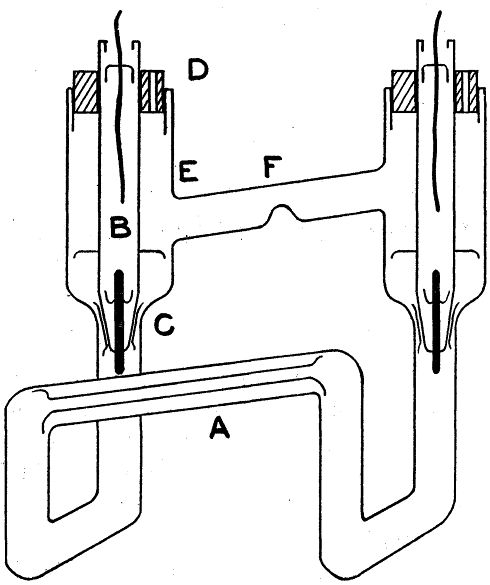

Fig. 1.—Capillary mercury arc.

In all later work the quartz capillary mercury arc shown in Fig. 1 was employed. It is a modification of the lamp described by Forbes and Heidt.[9] The capillary tube A has a slight slope and is 4 cm. long and about 2 mm. in internal diameter. The entire lamp is of quartz except for the tubes B, which are of Pyrex glass. The bottoms of those tubes have tungsten wires sealed in as shown and are ground to fit into the quartz tubes at C. The openings at C may be regulated by withdrawing the tubes B slightly. The tubes are thereafter held in fixed position by the rubber stoppers D, which are grooved to permit ready access of air into the reservoirs E. The tube F serves to permit flow of mercury from one reservoir to the other as described by Forbes and Heidt. (In the writer's experience with this lamp no such flow of mercury was observed even on three-hour periods of operation. The mercury levels were never that far displaced.) Contact is made by inserting nickel or iron wires in the mercury in the tubes B. The wires are so connected that the upper end of the capillary is negative. The lamp as described was used in a 110-volt battery circuit containing a rheostat so adjusted as to permit a current of 4.0 amperes. In starting the lamp the mercury column in A was broken by heating with a sharp flame. During operation a rapid stream of water was flowed over the capillary tube from an ordinary wing-top which had been cut down so that its edge would rest evenly on the full length of the tube. The lamp was supported in a glass funnel in such a way as to drain off the water. It was not necessary to keep the legs of the lamp immersed, for water was flowing down them constantly during operation. The filling of the tube was conducted simply by boiling out the air while holding the tube at a convenient angle to promote entrance of mercury. From time to time, between runs, the outer surface of the capillary was cleaned with hydrochloric acid.

Chemicals.—The acetic acid used was the analyzed product of General Chemical Co., of A. C. S. grade. It was subjected to four recrystallizations and decantations before introduction into the apparatus. Only about 25% of the original sample was used. The acetone was the A. C. S. grade of Eimer and Amend further purified by the method of Shipsey and Werner[10] to a constant boiling point of 56.0° uncorrected. The sodium bromide and sodium chloride were Eimer and Amend T. P. grades and were merely dried to constant weight at 130° before use.

Apparatus and Technique.—The methods used were very similar to those already described by Pearson.[7] The apparatus is indicated in Fig. 2. The purified liquid was introduced into reservoir A, frozen (or cooled) in carbon dioxide–toluene mixture, evacuated, and then allowed to warm to room temperatures (above the melting points both of acetone and of acetic acid). This process of cooling, evacuation and warming was repeated once in reservoir A. Then, by suitable manipulation of the stopcocks and application of the freezing mixture, the liquid could be distilled to either of the reservoirs B or C where it was subjected to further repeated cooling, evacuation and warming as already described for at least three additional successive times. In this way entrapped gases were eliminated.

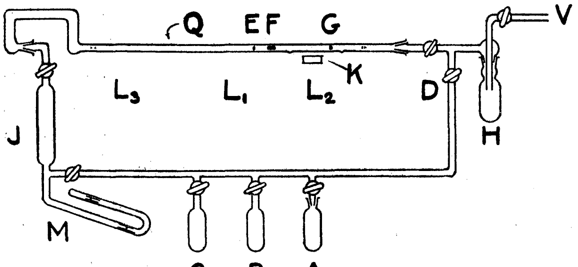

Fig. 2.—Reaction system.

Regular stopcock grease was used in all stopcocks and joints. The length of the constricted portion of the tubing, including the quartz reaction tube Q and allowing for the ground glass joints to which it was sealed, was fixed at 88 cm. The tube Q had an average internal diameter of almost exactly 5 mm. The tube J contained silver turnings intended to trap out mercury vapors. The mercury manometer M had a slope ratio of 25:1 and permitted

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[9] Forbes and Heidt, THIS JOURNAL, **53**, 4349 (1931).

[10] Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

TABLE I

SERIES OF EXPERIMENTS WITH LEAD GUARD MIRROR

Expt.	22	23	24[a]	25
Substance	Acetone	Acetic acid	Acetone	Acetic acid
Pres. at M, mm.	2.2–2.4	2.1–2.25	2.0	2.2
Mirror E (Pb)	Heavy	Very light	From expt. 23	Light
Distance of E from L_1, cm.	7	2.6	2.8	5.2
Guard mirror F (Pb) 1.5–2 cm. long	Heavy	Heavy	From expt. 23	Heavy
Mirror G (Sb)	Very light	From expt. 22	Very light	From expt. 24
Distance of G from L_1, cm	19.2	18.5	18.7	19
Time of run, minutes	85	75	78	180
Effect on E	Partly removed	Only trace left	Gone in 22 min.	Still present
Effect on F	....	None	Attacked near E in 65 min.	None
Effect on G	None	Gone	None	Gone

[a] Expt. 24 followed sixteen hours after expt. 23.

readings accurate to 0.01 mm. The apparatus was connected to a carbon dioxide–toluene trap and a mercury vapor pump system at V. During a run, the path of the vapors was from one of the reservoirs A, B or C through J and the reaction tube Q to the receiver H, which was cooled in a carbon dioxide–toluene mixture. After the reservoir was exhausted the liquid was then distilled back from the receiver H through the now opened stopcock D to the reservoir. It was found that the small amount of product impurity formed during the photolyses did not sensibly affect the results in subsequent runs. The irradiated zones were at either L_1, L_2 or L_3, as will be indicated below. K represents a light filter (cooled with flowing water during runs) containing a suitable solution between crystal quartz plates 1 cm. apart. A copper cylinder around the reaction tube served as a screen which was used while the arc and the flow of gas were adjusted. It was slipped aside at zero time, exposing the irradiated zone but shielding the mirror or mirrors. When the filter was not used, the reaction tube itself was cooled with running water. Under no circumstances did the temperature of the reaction tube rise above that of the room.

Part I. Detection of Atomic Hydrogen in the Presence of Methyl.—In these early experiments, the results of which have already been reported,[8] the apparatus was not quite the same as shown in Fig. 2. The reaction tube system was sealed to the rest of the apparatus and not affixed with ground glass connections. In other respects it was substantially the same as in the latter experiments.

In this part the depression between F and G contained a small pellet of lead; that after G contained one of antimony. A transparent lead test mirror of the weight desired was deposited at E (after suitable preparation of the surface[2]) and a heavy lead guard mirror was deposited at F. A very light antimony mirror was then deposited at G. Such mirrors were deposited only when desired. On some occasions, as is evident from Table I, a mirror might be used for more than one experiment.

In Table I there are indicated the results of a typical series of experiments on the vapors of acetone and of acetic acid. During the experiments of this part, the reaction tube was illuminated at L_1, approximately 40 cm. from its beginning, by the unfiltered Hanovia arc located about 0.7 cm. from the tube. The arc was not always located at the same distance from the beginning of the tube in this series. It is for that reason that the distances of the mirrors from the irradiated zone vary from experiment to experiment.

The efficacy of the heavy lead mirror as a guard to prevent the passage of methyl radicals is indicated with acetone as a known case[7] in expt. 22. It will be shown below that under similar conditions of operation irradiated acetone will yield more than ten times as many mirror-active particles as acetic acid. Lead mirrors may be shifted, but not removed, by hydrogen atoms, while antimony mirrors are attacked both by free methyl radicals and hydrogen atoms.[11] Consequently, it can be concluded from this experiment that, if acetic acid produces only free methyl radicals and no hydrogen atoms, it could be passed through the reaction tube under these same conditions for at least eight hundred and fifty minutes without any visible effect on the antimony mirror. However, expt. 23 showed that acetic acid vapor removed that mirror under similar conditions of operation in seventy-five minutes. A fresh lead mirror was simultaneously attacked in that experiment. The fact that the guard mirror used in expt. 23 was still effective at the end of the run was shown in expt. 24 with acetone, which again failed to remove a fresh antimony mirror. The fact that the antimony mirror used in expt. 24 was

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(11) Pearson, Robinson and Stoddard, *Proc. Roy. Soc.* (London), **142**, 275 (1933).

sensitive to mirror-active particles was verified in expt. 25 with acetic acid vapor.

Similar experiments were performed from time to time and on the basis of these results it appeared clear that acetic acid was yielding particles capable of attacking lead mirrors and others which would attack antimony although they had no effect on lead. It was concluded and reported[8] consequently that the photolysis of acetic acid yielded both methyl radicals and hydrogen atoms. However, the subsequent results of Part II showed that the effect on the lead mirror could not be quantitatively duplicated. A check-up of the results indicated that, although methyl radicals and hydrogen atoms had been observed simultaneously during the photolysis of acetic acid, they did not both originate in that compound. The hydrogen atoms came from the acetic acid; the methyl radicals came from the acetone which had been adsorbed in the system (perhaps in J) and swept along with the acetic acid. Whenever a series such as shown in Table I was run, there would be apparent formation of methyl radicals during the photolysis of acetic acid. It was only when particular precautions were taken to eliminate the last traces of acetone before the acetic acid runs that no lead mirror removal was observed with the latter.

The conclusions to be drawn from this part are: (1) hydrogen atoms can be detected by this process in the presence of methyl radicals. (2) Acetic acid vapor of itself does not interfere with the sensitivity of lead mirrors to free methyl radicals. (3) Hydrogen atoms apparently are produced during the photolysis of acetic acid vapor.

Part II. Comparisons of Rates of Mirror Disappearance.—The previous part is not conclusive as to the possibility of free methyl formation during the photolysis of acetic acid. It may well be, for example, that under the conditions of the experiments hydrogen atoms are more mirror-active than free methyl radicals, so much so that the latter would not be detected within the time required to establish the presence of the atoms.

This group of experiments was initiated when it was still believed that methyl radicals detected in such experiments as expt. 23 (Table I) were originating in the acetic acid. The purpose was to compare the rates of removal of standard lead and antimony mirrors by acetone and by acetic acid. The former yields only methyl radicals;[7] the product of the latter was in question.[12] The conditions of the test were kept constant for each of the mirrors. The pressure of the vapors was set at approximately 2.3 mm. at the manometer. Standard mirrors were deposited as described by Pearson[7] by comparison with a smoked-glass tube. To obtain some measure of accuracy by this method the results of a large number of runs were averaged. For convenience, the water filter was used with the arc light shown in Fig. 1 at L_2 2.3 cm. from the reaction tube in the antimony tests; in the lead tests the light was placed 1 cm. from the tube at L_1 without a filter. In the first experiments neither the standard lead mirrors nor the standard antimony mirrors were ever satisfactorily removed in the photolysis of acetic acid in a reproducible manner. As already indicated, the erratic results were finally traced to the presence of residual acetone. Satisfactory results for lead and antimony mirrors with acetic acid were obtained only either after the acetone had been thoroughly removed from the system or before it had been introduced. The averaged results of this part are shown in Table II.

TABLE II

COMPARISON OF TIMES OF REMOVAL OF MIRRORS BY ACETIC ACID AND BY ACETONE

	Acetic acid	Acetone
Antimony	35.5 min.	137 sec.
Lead	$\gg$120 min.	39 sec.

Under the conditions of the test it is clear that free methyl caused the disappearance of lead more quickly than that of antimony. If the mechanism of reactions 3, 4 were correct, it could be concluded that half the effect on the antimony mirror with acetic acid might be due to free methyl, *i. e.*, that such radicals by themselves would have caused the removal in about seventy minutes. It would then be expected that the photolyzed acetic acid would remove the lead mirrors in about twenty minutes. It consequently must be concluded either that no free methyl is formed during the photolysis of acetic acid or that its mirror-activity compared with that of hydrogen atoms is so slight that it is unobservable.

In check experiments to find what effect, if any, free methyl might have on the photolysis of acetic acid, a small amount of acetone was introduced deliberately into the acetic acid. The rate of

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[12] See Rice, ref. 2, pp. 51–54, for the treatment of a parallel case in a mixture containing free methyl and free methylene.

lead mirror removal was then found to depend on the actual quantity of acetone in the acetic acid.

Part III. Effect of Distance of Mirror from the Irradiated Zone.—The evidence so far presented is not absolutely conclusive that no free methyl is formed during the photolysis of acetic acid. It is known that at room temperatures hydrogen atom has a much greater half-life than free methyl.[2b] The shape of the curve showing variation of time of disappearance of the mirrors with distance from the irradiated zone might consequently be used to establish whether or not free methyl is formed during the photolysis of acetic acid.

In this group of experiments no filter was used. The arc of Fig. 1 was located at L_3 so that the edge of the irradiated zone near the mirrors was now 22.8 cm. from the beginning of the constricted portion of the system. The light itself was fixed 1 cm. from the reaction tube. The pressure of the vapors was set at approximately 2.3 mm. at the manometer corresponding to a streaming velocity for acetic acid vapor at the beginning of the constricted region of approximately 29.7×10^2 cm. per sec.

The results of all these experiments (not the averages) are shown graphically in Fig. 3. Pearson's values are plotted from his average figures[7] for acetone entering at a pressure of 1.65 mm. and a streaming velocity of 12.3×10^2 cm. per sec. No explanation is offered at this time for the opposed concavity of the curves obtained by Pearson and by this writer. It should be pointed out that the difference may be related to the different pressures at which the work was conducted as well as to the fact that Pearson's work may have a higher accuracy in view of the greater number of his experiments. It is, however, clear that the general trends of the two curves are similar and quite different from the curve for acetic acid, which is almost a horizontal straight line. Evidently, the half-life of the active product from the photolysis of acetic acid is much greater than that from acetone and is probably hydrogen atom. Also, we are forced to assume either that free methyl is far less effective than hydrogen atom in causing removal of antimony mirrors or that it is entirely absent in the photolysis of acetic acid.

The first assumption is excluded by the findings of Paneth and Lautsch,[13] who report that methyl and ethyl radicals adhere to a mirror on the first collision. It will be shown below that the slight slope of the acetic acid line is reasonably traceable to the clean-up reactions involving hydrogen atom. Consequently, there is evidence that no free methyl is formed during the photolysis of acetic acid. The upper curve of Fig. 3 shows the ratios of times of disappearance of mirrors under the influence of acetic acid and acetone, respectively. It is calculated from the two curves below. It is this curve which is the basis for the previous statement that under similar conditions acetone yields more than ten times as many mirror-active particles as does acetic acid.

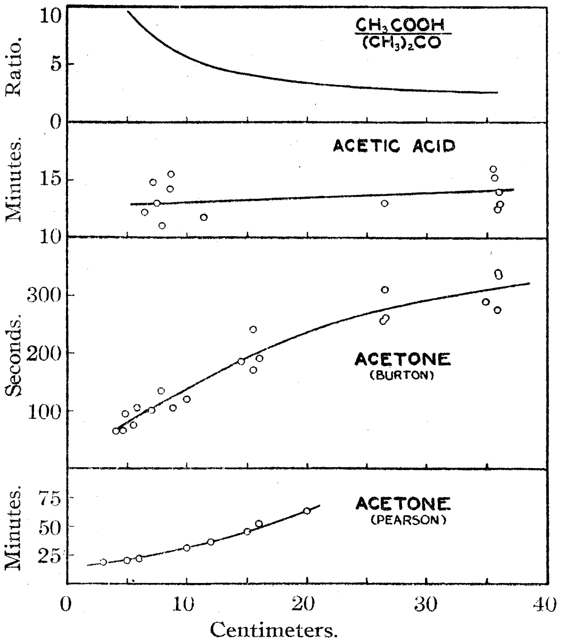

Fig. 3.—Effect of distance from irradiated zone on time of antimony mirror removal.

The formula, given by Paneth and Lautsch,[14]

$$t = \frac{X_2 - X_1}{V} - a\,\frac{(X_2^2 - X_1^2)}{2VP}$$

is used for an estimation of the time required for a particle to travel from the irradiated zone to any point under consideration. In that formula, X_1 and X_2 are, respectively, the distances of the edge of the irradiated zone and of the point from the beginning of the tube, V is the streaming velocity, a is the average pressure gradient, in this case 0.00261 cm. Hg per cm., and P is the pressure (*i. e.*, 0.23 cm.). The time required for a particle to travel 30 cm. from the irradiated zone comes out to be 0.58×10^{-2} sec. The average pressure between the irradiated zone and that

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(13) Paneth and Lautsch, *Ber.*, **64**, 2702 (1931).

(14) Paneth and Lautsch, *ibid.*, **64**, 2708 (1931).

point readily may be calculated to be about 0.13 cm. If N be the number of collisions which a hydrogen atom would suffer[15] in an atmosphere of acetic acid at 76 cm. pressure, then it is evident that the number of collisions suffered under the conditions of these experiments in these 30 cm. would be

$$N_{30} = N\frac{\text{Average press.} \times t}{76}$$

If $N = 10^{10}$, $N_{30} = 10^5$; on the other hand, if $N = 10^{11}$, $N_{30} = 10^6$.

If we now examine the acetic acid curve of Fig. 3, it may be seen that the extrapolated time of mirror disappearance at the irradiated zone is 12.1 minutes and that the estimated time at a distance of 30 cm. is 13.9 minutes. The difference of the reciprocals of the times is a measure of the fraction of hydrogen atoms which have disappeared in that 30 cm. That fraction is 1.8/13.9 or approximately 0.13 and is equal to the probability of an individual hydrogen atom undergoing reaction in that 30 cm.

Since the rate of reactive collisions may be expressed[16] by

$$k = Ae^{-E/RT}$$

where we may here take k as the total number of reactive collisions (in the unit of time chosen), A as the total number of collisions per hydrogen atom (in the same time), E as the energy of activation per mole, R as the gas constant and T as the absolute temperature, it is found that, substituting 0.13 for k and the appropriate values for A and T, at room temperature E is 8.1 kcal. if N is 10^{10} or 9.5 kcal. if N is 10^{11}. These figures are only approximate. There is the implicit assumption that the steric factor is 1. They also depend on the estimate of the decrease in the concentration of hydrogen atoms along the tube, which in turn depends upon data which are not extremely accurate. If we assume that the change in concentration may really be either a quarter or four times as great as the estimate, then the limiting values for E will be 7.3 and 10.3 kcal.

Part IV. Effect of Wave Length.—The absorption spectrum of acetic acid has been investigated by Ley and Arends.[17] The continuum begins at about 2300 Å., reaches a maximum at 2040 Å., falls to a slight minimum at about 1925 Å. and rises thereafter to the limit of the study at about 1850 Å. Inasmuch as Farkas and Wansbrough-Jones[4] indicate evidence for decomposition into stable molecules and this paper on the other hand offers evidence for a free radical mechanism, it may be surmised that the shape of the absorption curve is related to a variation in the production of free radicals with wave length. The following tests were conducted to discover whether there is any threshold of free radical production other than the beginning of the continuum.

All traces of acetone were removed from the system. The arc of Fig. 1 was removed to a distance of 2.3 cm. from the reaction tube at L_2. The filter vessel already described, containing either distilled water, 0.1 N sodium chloride or 0.125 N sodium bromide solutions, was inserted between them as indicated in Fig. 2. The data of Fromherz and Menschick[18] show that in 1-cm. layers of these concentrations sodium chloride cuts off fairly sharply at 2000 Å., whereas the sodium bromide solution cuts off at about 2300 Å. Tests of the arc lamp with a Moll thermopile and galvanometer indicated a slightly higher photon intensity in the region 2300–2000 Å. than in the 2000–1849 Å. region. About 94% of the energy was above 2300 Å. Standard antimony mirrors were deposited 2.5 cm. from the irradiated zone and the acetic acid was passed through, as before described, at a pressure of approximately 2.3 mm. The results of these experiments are summarized in Table III.

TABLE III

EFFECT OF WAVE LENGTH ON TIME OF ANTIMONY MIRROR REMOVAL BY PHOTOLYZED ACETIC ACID

Filter	Range, Å.	Index of energy intensity	Average time of mirror removal, min.
Water	>1849	10	35.5
0.1 N NaCl	>2000	9.74	95
.125 N NaBr	>2300	9.4	$\gg$133

No indication of mirror removal with the sodium bromide filter was ever obtained although after one such test the activity of the mirror was checked in a run with the water filter. Although one hundred and thirty-three minutes was the maximum time employed for such a test, it was not considered necessary to prolong it any further since no characteristic sharpening of the mirror, which always occurs long before complete removal, was ever observed.

The results show a somewhat higher yield of atomic hydrogen per photon below 2000 Å. than

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[15] *Cf.* Bonhoeffer and Harteck, "Grundlagen der Photochemie," Verlag von Theodor Steinkopff, Dresden, 1933, p. 183.

[16] Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932.

[17] Ley and Arends, *Z. physik. Chem.*, **B17**, 177 (1932).

[18] Fromherz and Menschick, *ibid.*, **B3**, 1 (1929).

above that value. If that be true, it may possibly indicate that the absorption maximum at 2040 Å. is associated with decomposition into stable molecules. At any rate, the evidence is clear that there is decomposition into atomic hydrogen in the range 2300–2000 Å. and that the beginning of the continuum is probably also the threshold of free radical production. The tests with the sodium bromide filter establish that it is a true photo decomposition which is being observed and not a secondary effect due to the intense line 2537 (*e. g.*, photosensitization by excited mercury vapor).

Discussion

The experimental results indicate that hydrogen atoms are formed in the photolysis of acetic acid but that methyl radicals are not. Reaction 3, suggested previously,[8] therefore cannot be the primary step of the photolysis. Also, all primary steps which yield radicals, such as CH_3CO, which decompose readily[19] into free methyl and another molecule, are eliminated. Consequently, although Terenin[20] reports the emission bands of hydroxyl during the photolysis of acetic acid, it cannot be formed in the primary decomposition. Finally, any mechanism suggested must account for the production of free hydrogen and free hydroxyl and must be the chemical equivalent of reactions 1 and 2 or otherwise agree with the analysis reported by Farkas and Wansbrough-Jones.[4]

Mechanism 1.—The mechanism summarized below meets the requirements just indicated.

$$\begin{array}{rl}
CH_3COOH + h\nu \longrightarrow CH_3COOH^* & (5')^{21,22} \\
CH_3COOH^* \longrightarrow CH_3COO + H & (6') \\
CH_3COO + H \longrightarrow CH_4 + CO_2 & (7') \\
CH_3COOH + H \longrightarrow CH_4 + COOH & (8') \\
COOH \longrightarrow CO + OH & (9) \\
CH_3COOH + OH \longrightarrow CH_3COO + H_2O & (10')^{23} \\
2CH_3COO \longrightarrow C_2H_6 + 2CO_2 & (11)
\end{array}$$

Hydrogen atom should also disappear by the reaction

$$CH_3COOH + H \longrightarrow CH_3COO + H_2 \qquad (12')$$

and to a very much smaller extent (of no quantitative significance) by

$$2H + M \longrightarrow H_2 + M \qquad (13)$$

The suggested mechanism fits previously estimated activation energies. Rice[2c] assigns a value of E for the reaction step 5,6 of 96 ± 8 kcal., well below the 123 kcal. corresponding to the beginning of the continuum at 2300 Å.[24] It is possible that Rice's value may be somewhat low and that the beginning of the continuum actually corresponds to the energy of activation. For the decomposition $CH_3COO \longrightarrow CH_3 + CO_2$ he assigns a value of 40–70 kcal. which would account for the fact that no free methyl is observed in this photolysis. On the other hand, he assigns a value of only 10–25 kcal. for reaction 9, which would indicate a fairly rapid reaction yielding hydroxyl and carbon monoxide.

If, in addition, we assume on the basis of the vapor pressure measurements of Holland,[25] as did Farkas and Wansbrough-Jones, that double molecules of acetic acid also enter into the decomposition reactions, the mechanism may be modified in the following respects

$$(CH_3COOH)_2^* \longrightarrow \left(\begin{matrix} CH_3COO \\ CH_3COOH \end{matrix}\right) + H \qquad (6'')$$

The hydrogen atom in this case will have somewhat less translational energy than in the single molecule case and the chances of recombination before the particles have left their mutual spheres of influence will be greater. The H will react then with the CH_3COO part of the molecule or the CH_3COOH part, with the probability that the former part, being nearer to the H atom, will enter into more frequent collisions. Thus, we have the reaction

$$\left(\begin{matrix} CH_3COO \\ CH_3COOH \end{matrix}\right) + H \longrightarrow CH_4 + CO_2 + CH_3COOH \qquad (7'')$$

which is equivalent to reaction 7′. On the other hand, if the H atom reacts with the CH_3COOH part of the molecule, we have reactions equivalent to 8′ and 12′ and all the accompanying and succeeding reactions. In order to explain the lower yield of carbon dioxide than might be expected on the basis of the evidence that there are only half as many single as double molecules present, Farkas and Wansbrough-Jones were forced to assume that the nature of the orientation in the molecule determined the direction of the reaction. While

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[19] Norrish, *Acta Physicochim. U. R. S. S.*, **3**, 171 (1935).

[20] Terenin, *ibid.*, **3**, 181 (1935).

[21] Reactions denoted by a single ′ refer to single acetic acid molecules; reactions denoted by double ″ refer to double molecules. When the primes are not indicated in a reaction involving the acetic acid molecule, the reference is to both reactions.

[22] The activation of acetic acid is chosen as the correct primary step in order to show a presumable relationship to results obtained with formic acid, as is discussed in a following report. However, in contradiction to the assumption of activation, the evidence in this report indicates immediate dissociation.

[23] The possibility of such reactions as $CH_3COOH + OH \longrightarrow CH_3OH + COOH$ and $CH_3COOH + OH \longrightarrow H_2O + CH_2COOH$ is generally excluded at low temperatures *Cf.* ref. 2, p. 190–191.

[24] The continuum may perhaps begin at 2400 Å., corresponding to 117 kcal.

[25] Holland, *Z. Elektrochem.*, **18**, 234 (1912).

such a view might also apply in this case, it is interesting to note that no special assumptions have to be adopted in order to explain all the products formed.

Farkas and Wansbrough-Jones give the following analysis of the products (neglecting water): 41% CO_2, 23% CH_4, 17.5% CO, 17.5% C_2H_6 and 1% H_2. The small yield of H_2 compared with CO indicates that reaction 8 proceeds much faster than reaction 12. Reaction 7 must be presumed to occur as a primary reverse reaction before the product particles of reaction 6 have had an opportunity to depart from each other's fields of influence. In other words, reaction 7 must be expected to take place entirely within the irradiated zone in a time too small for the particles to move any perceptible distance in the streaming vapor. Consequently, it seems logical to conclude that the energy of activation determined in Part III corresponds to reaction 8; *i. e.*, the energy of activation of reaction 8 is 7.3–10.3 kcal. per mole. From the ratio of H_2 yield to CO yield it may be calculated that the energy of activation of reaction 12 is correspondingly 9.0–12.1 kcal. per mole if the steric factor be assumed to be unity. However, the energy emitted in the reaction $2H + M \longrightarrow H_2 + M$ is known to be about 102 kcal.[26] and the difference between that figure and the energy of activation of step 5,6 is certainly higher than the just calculated value for reaction 12. This seems improbable and it accordingly appears likely either that the calculated values for reactions 8 and 12 are too low and that the acetic acid curve of Fig. 3 should correspond more closely to a horizontal straight line than is indicated by the data or that the beginning of the continuum may be nearer 2500 Å. than supposed. The latter conclusion would be contradictory to the results of Part IV.

Mechanism 1 is not the chemical equivalent of reactions 1 and 2. This may readily be seen by reference to reactions 8 and 11 from which it is evident that the production of one ethane molecule is necessarily accompanied by the formation of one methane and two carbon dioxide molecules. There is no such requirement in reaction 2. On the other hand, the requirements of the analysis of the product are met. The total yield of carbon dioxide according to mechanism 1 is equal to twice that of ethane plus that of methane minus that of carbon monoxide or $2 \times 17.5 + 23 - 17.5 = 40.5\%$, which is in good agreement with the analysis. The correspondence of yields of carbon monoxide and ethane is also required by this mechanism. Furthermore, the free radical mechanism explains the formation of hydrogen quite naturally. There is no need to make special assumptions. The traces of acetylene are not explained by this mechanism but they might well arise from some rarer reactions of atomic hydrogen.

The conclusions of Farkas and Wansbrough-Jones are founded on the assumptions of associated acetic acid molecules at extremely low pressures, not all of which are properly orientated. The mechanism suggested here does not involve such an assumption. Reference to the reactions indicates that the quantum yield of carbon dioxide will vary depending on the relative rates of the competing reactions 7 and 8. At higher wave lengths where reaction 7 would be favored, the quantum yield of carbon dioxide should be nearer 1; at lower wave lengths, because of the greater initial velocities of the product particles, reaction 8 would be favored and the quantum yield would be raised with 2 as the upper limit. Similarly, the observed yield of atomic hydrogen should be favored by lower wave lengths. The conclusion as to hydrogen is in agreement with the results of Table III. The conclusion as to carbon dioxide is in disagreement with the figure of approximately 1 for the quantum yield reported by Farkas and Wansbrough-Jones. Using their figures for the analysis of the products, it is apparent that the calculated quantum yield, using mechanism 1, is approximately 1.9. Either their single estimate of the quantum yield has even less accuracy than they indicate or mechanism 1 must be incorrect.

Mechanism 2.—There is, however, another free radical mechanism which may be valid. It is based entirely on the assumption that both single and double molecules are present, and is given below because its calculated quantum yield of carbon dioxide, assuming that each photon absorbed leads to reaction, is 1. Until there is more accurate information about the quantum yield of the photolysis of acetic acid, there is no basis for choice between mechanism 1 and this one.

For single molecules the principal reactions are 5′, 6′ and 7′. For double molecules the principal reaction is

$$(CH_3COOH)_2 + h\nu \longrightarrow (CH_3COOH)_2^* \qquad (5'')$$

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[26] Birge, *Proc. Nat. Acad. Sci.*, **14**, 12 (1928).

followed by 6′′ and either 7′′ or

$$\begin{pmatrix} CH_3COO \\ CH_3COOH \end{pmatrix} + H \longrightarrow C_2H_6 + CO_2 + CO + H_2O \qquad (14'')^{27}$$

The reactions just indicated are the exact stoichiometric equivalent of Farkas and Wansbrough-Jones' suggested mechanism. They are consequently in agreement with the analysis of the products and the reported quantum yield of one for carbon dioxide. Reactions 7″ and 14″ are the equivalent in effect of their so-called properly orientated double molecules. Reactions 5′ and 5″ are the activation reactions, 6′ and 6″ the decomposition reactions. In the latter are produced the hydrogen atoms reported herein. Not all of them, however, escape from the field of influence of the other product radical. At the longer wave lengths nearly all of them react with the residual body in reactions 7′ and 7″ or 14″. No such hydrogen atoms can be detected by the mirror method. Only those that escape are detectable. Evidently, as the wave length decreases beyond the limit required to effect decomposition, the excess energy is divided up among the various degrees of freedom and some of it goes to give the radicals increased velocity relative to each other. For the double molecule, more excess energy is required to produce the same velocity of separation, so that it might be expected that somewhat more of the hydrogen atoms will escape the back reaction after 6′ than after 6″. Once free of the residue, however, there is no distinction between them. When the residue is that of a double molecule, a simple decomposition may be expected to occur

$$\begin{pmatrix} CH_3COO \\ CH_3COOH \end{pmatrix} \longrightarrow CH_3COO + CH_3COOH \qquad (15'')$$

The hydrogen atoms may then enter reactions 8′, 12′ and 13. On energetic grounds reaction 8′ might be favored over reaction 12′ since the C–C bond is weaker than the O–H bond.[28] The termolecular reaction 13, because of the relative scarcity of hydrogen atoms, may be considered so rare that it is non-occurring. The hydrogen atoms may also enter equivalent reactions with double acetic acid molecules. In effect they will be the same as those just given for 8′ and 12′.

As a result of the escape of the hydrogen atoms and their entrance into reactions 8 and 12, the radicals CH_3COO and COOH are liberated. The reaction $CH_3COO \longrightarrow CH_3 + CO_2$, as has been shown, would not be expected to occur. Reaction 9 would occur as already indicated and account for Terenin's observation of OH; the OH might also enter into reactions such as 10′. Reaction 11 would also follow. The relative scarcity of products other than CH_4, C_2H_6, CO, CO_2 and H_2 would indicate either that very little atomic hydrogen becomes available for reactions 8 and 12 or that reaction 12 is favored over 8 or that reaction 10 is favored over other possible reactions involving OH.[23] If mechanism 2 is correct, the first hypothesis must be near the truth (irrespective of the others); it is supported by the only available data for the quantum yield of carbon dioxide, *i. e.*, approximately 1.0. Were reaction 11 to occur to any great extent, the observed quantum yield might be nearer 2.0. (It may be said that the principal weakness of mechanism 2 lies in the necessity of this hypothesis. It seems unreasonable to believe that the great majority of the hydrogen atoms should not escape the influence of the other product particle even at very short wave lengths.)

It may now be seen that the suggested mechanism fits all the known data on this reaction including estimated energies of activation.

It has been shown that the energy of activation for the reaction involving the disappearance of hydrogen atom may be about 7.3–10.3 kcal. If the quantum yield of carbon dioxide be nearly 1.0, reaction 8 could not be an important factor in the production of CH_4. Therefore, reaction 12, which is known to produce 1% of H_2, would account for most of the disappearance of atomic hydrogen. The value of E of 7.3–10.3 kcal. would then apply to that reaction. It is probably much too low, as already indicated under mechanism 1. (The discrepancy here is even greater than for mechanism 1 and may be interpreted against the validity of mechanism 2.)

The principal advantage of the free radical mechanism here suggested over that indicated in reactions 1 and 2 is that it explains the formation of molecular hydrogen quite naturally as well as the formation of hydroxyl, which incidentally need be present in but very small concentration

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(27) Reasoning *ad hoc*, the explanation of reaction 14″ is that the close proximity of the CH_3COO group with its free valence force loosens the C–O bond in the CH_3COOH and thus causes the H to act preferentially on that bond to form water with the —OH.

(28) The C–C bond has in general a strength of about 84 kcal. while that of the O–H bond in acetic acid has been estimated to be 96 ± 8 kcal. (see Rice, ref. 2c) and according to these results may have an even higher value. On the other hand, steric factors may retard 8′ as compared with 12′ (ref. 2, Chap. VI).

to be detected by its emission spectrum.[29] The remarks as to traces of acetylene and variation of yield of atomic hydrogen and of quantum yield of carbon dioxide with wave length made in reference to mechanism 1 also apply to mechanism 2. However, the effect on quantum yield of carbon dioxide would not be so marked in this case as in mechanism 1. The increased production of atomic hydrogen at the lower wave lengths would be just as perceptible and in agreement with Table III.

Patat and Sachsse[30] and Rollefson[31] have both indicated reasons why, in the event of competition between decompositions into stable molecules and into free radicals, the free radical yield should be favored by the lower wave lengths. Consequently, there appears to be no way with the data at hand to decide whether a decomposition into stable molecules is occurring.

Furthermore, the interpretation to be put on the data is questionable. Either of mechanisms 1 or 2 will fully explain all the reactions involved. Apart from the doubts expressed above as to mechanism 2, there is no fundamental reason why either one may not be correct. There is no *a priori* reason why we should expect a quantum yield of one molecule decomposed per photon absorbed in the case of a molecule as complicated as that of acetic acid.[32] Norrish, Crone and Saltmarsh[33] have shown, for example, in the case of acetone that the low quantum yield in the continuum may be ascribable to an intramolecular stabilization because of the dissipation of energy within the large number of degrees of freedom before it becomes available for disruption of a bond. In that case they have also established the existence of decomposition in the discrete fluorescence region before the continuum. If the quantum yield of decomposed molecules were actually one, it would be expected that rupture takes place at the locus of absorption and that there would be no decomposition (*i. e.*, predissociation) before the continuum.

The results of Table III indicate that acetic acid suffers no photolysis (yielding atomic hydrogen) before the continuum. Farkas and Wansbrough-Jones' estimate of a quantum yield of carbon dioxide of 1.0 may be interpreted as evidence in favor of mechanism 2 and a conclusion that rupture takes place immediately and at the locus of absorption. A decisive choice between mechanisms 1 and 2, however, awaits a more certain determination of the quantum yield.

Conclusions.—The only well-founded conclusions are that at least part of the reaction takes place by a free radical mechanism such as here indicated and that no other mechanism is required to explain all the facts so far known.

Acknowledgment.—The author wishes to express his appreciation to Professor James Franck of Johns Hopkins University, who suggested this investigation, and to Professor H. Austin Taylor for his frequent advice and suggestions.

Summary

1. Details are given of a method for detecting hydrogen atoms in the presence of free methyl.
2. Hydrogen atoms but no free methyl radicals are formed during the photolysis of acetic acid.
3. A free radical mechanism is indicated which fits all the facts known about that photolysis.
4. Energies of activation have been computed for two reactions involving atomic hydrogen and acetic acid.
5. It is shown that according to the mechanism suggested the quantum yield of carbon dioxide should increase at shorter wave lengths, the lower and upper limits being 1 and 2, respectively. Farkas and Wansbrough-Jones report a quantum yield of approximately 1.0.
6. The production of atomic hydrogen is apparently slightly favored by decrease in wave length.
7. No production of atomic hydrogen is observed above 2300 Å. The results and other data available are in harmony with a conclusion that the acetic acid spectrum does not have a predissociation region and that in the continuum rupture takes place immediately at the locus of absorption.

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NEW YORK, N. Y.

RECEIVED JULY 9, 1936

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[29] Oldenberg, *J. Chem. Phys.*, **3**, 266 (1935).

[30] Patat and Sachsse, *Z. physik. Chem.*, **B31**, 105 (1935).

[31] Rollefson, Paper presented before Physical Section, A. C. S. meeting, Kansas City, April, 1936.

[32] Franck, Sponer and Teller, *Z. physik. Chem.*, **18**, 88 (1932).

[33] Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1456 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Studies in the Mechanism of Decomposition. II. Note on the Photolysis of Formic Acid

BY MILTON BURTON

Using the para–ortho hydrogen conversion method of Farkas[1] and of Geib and Harteck,[2] Gorin and H. S. Taylor[3] adduced good evidence that no atomic hydrogen is produced during the photolysis of formic acid and that the decomposition probably proceeds by a rearrangement of bonds to yield stable molecules in one primary act by one of the two reactions

$$HCOOH + h\nu \longrightarrow H_2O + CO \quad (1)$$
$$HCOOH + h\nu \longrightarrow H_2 + CO_2 \quad (2)^4$$

Inasmuch as evidence has been presented[5] that hydrogen atom is formed during the photolysis of acetic acid, the question naturally arose as to whether Gorin and Taylor's failure to observe similar results for formic acid might not be a consequence of the method they employed. Accordingly, the tests described below were undertaken to discover whether the mirror method might detect hydrogen atoms in the photolysis of formic acid.

Experimental

The apparatus and methods used were similar to those described for acetic acid.[5] A sample of Kahlbaum Formic Acid 95% was dried over Drierite for three days, introduced into the carefully evacuated system and degassed as already described for acetic acid. In the runs the pressure of formic acid was fixed at about 2.4 mm. at the sloping manometer before the constricted region of the reaction system. Only antimony mirrors were used in the reaction tube. With the capillary mercury arc previously described[5] located 22.8 cm. from the beginning of the reaction tube and 1 cm. from it, antimony mirrors were deposited in the usual manner at about 9 cm. from the irradiated zone.

Tests for Atomic Hydrogen.—In none of the experiments with illuminated formic acid was removal of the antimony mirrors ever observed. In one case, a typical run failed to affect a very light antimony mirror, which would not have lasted four minutes with acetic acid under the same conditions, even though continued for seventy-eight minutes. The system was checked with fresh acetic acid according to the methods previously described and the mirrors were found to possess their normal sensitivity.

There is, of course, the possibility that the energy of activation of secondary reactions between H and HCOOH may be so low that reaction takes place on the first collision or, at most, after a very few collisions and that consequently the hydrogen atoms, though formed, never reach the mirror. This possibility was checked by making a run with a mixture containing approximately 4 parts of acetic acid to about 1 of formic acid. It being already known that photolyzed acetic acid yields hydrogen atoms, such a run should afford a direct test of a possible very fast reaction between H and HCOOH. With the pressure of the mixed vapor adjusted at about 2.4 mm. at the sloping manometer and the other conditions being as already described, it was found that a mirror which would not last in pure acetic acid vapor for more than about four minutes now took about sixteen minutes to disappear. It may be concluded from this test either that formic acid acts like acetaldehyde[6] and reduces normal mirror activity or that there is a rather rapid reaction between H and HCOOH, faster than that between H and CH_3COOH but not fast enough to account for a failure to observe hydrogen atoms during the photolysis of formic acid if there formed.

In order to check the first alternative a formic acid run was made in which the antimony mirror was heated with live steam. Although continued for fifty-two minutes, not the slightest effect was observed on a very light antimony mirror such as used in this group of experiments. Inasmuch as the mixed run with acetic acid had already demonstrated that formic acid did not have a completely deadening effect on the antimony mirror, it may be concluded from this experiment that the failure to observe mirror removal was not due to a cause similar to that reported for acetaldehyde; *i. e.*, the mirrors were not being made inactive by a condensed layer of formic acid.

In a final experiment with formic acid, the arc was brought up to within 0.7 cm. of the reaction tube and a very light antimony mirror deposited 1.9 cm. from the irradiated zone. Although the run was continued for forty-seven minutes, no indication of sharpening of the mirror (a phenomenon always occurring long before removal) was observed.

The absorption spectra of formic acid and of acetic acid are very similar,[7] the extinction coefficients throughout the continua being almost the same, except that the spectrum of formic acid is displaced slightly toward the long wave side. Inasmuch as decomposition of acetic acid has been detected under the conditions of these experiments and Gorin and Taylor have already demonstrated the photolysis of formic acid at wave lengths which the arc used has been shown to cover,[5] it appears reasonable to assume that decomposition of the formic acid also occurred. Consequently, the evidence recited above appears to indi-

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[1] Farkas, *Z. physik. Chem.*, **B10**, 419 (1930).

[2] Geib and Harteck, *ibid.*, Bodenstein-Festband, 849 (1931).

[3] Gorin and Taylor, THIS JOURNAL, **56**, 2042 (1934).

[4] These are the over-all reactions. The mechanism was not suggested but the intimation was that it would be quite different, since double molecules are mainly involved in reaction 2.

[5] Burton, THIS JOURNAL, **58**, 1645 (1936).

[6] Pearson, *J. Chem. Soc.*, 1718 (1934); Pearson and Purcell, *ibid.*, 1151 (1935).

[7] Ley and Arends, *Z. physik. Chem.*, **B17**, 177 (1932).

cate that no hydrogen atoms are formed during the photolysis of formic acid.

The stability of HCO.—The results of Blacet and Roof[8] on the photolysis of acetaldehyde indicate that the HCO radical is rather stable. On the other hand, although the data used by Rice and Herzfeld[9] in considering the chain mechanism involved in the pyrolysis of that compound would indicate a fair stability of HCO at room temperature, Mecke,[10] in discussing the photolysis of formaldehyde, favored the idea that HCO is very unstable and requires only about 4 kcal. to dissociate it further.

Using the guard mirror method previously described[5,11] and employing the precautions indicated to be necessary by the work of Pearson and Purcell,[6] it was found in a preliminary experiment with acetaldehyde, purified[12] and evacuated (using liquid air) in the regular manner, that the light lead mirror, before the lead guard mirror, was removed in five minutes while the light antimony mirror, after the guard, was not in the slightest degree affected after seventy-one minutes.

Inasmuch as CH_3 was formed, HCO must have been formed and the inference logically follows that HCO must be very stable at room temperatures since, had it decomposed, atomic hydrogen would have been formed and would have removed the antimony mirror.

Discussion

Terenin[13] has reported the emission spectrum of hydroxyl during the photolysis of formic acid. If we assume a possible mechanism to account for this production as follows

$$HCOOH + h\nu \longrightarrow HCOOH^* \qquad (3)$$
$$HCOOH^* \longrightarrow HCO + OH \qquad (4)$$

it is evident that no H atom need be observed, since, as has been shown, HCO does not appear to decompose readily. Although OH had been similarly discovered in the photolysis of acetic acid, its formation in a primary step had been excluded because of the known instability of CH_3CO.[14] In the case of formic acid the strength of the C–H bond may be presumed to be greater than that of the C–C bond in acetic acid.[15] It consequently seems that the C–O bond may be much weaker in formic acid than in acetic acid. Since the evidence of absorption spectra indicates that absorption in both compounds is in the COOH group, it may well be possible that the C–O bond is weaker than the O–H bond in formic acid and that the decomposition takes place at the weaker bond.

The para–ortho hydrogen conversion should be as sensitive to a free radical such as OH as to free H.[16] However, if it be ignored for the moment that the results of Gorin and Taylor, contrary to the findings of Terenin, exclude the possibility of any considerable formation of OH, it would still be difficult to write a completely satisfactory free radical reaction mechanism to fit the known data (except by a process of strictly *ad hoc* reasoning) because of the complication introduced by the predominance of double formic acid molecules at pressures greater than 10 mm. and temperatures below 30°.[17] It would be hard to explain why double molecules decompose exclusively by reaction 2. It consequently appears advisable in view of the present state of knowledge of this reaction not to attempt the hypothesis of a mechanism beyond reactions 3 and 4.

The antimony mirror indicates, in agreement with the results of Gorin and Taylor, that no hydrogen atoms are formed in the photolysis of formic acid at room temperatures. This result, it has been shown, is not inconsistent with the findings of Terenin that OH is formed during such photolysis. However, it appears that it may be difficult to reconcile Terenin's results with those of Gorin and Taylor. In view of the evidence, it still appears advisable to consider the photolysis of formic acid as being predominantly a decomposition into stable molecules in one primary act[18] for very little OH has to be produced to be detectable by its emission spectrum.[19]

Acknowledgment.—The author wishes to express his appreciation to Professor H. Austin Taylor for his advice and suggestions.

Summary

1. No hydrogen atoms are detectable by the antimony mirror method during the photolysis of formic acid. This agrees with the findings of Gorin and Taylor.

2. Evidence presented indicates that a reaction takes place between H and HCOOH with a fairly low energy of activation.

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[8] Blacet and Roof, THIS JOURNAL, **58**, 278 (1936).

[9] Rice and Herzfeld, *ibid.*, **56**, 284 (1934).

[10] Mecke, *Nature*, **125**, 526 (1930).

[11] Burton, THIS JOURNAL, **58**, 692 (1936).

[12] The vapor pressure at 0° was 336.7 ± 0.8 mm. which checks with the value of 337 mm. given by Emeleus [*J. Chem. Soc.*, 1733 (1929)].

[13] Terenin, *Acta Physicochim. U. R. S. S.*, **3**, 181 (1935).

[14] Norrish, *ibid.*, **3**, 171 (1935).

[15] For a full discussion of bond strengths see Rice and Rice, "The Aliphatic Free Radicals," Johns Hopkins University Press, Baltimore, 1935, Chap. VI.

[16] *Cf.* L. Farkas and Sachsse, *Z. physik. Chem.*, **B23**, 1 (1933); *Trans. Faraday Soc.*, **30**, 331 (1934); A. Farkas, "Ortho-Hydrogen, Para-Hydrogen, Heavy Hydrogen," Cambridge University Press, 1935, p. 102; W. West, THIS JOURNAL, **57**, 1931 (1935).

[17] *Cf.* ref. 10; also Ramsperger and Porter, THIS JOURNAL, **48**, 1267 (1926); Coolidge, *ibid.*, **50**, 2166 (1928).

[18] *Cf.* Franck and Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[19] Oldenberg, *J. Chem. Phys.*, **3**, 266 (1935).

3. A mechanism is suggested for the formation of OH during the photolysis of formic acid. This mechanism is consistent with the mechanism previously suggested for acetic acid.

4. A preliminary experiment with acetaldehyde showed HCO to be a stable radical at room temperature.

5. In view of the difficulty in reconciling the results of Gorin and Taylor with those of Terenin, it appears probable that the major portion of the photolysis of formic acid takes place by decomposition into stable molecules in one primary act.

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RECEIVED JULY 9, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF MONTANA STATE UNIVERSITY]

Cyclohexyltrichloromethylcarbinol

BY JOSEPH W. HOWARD AND ROBERT J. BROWN

This compound was prepared by the reaction of chloral and cyclohexylmagnesium bromide. The most satisfactory results were obtained when this was carried out as an "inverse Grignard" reaction.

The Grignard reagent was prepared by adding 82 g. of monobromocyclohexane in 60 cc. of ether to 14 g. of magnesium ribbon and a crystal of iodine in 70 cc. of ether. The reaction was completed after three hours of stirring and gentle heating. The resultant solution was decanted from any unchanged magnesium and added with stirring over a two-hour period to 74 g. of freshly distilled chloral in 150 cc. of ether. The product was decomposed with 30% sulfuric acid and the ether washed in turn with water, sodium bicarbonate solution, sodium bisulfite solution and water. It was dehydrated over anhydrous sodium sulfate, the ether removed by distillation and the alcohol distilled in vacuum. A yield of 35 g. of an oily liquid boiling at 119 to 121° at 15 mm. was obtained; d^{20}_{20} 1.2839, n_{25} 1.4820. *Anal.* Calcd. for $C_8H_{13}OCl_3$: Cl, 45.95. Found: Cl, 45.99.

This carbinol darkens on standing. It is insoluble in water but soluble in ether, ethyl alcohol, methyl alcohol, acetone, benzene, chloroform and carbon tetrachloride.

Preparation of the Esters

The acetate and propionate were prepared by refluxing the carbinol for one and one-half hours at 135° with the corresponding acid chloride. The same method was used to prepare the butyrate but butyric anhydride was found to give more satisfactory results than butyryl chloride. The benzoate was prepared by treatment with benzoyl chloride according to the usual procedure of the Schotten–Baumann reaction.

ESTERS OF CYCLOHEXYLTRICHLOROMETHYLCARBINOL

		Formula	Analysis for Cl, % Calcd.	Found
1	Acetate	$C_{10}H_{15}O_2Cl_3$	38.89	39.08
2	Propionate	$C_{11}H_{17}O_2Cl_3$	36.97	37.14
3	Butyrate	$C_{12}H_{19}O_2Cl_3$	35.44	35.28
4	Benzoate	$C_{15}H_{17}O_2Cl_3$	31.71	31.56

	B. p., °C.	Mm.	d^{20}_{20}	n_{25}
1	173	680	1.3612	1.4945
2	188	681.6	1.2119	1.4989
3	185	682.6	1.1872	1.4995
4	210	683.3	1.2893	1.5259

The average yields of these esters was 85%. They are all insoluble in water but soluble in ether, ethyl alcohol, methyl alcohol, acetone, benzene, chloroform and carbon tetrachloride.

Summary

Cyclohexyltrichloromethylcarbinol as well as its acetic, propionic, butyric and benzoic esters have been prepared and studied.

MISSOULA, MONTANA

RECEIVED JUNE 15, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Synthesis of Some Dioxole Derivatives from Alkylacetylenes[1]

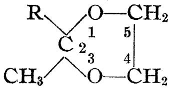
BY D. B. KILLIAN, G. F. HENNION AND J. A. NIEUWLAND

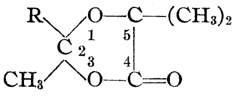
Glycol ethylidene oxide, or 2-methyl-1,3-dioxolane, was first prepared by Wurtz[2] by heating glycol and acetaldehyde in sealed tubes for eight days on a water-bath. Later work[3,4,5] showed that aldehydes could be condensed with polyhydric alcohols with greater ease when phosphoric or sulfuric acid was used as a catalyst. Acetylene reacts with polyhydroxy compounds, in the presence of mercuric sulfate and sulfuric acid, to yield dioxolanes and dioxolones.[6,7] Nieuwland, Vogt and Foohey[8] have shown that cyclic acetals result in high yields from acetylene and polyhydroxy compounds when mercuric oxide and a solution of boron fluoride in methanol are used as catalysts.

The 2,2-dialkyl-1,3-dioxolanes have been reported in the literature in a limited number only. Acetone or other ketones of low molecular weight may be condensed with polyhydroxy compounds in the presence of mineral acids to yield cyclic ketals. Various methods[9,10,11] have been proposed for the synthesis of these compounds, but none of them is generally applicable. The number of references to this field is so large that an exhaustive literature survey of the subject cannot be made here.

Staedler[12] first described chloralide, 2,5-bis-trichloromethyl-1,3-dioxol-4-one, prepared by the action of sulfuric acid on chloral. Other 1,3-dioxol-4-ones have been described from time to time by various investigators.[13–15] Many techniques have been described for the preparation of such compounds by condensing an α-hydroxy acid with a ketone, an aldehyde or acetylene.

The authors have previously shown[16] that amylacetylene reacts with ethylene glycol, in the presence of mercuric oxide and boron fluoride, to yield 2-amyl-2-methyl-1,3-dioxolane. The addition of polyhydroxy alcohols and α-hydroxy acids to an alkylacetylene furnishes a convenient method for the synthesis of many dioxole derivatives. Dihydric alcohols, such as ethylene glycol, yield with alkylacetylenes compounds of type I; α-hydroxy acids, for example α-hydroxyisobutyric acid, give rise to compounds of type II; and polyhydric alcohols, such as mannitol, produce compounds of type III.


I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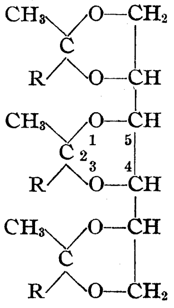
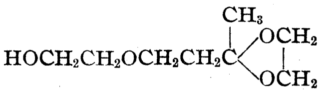
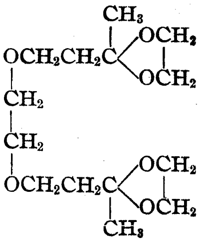

III

The addition of polyhydroxy alcohols to monovinylacetylene is of some interest since it has been shown that methanol reacts with monovinylacetylene in the ratio of three molecules of the alcohol to one of the acetylene to produce 1,3,3-trimethoxybutane.[17] We have found that ethylene glycol and monovinylacetylene yield two addition compounds, one formed from two molecules of glycol and one of the acetylene (IV); and the other from three molecules of glycol and two of the acetylene (V).


IV


V

Experimental

General Procedure.—The catalyst was prepared by heating together momentarily, 5 g. of red mercuric oxide, 2 ml. of $(C_2H_5)_2O \cdot BF_3$, and 2 ml. of anhydrous methanol. To this was added 1–2 g. of trichloroacetic acid, and the

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[1] Paper XIV on the chemistry of the alkylacetylenes and their addition products; previous paper, *J. Org. Chem.*, **1**, 159 (1936).

[2] Wurtz, *Compt. rend.*, **53**, 378 (1861).

[3] Verley, *Bull. soc. chim.*, [3] **21**, 276 (1899).

[4] Clarke, *J. Chem. Soc.*, **101**, 1804 (1912).

[5] Read, Lathrop and Chandler, THIS JOURNAL, **49**, 3116 (1927).

[6] Reichert, Bailey and Nieuwland, *ibid.*, **45**, 1552 (1923).

[7] Hill and Hibbert, *ibid.*, **45**, 3108 (1923).

[8] Nieuwland, Vogt and Foohey, *ibid.*, **52**, 1018 (1930).

[9] E. Fischer and Rund, *Ber.*, **49**, 88 (1916).

[10] Böeseken, *Rec. trav. chim.*, **48**, 931 (1929).

[11] Bogert and Roblin, THIS JOURNAL, **55**, 3741 (1933).

[12] Staedler, *Ann.*, **61**, 104 (1847).

[13] Van Ekenstein and Blanksma, *Rec. trav. chim.*, **25**, 162 (1906).

[14] Blaise, *Bull. soc. chim.*, [4] **15**, 661 (1914).

[15] H. O. L. Fischer and Taube, *Ber.*, **60B**, 485 (1927).

[16] Hennion, Killian *et al.*, THIS JOURNAL, **56**, 1130 (1934).

[17] Killian, Hennion and Nieuwland, *ibid.*, **56**, 1786 (1934).

TABLE I

CHARACTERISTICS AND ANALYSES OF THE DIOXOLES

Compound	Reactant + butyl- or monovinyl-acetylene	B. p., °C.	Mm.	n_D	°C.	d	MR Calcd.	MR Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2-Butyl-2-methyl-1,3-dioxolane	Ethylene glycol	62–63	20	1.4232	21	0.922	40.23	40.36	66.22	66.50	11.19	11.23
2-Butyl-4-chloromethyl-2-methyl-1,3-dioxolane	Glycerol monochlorohydrin	109	25	1.4420	25	1.032	49.72	49.45		Cl,	18.41	18.05
2-Butyl-2-methyl-5-phenyl-1,3-dioxol-4-one	Mandelic acid	136–138	19	M. p., 44–45					71.75	71.14	7.75	7.68
2-Butyl-2,5,5-trimethyl-1,3-dioxol-4-one, II	α-Hydroxyisobutyric acid	104	25	1.4225	25	0.953	49.48	49.69	64.47	64.91	9.75	9.95
2-[β-(2-Methyl-1,3-dioxolan-2-yl)-ethoxy]-ethanol, IV	Ethylene glycol[a]	140–142	20	1.4430	22	1.094	43.40	42.63	54.54	53.51	9.09	8.73
1,2-Bis-[β(2-methyl-1,3-dioxolan-2-yl)-ethoxy]-ethane, V	Ethylene glycol[a]	204–206	20	1.4572	21	1.098	72.31	72.01	57.89	58.21	9.03	9.13
Dimethyl 2-butyl-2-methyl-1,3-dioxolane-4,5-dicarboxylate	Dimethyl tartrate	141–142	9	1.4412	25	1.103	62.03	62.32	55.35	55.88	7.75	7.93
2-Butyl-2-methyl-4,5-bis-(2-butyl-2-methyl-1,3-dioxolan-4-yl)-dioxolane, III	Mannitol	210–212	9	1.4572	20	0.999	116.30	116.68	67.23	67.24	10.35	10.95

[a] Second reactant, monovinylacetylene.

resulting mixture placed in a three-necked flask equipped with a mercury-sealed motor-driven stirrer, a reflux condenser and a dropping funnel. The appropriate polyhydroxy compound was then added to the catalyst mixture and the alkylacetylene added dropwise, if liquid, and, if a gas, as is the case with monovinylacetylene, in a slow stream using a liquid ammonia condenser[18] on the reaction flask.

The reactions were spontaneous and occasionally required cooling by immersing the flask in a water-bath. After stirring for two hours the contents of the flask was mixed with a small amount of sodium methylate and fractionated *in vacuo*. The yields were in all cases good, namely, between 70 and 90% of the theoretical amounts.

The characteristics and analyses of the dioxoles synthesized are given in Table I.

Acknowledgment.—The authors gratefully acknowledge the kind assistance of Dr. Austin M. Patterson for reading the manuscript of this article and suggesting the nomenclature used.

Summary

1. Various dioxolanes and dioxolones have been synthesized from polyhydric alcohols and α-hydroxy acids with butylacetylene and monovinylacetylene.

2. Monovinylacetylene reacted with ethylene glycol to yield two products. The first was formed by the condensation of two moles of glycol with one of monovinylacetylene; the second by the condensation of three moles of glycol with two of the vinylacetylene.

NOTRE DAME INDIANA RECEIVED JUNE 12, 1936

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(18) Vaughn and Pozzi, *J. Chem. Ed.*, **8**, 2433 (1931).

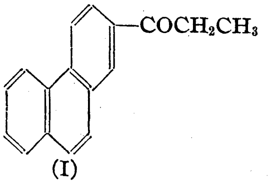
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Synthesis of Phenanthrene Derivatives. IV. Propionylphenanthrenes

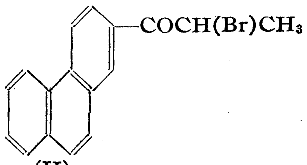
BY W. E. BACHMANN AND W. S. STRUVE

From the reaction between propionyl chloride, phenanthrene and aluminum chloride in nitrobenzene a mixture of propionylphenanthrenes is formed from which it is possible to isolate 2-propionylphenanthrene (I) and 3-propionylphenanthrene. This result is similar to those obtained with acetyl chloride,[1] benzoyl chloride[2] and *o*-toluyl chloride.[3]

The structures of the propionylphenanthrenes were established by their oxidation to 2- and 3-phenanthroic acid by sodium hypochlorite solution as well as by synthesis from the corresponding 2- and 3-cyanophenanthrenes by means of ethylmagnesium bromide. By the Grignard reaction we have also synthesized 9-propionylphenanthrene.



(I)



(II)

By interaction of bromine and 2- and 3-propionylphenanthrene α-bromo-2-propionylphen-

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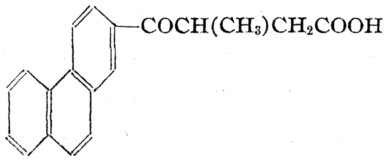
(1) Mosettig and van de Kamp, THIS JOURNAL, **52**, 3704 (1930).

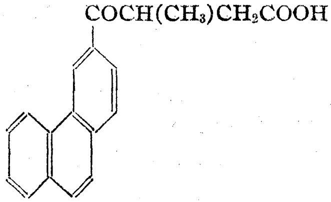
(2) Bachmann, *ibid.*, **57**, 555 (1935).

(3) Bachmann and Pence, *ibid.*, **57**, 1130 (1935).

anthrene (II) and α-bromo-3-propionylphenanthrene are formed. By condensation of the bromopropionylphenanthrenes with sodiomalonic ester, followed by decarboxylation of the malonic acids obtained on hydrolysis of the esters, β-(2-phenanthroyl)-butyric acid (III) and β-(3-phenanthroyl)-butyric acid (IV) were obtained.



(III)



(IV)

Experimental

Reaction of Propionyl Chloride with Phenanthrene.—To an ice-cold solution of 320 g. of aluminum chloride and 200 g. of phenanthrene in 1750 cc. of nitrobenzene was added 140 g. of propionyl chloride at one time. After being kept cold for half an hour, the mixture was allowed to stand at room temperature for twelve hours. After hydrolysis by ice and dilute hydrochloric acid, followed by removal of the nitrobenzene by steam distillation, the product was dissolved in a hot mixture of acetone and alcohol. On cooling 20 g. of 2-propionylphenanthrene crystallized out. By recrystallization from alcohol the 2-propionylphenanthrene was obtained in the form of colorless needles; m. p. 104–105°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.2; H, 6.0. Found: C, 87.1; H, 6.2.

After standing in a refrigerator for three weeks the filtrate from which the 2-isomer had been removed deposited 60 g. of 3-propionylphenanthrene. By recrystallization from alcohol the 3-propionylphenanthrene was obtained as colorless needles; m. p. 55–57°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.2; H, 6.0. Found: C, 87.3; H, 6.1.

A further quantity of the two ketones was obtained from the filtrate through their picrates.

Oxidation of 2- and 3-Propionylphenanthrenes.—A suspension of 1 g. of propionylphenanthrene in 100 cc. of 3% sodium hypochlorite solution containing 1 g. of potassium hydroxide was refluxed for four hours. The solution was filtered and the filtrate was acidified; the phenanthroic acid which precipitated was filtered off and recrystallized from chlorobenzene. From the 2-propionylphenanthrene 2-phenanthroic acid (m. p. 258–260°) was obtained; it gave a methyl ester whose melting point was not depressed when the compound was mixed with authentic 2-phenanthroic acid methyl ester. Similarly 3-propionylphenanthrene gave 3-phenanthroic acid (m. p. 265–270°) whose identity was likewise established through the methyl ester.

Synthesis of Propionylphenanthrenes.—To the Grignard reagent which had been prepared from 10 g. of ethyl bromide in 30 cc. of ether was added 30 cc. of benzene and 10 g. of cyanophenanthrene (2-, 3- or 9-isomer). After the mixture had been refluxed for four hours, it was cooled and hydrolyzed with ice-cold ammonium chloride solution. The aqueous solution was removed and the ether-benzene solution was shaken with dilute hydrochloric acid; from the aqueous solution of the ketone-imine hydrochloride the ketone was obtained by hydrolysis. The 2- and 3-propionylphenanthrenes were identical with those obtained by reaction of propionyl chloride with phenanthrene. The yields were: 2-propionylphenanthrene, 77%; 3-propionylphenanthrene, 22%; 9-propionylphenanthrene, 86%. The 9-propionylphenanthrene was purified by distillation under reduced pressure followed by recrystallization from alcohol; from this solvent it was obtained in the form of colorless, heavy hexagonal plates; m. p. 55–57°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.2; H, 6.0. Found: C, 87.6; H, 6.3.

Picrates of Propionylphenanthrenes.—On cooling hot saturated alcoholic solutions of equal parts of propionylphenanthrene (2-, 3- and 9-isomer) and picric acid the picrates crystallized in the form of yellow needles composed of ketone and picric acid in a 1:1 ratio.

TABLE I

PROPIONYLPHENANTHRENE PICRATES

Picrate of	M. p., °C.	Anal. for N Calcd.	Anal. for N Found
2-Propionylphenanthrene	104.5–107	9.05	9.01
3-Propionylphenanthrene	111–113	9.05	9.05
9-Propionylphenanthrene	105.5–107	9.05	9.01

Bromopropionylphenanthrenes.—A solution of 21.6 g. of 3-propionylphenanthrene in 500 cc. of absolute ether was treated at 0° with a solution of 4.6 cc. of bromine in 125 cc. of ether. After forty minutes the precipitate of α-bromo-3-propionylphenanthrene was filtered off; an additional quantity of the compound was obtained by evaporation of the filtrate after the latter had been treated with anhydrous sodium carbonate in order to neutralize the hydrogen bromide. α-Bromo-3-propionylphenanthrene crystallizes from methyl alcohol and benzene in the form of long colorless needles; m. p. 117–118°; yield, 20 g. (70%).

Anal. Calcd. for $C_{17}H_{13}OBr$: Br, 25.6. Found: Br, 26.3.

For the preparation of the 2-isomer 10 g. of 2-propionylphenanthrene was treated with 2.2 cc. of bromine in 800 cc. of ether; after two hours the mixture was worked up in the manner described for the 3-isomer. α-Bromo-2-propionylphenanthrene crystallizes from benzene–alcohol in colorless plates; m. p. 131.5–133°; yield 11 g. (82%).

Anal. Calcd. for $C_{17}H_{13}OBr$: Br, 25.6. Found: Br, 25.5.

β-Phenanthroylbutyric Acids.—Five grams of α-bromo-3-propionylphenanthrene was added to a solution of sodiomalonic ester which had been prepared from 5 g. of malonic ester and 0.5 g. of sodium in 20 cc. of benzene. After being refluxed for four hours the mixture was hydrolyzed and the substituted malonic ester was heated with 40 cc. of 5% sodium hydroxide solution. From the aqueous solution the phenanthroyl-isoglutaric acid was obtained by acidification. The acid was decarboxylated by heating a suspension of the acid in water for three hours. The β-(3-phenanthroyl)-butyric acid which was formed was purified through its ammonium salt followed by recrystallization of the acid from acetic acid. β-(3-Phenanthroyl)-butyric acid crystallizes from acetic acid in colorless prisms; m. p. 144–146°; yield 1.5 g. (32%).

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 78.0; H, 5.6.

In a similar manner α-bromo-2-propionylphenanthrene was condensed with sodiomalonic ester. The substituted malonic acid which was obtained was heated at 180° for one hour in order to decarboxylate it to β-(2-phenanthroyl)-butyric acid. The latter acid was obtained as fine colorless crystals from acetic acid; m. p. 173–174°; yield 32%.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 78.0; H, 5.8.

Summary

2- and 3-Propionylphenanthrene have been isolated from the reaction between propionyl chloride, phenanthrene and aluminum chloride in nitrobenzene. The same ketones in addition to 9-propionylphenanthrene have been synthesized from the corresponding cyanophenanthrenes through the Grignard reaction.

β-(2-Phenanthroyl)-butyric acid and β-(3-phenanthroyl)-butyric acid have been synthesized.

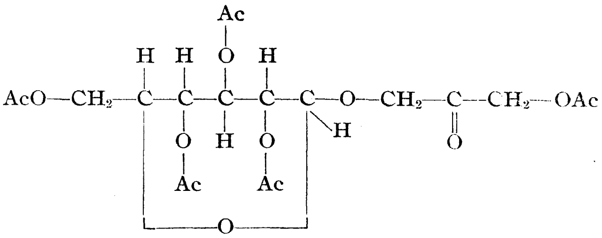
ANN ARBOR, MICHIGAN RECEIVED JUNE 30, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

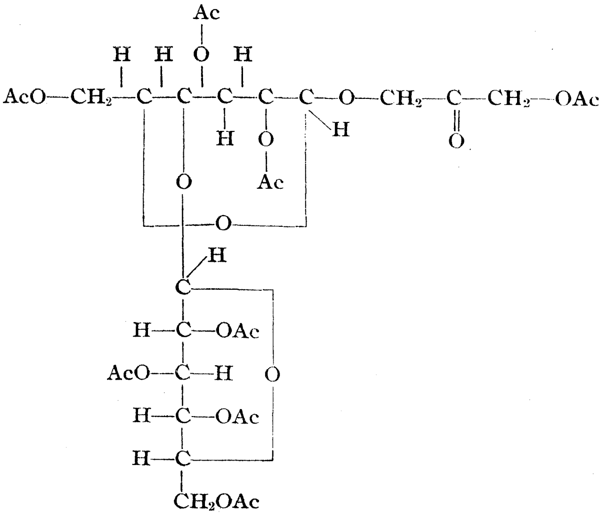
The Mechanism of Carbohydrate Oxidation. XX.[1] The Preparation of Oligosaccharide Acetates Containing Dihydroxyacetone Constituents

BY LEONARD C. KREIDER AND WM. LLOYD EVANS

When Evans and Hockett[2] advanced a mechanism to explain the action of potassium hydroxide on gentiobiose (6-glucosidoglucose) to produce lactic acid, they pointed out that 3-glucosidoglyceraldehyde was a theoretically possible intermediate in this degradation. In the alkaline environment of this reaction it is possible for this glyceraldehyde derivative to undergo the well-known Lobry de Bruyn and van Ekenstein rearrangement to give 3-glycosidodihydroxyacetone. In order to test the Evans and Hockett mechanism it was desirable to subject a 3-glucosidotriose, the postulated reaction intermediate, to the action of potassium hydroxide. At that time glucosidotrioses were unknown. We then succeeded in devising a general method for the synthesis of oligosaccharides that contain dihydroxyacetone as the reducing portion of the molecule. This synthesis has already been applied to the preparation of 3-glucosidodihydroxyacetone (described in a preliminary report[3]), β-*d*- and β-*l*-arabinosidodihydroxyacetone and β-*d*- and β-*l*-xylosidodihydroxyacetone, all as their acetates.[1] The present paper gives detailed directions for the preparation, in a pure crystalline form, of



β-*d*-Glucosidodihydroxyacetone pentaacetate



β-Cellobiosidodihydroxyacetone octaacetate

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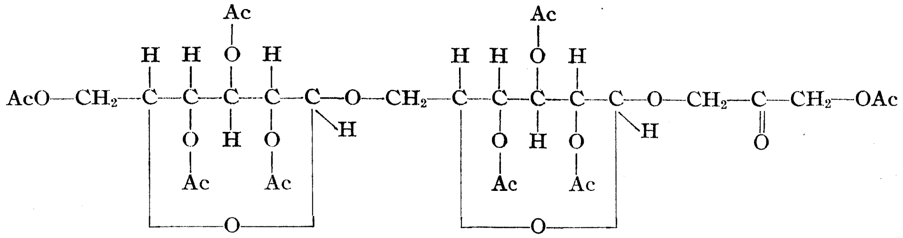
[1] Number XIX of this series: L. C. Kreider and W. L. Evans, THIS JOURNAL, 58, 797 (1936).

[2] W. L. Evans and R. C. Hockett, *ibid.*, 53, 4384 (1931).

[3] L. C. Kreider and W. L. Evans, *ibid.*, 57, 229 (1935).



β-Gentiobiosidodihydroxyacetone octaacetate

Their crystalline *p*-nitrophenylhydrazones were also prepared and characterized.

The action of potassium hydroxide on the three oligosaccharides described here will be published later.

Experimental Part

Preparation of Starting Materials.—Dihydroxyacetone monoacetate was prepared according to the directions of Fischer, Baer and Feldmann.[4] Acetobromoglucose was made by the classical method of Fischer[5] except that the final crystallization was from absolute ether instead of amyl alcohol. Acetobromocellobiose was prepared from cellobiose octaacetate following the directions of Fischer and Zemplén,[6] and acetobromogentiobiose was prepared from gentiobiose octaacetate by the method of Brauns.[7] The final recrystallizations were made again from absolute ether. The acetobromo sugars were each left in a vacuum desiccator for a day over phosphorus pentoxide before being used. The benzene, Drierite and silver carbonate were prepared as before.[1]

All the following compounds reported here were obtained in crystalline condition and were recrystallized to constant melting point and rotation.

β-*d*-Glucosidodihydroxyacetone Pentaacetate.—The preparation of this compound was conducted in a 500-cc. three-necked round-bottomed flask which carried in the middle neck a high speed motor stirrer of efficient design running under a mercury seal. One side neck carried a drying tube charged with granular Drierite and the other a solid stopper. The stirring was then started and the following materials added: 14.1 g. (2.0 moles) of dihydroxyacetone monoacetate, 115 cc. (25 moles) of benzene, 14.5 g. (1.0 mole) of silver carbonate and 50 g. (7 moles) of finely powdered Drierite. That the reactants might be absolutely anhydrous the above mixture was stirred vigorously for twenty minutes and then 22.0 g. (1.0 mole) of β-acetobromo-*d*-glucose was added in ten equal portions at fifteen-minute intervals. Vigorous stirring was continued throughout this time and for at least three hours after the last addition of acetobromoglucose.

At this point the stirring was stopped and the solid materials removed from the benzene solution by suction filtration. The residue was washed twice with small amounts of benzene and the washings added to the filtrate. The combined benzene solutions were then placed in a separatory funnel and washed four times with about equal volumes of water to remove the excess dihydroxyacetone monoacetate. The resulting benzene solution was dried over calcium chloride and then evaporated under vacuum to a thick, light yellow sirup at a bath temperature below 45°. This sirup was dissolved in 100 cc. of warm ether to which was added about one-third of its volume of isoamyl alcohol. This was then placed in the ice box in a stoppered flask. Crystallization began after a few hours and was practically complete after four days.[8] The crystals were filtered from the mother liquor and washed with a little cold ether. The yield of crude product was 11.4 g. or 46% of the theoretical based on the amount of β-acetobromo-*d*-glucose used. For purification, the crystals were dissolved in chloroform, warmed and treated with Norite, filtered and then carefully evaporated to a sirup of moderate consistency. This was warmed to 40° and then ten times its volume of warm ether was added and mixed to homogeneous solution. Crystallization usually took place on cooling, but when it was not spontaneous it was induced by gentle rubbing with a glass rod. After the fourth recrystallization as above was completed both the melting point and the rotation were constant: m. p. 103° (corr.); $[\alpha]^{18}\text{D}$ −25.2° (*c*, 4.2; $CHCl_3$). This compound is very soluble in acetone and chloroform, fairly soluble in benzene, ether, and ethyl alcohol, sparingly soluble in butyl and amyl alcohols and insoluble in petroleum ether and water.

Anal. Calcd. for $C_9H_{11}O_8(COCH_3)_5$: acetyl, 10.82 cc. 0.1 *N* NaOH per 100 mg. Found: acetyl, 10.81 cc.

β-*d*-Glucosidodihydroxyacetone Pentaacetate *p*-Nitrophenylhydrazone.—This compound was most easily prepared by taking 1.0 g. (1.0 mole) of β-*d*-glucosidodihydroxyacetone pentaacetate and 0.39 g. (1.05 moles) of *p*-nitrophenylhydrazine and dissolving them in 25 cc. of absolute alcohol. Complete solution was effected by heating under slow reflux, which was continued for two hours. Often during this heating, and always after cooling in the ice box, feathery light yellow needles separated. It was recrystallized four times from ethanol. The yield was

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[4] H. O. L. Fischer, E. Baer and L. Feldmann, *Ber.*, **63**, 1732 (1930).

[5] E. Fischer, *ibid.*, **49**, 584 (1916).

[6] E. Fischer and G. Zemplén, *ibid.*, **43**, 2536 (1910).

[7] D. H. Brauns, THIS JOURNAL, **49**, 3170 (1927).

[8] In case crystallization does not begin at the end of the first day it is because there has been some mistake made in following the directions as they are given here. Of all the Königs-Knorr reactions we have run, this is by far the most sensitive to changed conditions, and if the stipulated procedure is not carried out exactly as directed the yield may fall as low as half the amount this preparation records. When this happens the first crystallization of the product is often difficult, but we have found from experience that crystallization can nearly always be effected by the following simple device. Add another volume of isoamyl alcohol equal to the amount already in the flask, mix thoroughly and then leave the flask unstoppered in a warm place (25°) to allow the ether to evaporate spontaneously. Crystals often do not form for several days until the ether concentration is considerably diminished, and it may take as long as two weeks for crystallization to be complete, but if one is patient the method seldom fails. The last day before the crystals are removed the flask should be stoppered and placed in the ice box. From this point, proceed as in the regular directions.

nearly quantitative: m. p. 187° (corr.); $[\alpha]^{19}\text{D}$ −129.8° (*c*, 1.76; $CHCl_3$).

Anal. Calcd. for $C_{15}H_{16}O_9N_3(COCH_3)_5$: acetyl, 8.37 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 8.37 cc.

β-Cellobiosidodihydroxyacetone Octaacetate.—The following materials were used: 4.0 g. (2.0 moles) of dihydroxyacetone monoacetate, 65 cc. (50 moles) of benzene, 4.2 g. (1.0 mole) of silver carbonate, 14 g. (7.0 moles) of Drierite and 10.5 g. (1.0 mole) of acetobromocellobiose. The procedure for the synthesis and subsequent purification of this compound was exactly like that for β-*d*-glucosidodihydroxyacetone pentaacetate through the point where the benzene solution had been evaporated to a thick sirup. Here the product was dissolved in warm, absolute ethanol, treated with Norite, filtered and concentrated to about 40 cc. by boiling. Crystallization occurred by allowing this solution to cool to room temperature and was completed after the solution had been left in the ice box for an additional three hours. The yield of well crystallized product was 5.92 g. or 52.5% of the theoretical based on the amount of acetobromocellobiose used. It was recrystallized for analysis alternately from chloroform–ether and from acetone–ether, using each thrice, after which its melting point and rotation did not change further: m. p. 169° (corr.); $[\alpha]^{20}\text{D}$ −27.1° (*c*, 3.78; $CHCl_3$). This compound is very soluble in acetone and chloroform, moderately soluble in hot ethyl alcohol, sparingly soluble in warm ether and benzene and practically insoluble in cold petroleum ether and water.

Anal. Calcd. for $C_{15}H_{18}O_{13}(COCH_3)_8$: acetyl, 10.67 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 10.59 cc.

β-Cellobiosidodihydroxyacetone Octaacetate *p*-Nitrophenylhydrazone.—The preparation of this compound was similar to that of β-*d*-glucosidodihydroxyacetone pentaacetate *p*-nitrophenylhydrazone as described above. A nearly quantitative yield of fine, light yellow needles resulted. This was recrystallized from ethanol twice and then from benzene once, after which it had a constant melting point and rotation: m. p. 176° (corr.); $[\alpha]^{20}\text{D}$ −72.9° (*c*, 1.4; $CHCl_3$).

Anal. Calcd. for $C_{21}H_{23}O_{14}N_3(COCH_3)_8$: acetyl, 9.04 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 8.98 cc.

β-Gentiobiosidodihydroxyacetone Octaacetate.—The procedure for the preparation of this compound is exactly like that of β-cellobiosidodihydroxyacetone octaacetate. The following materials were used in a typical experiment: 3.6 g. (2.0 moles) of dihydroxyacetone monoacetate, 60 cc. (50 moles) of benzene, 3.75 g. (1.0 mole) of silver carbonate, 13.0 g. (7 moles) of finely powdered Drierite, and 9.5 g. (1.0 mole) of acetobromogentiobiose.

The yield of well crystallized product was 6.0 g. or 59% of the theoretical based on the acetobromogentiobiose used. Its solubility behavior is very nearly the same as that of its cellobiosido analog: m. p. 172° (corr.); $[\alpha]^{23}\text{D}$ −25.9° (*c*, 3.3; $CHCl_3$).

Anal. Calcd. for $C_{15}H_{18}O_{13}(COCH_3)_8$: acetyl, 10.67 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 10.55 cc.

β-Gentiobiosidodihydroxyacetone Octaacetate Methyl Alcoholate.—When β-gentiobiosidodihydroxyacetone octaacetate is recrystallized from methyl alcohol, a crystalline alcoholate appears to be formed. When this substance is heated slowly it melts at 110–112°, but on heating further it crystallizes again, melting the second time more sharply at 171–172°. The methyl alcohol may also be removed from the complex by heating it in a vacuum oven at 50° at 20 mm. of mercury pressure. A micro-rotation of this alcoholate was made and gave $[\alpha]^{20}\text{D}$ −25.0° (*c*, 2.1; $CHCl_3$). If the alcoholate would readily dissociate in chloroform solution we might expect this ratio to hold:

$$\frac{\text{mol. wt. alcoholate}}{\text{mol. wt. gentiobiosido-}} = \frac{\text{rotation gentiobiosido-}}{\text{rotation alcoholate}}$$

$$782/750 = -25.9/X$$

X may be calculated to be $[\alpha]\text{D}$ −24.9°, which is in good agreement with the observed $[\alpha]^{20}\text{D}$ −25.0°. Hence, it is probable that this compound is β-gentiobiosidodihydroxyacetone octaacetate methyl alcoholate, in which one molecule of the methyl alcohol is loosely bound.

β-Gentiobiosidodihydroxyacetone Octaacetate *p*-Nitrophenylhydrazone.—The method of its preparation and purification was very similar to that used for β-cellobiosidodihydroxyacetone octaacetate *p*-nitrophenylhydrazone. Again a nearly quantitative yield of fine light yellow needles was obtained, which after recrystallization twice from ethanol and once from benzene gave a constant melting point and rotation; m. p. 155° (corr.); $[\alpha]^{20}\text{D}$ −77.2° (*c*, 1.5; $CHCl_3$).

Anal. Calcd. for $C_{21}H_{23}O_{14}N_3(COCH_3)_8$: acetyl, 9.04 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 9.00 cc.

Deacetylation of the Oligosaccharide Acetates.—It is known that great care must always be exercised in the deacetylation of any carbohydrate if it contains either a free aldehyde or a free ketone group. Ketone sugars are especially sensitive in this respect.[9] As all the new oligosaccharide acetates contained the alkali-sensitive ketone group, only the mildest deacetylation agents were employed. The acetyl groups were easy to remove, but we invariably encountered the difficulty of the deacetylating agent attacking the sensitive free ketone group and causing deep-seated changes in the free oligosaccharide that had been liberated. This yielded a complex mixture of substances from which it was impossible to separate a pure crystalline product.

For this work we chose what appeared to be the three mildest deacetylating agents in the literature: the barium methylate–methyl alcohol method of Isbell[10] where the barium methylate is eventually decomposed by an exact titration with sulfuric acid; Levene and Tipson's modification[11] of Isbell's method where the excess reagent is decomposed with carbon dioxide; and finally the slightly more vigorous ammonia–methyl alcohol method where the directions of Fischer and Taube[12] were followed. All three methods caused the formation of small amounts of yellow to brown decomposition products that seemed similar in character, but much smaller in amount, to the prod-

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(9) C. S. Hudson and D. H. Brauns, This Journal, **37**, 1283 (1915).

(10) H. S. Isbell, *Bur. Standards J. Research*, **5**, 1185 (1930).

(11) P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, **93**, 637 (1931).

(12) H. O. L. Fischer and C. Taube, *Ber.*, **60**, 1704 (1927).

ucts formed by sugars through alkaline degradation according to methods of Evans and co-workers.[13]

Discussion

It should be pointed out that the use of finely powdered Drierite as an internal desiccant in Königs–Knorr reactions is a very worthwhile practice. In the past when this reaction was used to prepare oligosaccharides (without the use of internal desiccants), yields ranging from a low of 0.25%[14] to a maximum of about 25%[15] were recorded. Yields of from 10 to 20% were the most common.[16] This is in sharp contrast to the 46, 52 and 59% yields recorded in this paper for the preparation of the same type of compounds.

The use of the new oligosaccharide acetates reported here in further elucidating the mechanism of the alkaline degradation of the more complex carbohydrates will be discussed in detail in a later paper.

The assignment of the β-configuration follows from the fact that the values of Hudson's *A* for the new oligosaccharide acetates are in each case positive, as was explained in a previous paper.[1]

β-*d*-glucosidodihydroxyacetone pentaacetate $A = +32{,}200$
β-cellobiosidodihydroxyacetone octaacetate $A = +29{,}300$
β-gentiobiosidodihydroxyacetone octaacetate $A = +35{,}400$

The configuration of the *p*-nitrophenylhydrazones and of the methyl alcoholate follows from the configuration proved for the parent oligosaccharide acetates from which they were prepared.

In connection with the deacetylation of the oligosaccharide acetates it is very interesting to note that C. L. Bernier[17] found that the Kunz method[18] of acetyl determination was inapplicable to dihydroxyacetone monoacetate, as the results were invariably high. We also observed that the Kunz method failed for oligosaccharide acetates that contained dihydroxyacetone as a reducing constituent, for here too the results were about ten per cent. high. (In a typical analysis, 0.2132 g. of β-*d*-glucosidodihydroxyacetone pentaacetate required 25.42 cc. of 0.1 *N* NaOH; calcd. is 23.07 cc.) The acetyl analyses recorded in this paper were all made by the Freudenberg absolute method[19] and in no case was there any difficulty in either duplicating results or getting values that checked closely with theory. These facts indicate an unusual susceptibility of dihydroxyacetone to degradation by alkali.

Attention should also be called to the fact that the preparation of β-*d*-glucosidodihydroxyacetone pentaacetate and of β-gentiobiosidodihydroxyacetone octaacetate now make possible the study of a fairly complete sugar series where each higher member differs from the preceding one by the addition of three carbohydrate carbons to the carbohydrate chain as it lengthens:

	M. p., °C.	$[\alpha]_D$ in $CHCl_3$
Dihydroxyacetone diacetate[20]	42–45	...
β-*d*-Glucose pentaacetate[21]	132	+3.8°
β - *d* - Glucosidodihydroxyacetone pentaacetate	103	−25.2°
β-Gentiobiose octaacetate[22]	192–193	−5.3°
β - Gentiobiosidodihydroxyacetone octaacetate	172	−25.9°
6 - β - Gentiobiosido - β - *d* - glucose hendecaacetate	221	−8.0°

These may be thought of as constituting an "homologous series" among the carbohydrates, as it is analogous to the various homologous series among the hydrocarbons. A detailed study of the physical and chemical properties of the members of this series should prove interesting and profitable. The periodic rise and fall both of the melting points and the magnitude of the optical rotations are apparent from the data presented above.

Summary

1. The following new compounds were prepared in pure crystalline form and their characteristic properties determined: β-*d*-glucosidodihydroxyacetone pentaacetate, β-*d*-glucosidodihydroxyacetone pentaacetate *p*-nitrophenylhydrazone, β-cellobiosidodihydroxyacetone octaacetate, β - cellobiosidodihydroxyacetone octaacetate *p* - nitrophenylhydrazone, β-gentiobiosidodihydroxyacetone octaacetate, β-gentiobiosidodihydroxyacetone octaacetate methyl alcoholate and β-gentiobiosidodihydroxyacetone octaacetate *p*-nitrophenylhydrazone.

2. The first trisaccharide to contain a triose

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[13] G. F. Nadeau, M. R. Newlin and W. L. Evans, THIS JOURNAL, **55**, 4957 (1933); W. L. Evans and C. C. Clark, *ibid.*, **54**, 698 (1932).

[14] B. Helferich and H. Bredereck, *Ann.*, **465**, 166 (1928).

[15] B. Helferich and W. Schafer, *ibid.*, **450**, 229 (1926).

[16] H. O. L. Fischer and L. Feldmann, *Ber.*, **62**, 854 (1929); B. Helferich and H. Rauch, *ibid.*, **59**, 2655 (1926); *Ann.*, **455**, 168 (1927).

[17] C. L. Bernier, unpublished work.

[18] A. Kunz and C. S. Hudson, THIS JOURNAL, **48**, 1978 (1926).

[19] K. Freudenberg and M. Harder, *Ann.*, **443**, 230 (1923).

[20] H. O. L. Fischer and H. Mildbrand, *Ber.*, **57**, 707 (1924).

[21] C. S. Hudson and J. K. Dale, THIS JOURNAL, **37**, 1264 (1915).

[22] C. S. Hudson and J. M. Johnson, *ibid.*, **39**, 1272 (1917).

constituent has been synthesized as its acetate.

3. A postulated intermediate in alkaline degradation of gentiobiose has been synthesized in a pure form as its acetate.

4. Attention is directed to the importance of using Drierite as an internal desiccant when the Königs–Knorr reaction is used to prepare oligosaccharides.

5. The susceptibility of dihydroxyacetone to degradation by alkali is pointed out.

6. With the synthesis of β-*d*-glucosidodihydroxyacetone pentaacetate and β-gentiobiosidodihydroxyacetone octaacetate the first six members of a homologous series among the carbohydrates are now available for study.

COLUMBUS, OHIO RECEIVED JULY 6, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Relative Rates of Combination of Hydrogen and Deuterium with Ethylene

BY A. WHEELER AND R. N. PEASE

In the present investigation the relative rates of combination of hydrogen and deuterium with ethylene have been measured, both for the homogeneous reaction and on a copper catalyst at 0°. Preliminary results with deuterium of unknown purity have already been published.[1] The present data are in good agreement with the earlier experiments, indicating that the heavy hydrogen used in the first experiments contained about 20% of the light isotope. This considerable contamination in the earlier experiments was due to the fact that, for the removal of oxygen, the heavy isotope was passed through a supported nickel catalyst often exposed to the light isotope for the same purpose. (The contamination of light hydrogen by deuterium probably did not occur, since the catalyst was always subjected to copious sweeping out before a sample of the light isotope was taken.) As is obvious, the earlier experiments were performed before the importance of exchange reactions between hydrogen and deuterium was realized.

Experimental Procedure

The apparatus and experimental procedure have been described by one of us elsewhere.[2] Both light and heavy hydrogen were prepared by electrolysis from caustic solution. The light hydrogen was passed subsequently through a calcium chloride tube, over a supported nickel catalyst at 500°, and finally through a trap at −80°. The deuterium was led over a hot platinum wire spiral and through a trap at −80°. Analysis (mass spectrographic and gas balance) showed the purity of the deuterium to be >99%. Compressed ethylene of high purity was subjected to fractional distillation before use. For the catalytic experiments, Kahlbaum copper oxide granules, "zur analyse," were reduced in light hydrogen at 200°, and the resulting product deactivated by heating *in vacuo* for one hour at 500°.

Since preliminary experiments indicated that exchange reactions of the type $D_2 + C_2H_4 \longrightarrow C_2H_3D + HD$ were to be looked for in the runs with deuterium, provision was made for the analysis of the light hydrogen content in the residual gas at the end of a run. The analysis was effected by freezing out ethylene and ethane with liquid air, and measuring the viscosity of the residual hydrogen gas in a Rankine-type viscometer.[3] By comparing the viscosity of the residual gas with that of pure deuterium, the approximate light hydrogen content of the sample could be found. The reproducibility of the viscometric readings was better than 1%, but the presence of methane (vapor pressure about 93 mm. at liquid air temperature) in the high temperature homogeneous runs, together with the possibly incomplete freezing out of the ethylene and ethane, make the viscometric results somewhat uncertain. However, they should set an upper limit for the light hydrogen content in the residual gas at the end of any given run.

I. The Homogeneous Reaction.—Reaction was carried out at four temperatures, namely, 534, 555, 567 and 574°. In agreement with the earlier work[2b] on the reaction of light hydrogen with ethylene, it was observed that one does not obtain good second order rate constants by extrapolating the pressure measurements to zero time and computing the rate constants from this point. Instead the procedure adopted, as before,[2b] was to use the fifth minute as zero time, the partial pressure of hydrogen and ethylene at this point being calculated from the extrapolated value for the initial pressure. In this way good rate constants were obtained, leading to the same value for the relative rates of the hydrogen and deuterium reaction which one calculates by comparing directly the times necessary for corresponding pressure drops. In Table I the rate constants are in the units (mm. × sec.)$^{-1}$. The second column indicates whether light hydrogen or deuterium was used in a given run, while the fifth column gives the ratio of the rate of the light hydrogen reaction to the rate of the deuterium reaction. The sixth and seventh columns contain the extrapolated initial partial pressures of hydro-

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[1] R. N. Pease and A. Wheeler, THIS JOURNAL, **54**, 1144 (1935).

[2] R. N. Pease (a) *ibid.*, **45**, 1196 (1923); (b) *ibid.*, **54**, 1876 (1932).

[3] A. O. Rankine, *J. Sci. Instruments*, **1**, 4 (1934).

gen and ethylene. In all runs three parts of hydrogen to one of ethylene were used, in order to cut the methane formation to a minimum.[2b]

It is to be noted that the observed temperature coefficient of the light hydrogen reaction agrees well with that found in the earlier research on this reaction. There is, however, a small discrepancy in the absolute values of the rate constants at a given temperature. This consistent discrepancy undoubtedly is due to temperature calibration errors, amounting to about four degrees. An error of two degrees in each research, working in opposite directions, is well within the realm of possibility.

Table I shows that over the temperature range investigated light hydrogen reacts with ethylene two and a half times as fast as the heavy isotope. Although this would apparently point to no difference in the activation energies of two reactions, a difference of one thousand calories might easily escape detection.

The evidence with regard to exchange reactions given by the viscometric measurements is as follows: (1) at 580° deuterium does not exchange with Pyrex glass previously exposed to the light isotope.

TABLE I

Run	H_2 or D_2	T, °C.	$k \times 10^7$ (mm. × sec.)$^{-1}$	$\alpha = \frac{k_{H_2}}{k_{D_2}}$	$P^0_{\text{Hyd.}}$ mm.	$P^0_{C_2H_4}$, mm.
17	H_2	534	6.5	2.5	577.5	192.5
21	D_2	534	2.6		580.8	193.6
22	H_2	555	14.8	2.57	583.2	194.4
23	D_2	555	5.75		577.5	192.5
6	H_2	567	21.7	2.47	596.4	198.8
7	D_2	567	8.8		590.4	196.8
26	D_2	574	11.0		613	204.3

A sample of pure deuterium was allowed to remain for three hours in a Pyrex bulb maintained at 580°. The time of fall for the mercury pellet in the viscometer was 50.5 seconds for the sample, while for untreated deuterium it was 50.7 seconds, and for pure light hydrogen 36.4. It is to be noted that the ratio of viscosities η_{D_2}/η_{H_2} was consistently observed to be 1.395 ± 0.003. This is to be compared with the theoretical ratio of 1.41 obtained by Maass.[4] (2) Below 534° exchange reactions such as $D_2 + C_2H_4 \longrightarrow C_2H_3D + HD$ are absent or of negligible importance. The time of fall for the mercury pellet with pure D_2 filling the viscometer was 72.7 seconds, and with the D_2 residue from a run at 534° the time was 72.5. For pure light hydrogen the time was 52.0 seconds. (3) In the temperature region 570° exchange reactions may play roles of some importance. The time of fall for the mercury pellet with the deuterium residue from a run at 567° was 70.5 seconds, for pure D_2, 72.7 seconds, and for pure H_2, 52.0 seconds. For the deuterium residue from a 3 to 1 deuterium–ethylene mixture maintained at 567° for twenty-four hours, the time of fall was 66.5 seconds, indicating a maximum of about 20% light hydrogen.

Discussion of Homogeneous Reaction.—It has been shown[2b] that the reaction of ethylene with hydrogen in Pyrex bulbs is unambiguously homogeneous and second order. The actual mechanism of the reaction is, however, in dispute at the present time. Two mechanisms have been put forward: (1) that the reaction is a straightforward bimolecular association reaction[2b] and (2) that reaction proceeds through the following free-radical chain mechanism[5]

$$\begin{array}{llll}
\text{I} & C_2H_4 + H_2 \rightleftarrows C_2H_5 + H & E_1, E_1' \\
\text{II} & C_2H_4 + H \rightleftarrows C_2H_5 & E_2, E_2' \\
\text{III} & C_2H_5 + H_2 \longrightarrow C_2H_6 + H & E_3 \\
\text{IV} & C_2H_5 + H \longrightarrow C_2H_6 & E_4
\end{array}$$

The double arrows in reactions I and II indicate that the reactions are reversible, not that equilibrium is maintained. E_1 is the activation energy for reaction I in the forward direction; E_1' the activation energy for the reverse reaction, etc. It has been shown[5] that the above mechanism gives a second order rate of formation of ethane, with approximately the correct temperature coefficient. The actual expression is

$$-\frac{d\,C_2H_4}{dt} = \sqrt{\frac{k_1k_2}{k_1' + k_4}}\,(C_2H_4)(H_2)$$

Here the k's and k''s are the rate constants for the corresponding forward and reverse reactions. It was hoped that the difference in the rates of hydrogenation and deuterization of ethylene might enable one to decide whether the reaction is a straightforward association or a chain reaction. Unfortunately no clear-cut decision may be made. However, the following evidence may be brought forward. Since in the chain mechanism $k_2/(k_1' + k_4)$ involves in each k only the reaction of a hydrogen or a deuterium *atom* (no zero point considerations for reactants) it is reasonable to suppose that this ratio is the same for both the hydrogen and deuterium reactions. This being so, according to the chain mechanism the ratio of rates of the hydrogenation and deuterization processes must depend solely on the ratio of $\sqrt{k_1}$ for the two processes. In terms of a collision theory this means that

$$2.5 = \left[1.4\,e^{-\frac{\Delta E_0}{RT}}\right]^{1/2}$$

where ΔE_0 is the difference in zero-point energy for H_2 and D_2 as they enter into reaction I of the chain mechanism. In order for the above equation to be fulfilled, ΔE_0 must equal 2400 calories. It is well known,[6] however, that the *maximum* zero-point energy difference for reaction involving H_2 or D_2 is 1800 calories. It would appear, then, that the chain mechanism given above is

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(4) Maass, *Can. J. Research*, **12**, 57–62 (1935).

(5) F. O. Rice and K. F. Herzfeld, THIS JOURNAL, **56**, 284 (1934).

(6) Eyring and Sherman, *J. Chem. Phys.*, **1**, 6 (1933).

in questionable agreement with the experiments. In addition it may be cited that packing the reaction vessel[2b] in no way affects the rate of formation of ethane, and that in the present investigation the addition of one-half an atmosphere of nitrogen to a deuterium–ethylene mixture had no marked effect on the observed rate. Recent experiments on the reverse reaction[7] (*i. e.*, the decomposition of ethane) indicate that free radicals are absent during the initial stages of reaction. In view of the total lack of evidence for a chain reaction, it seems more likely that the hydrogenation of ethylene proceeds by a straightforward association mechanism.[8]

If, then, the hydrogenation of ethylene proceeds through a bimolecular association, the observed ratio of 2.5 for the hydrogen and deuterium reactions is easily accounted for. In terms of collision theory

$$k_{H_2}/k_{D_2} = 2.5 = 1.4\ e^{+\Delta E_0/kT}$$

where ΔE_0 is the effective difference in zero-point energy of H_2 and D_2, as they enter into this reaction. At 550°, ΔE_0 must be 950 cal. in order to satisfy the above equation.

According to an activated complex picture

$$\frac{k_{H_2}}{k_{D_2}} = \left(\frac{m^*_{H_2}}{m^*_{D_2}}\right)^{3/2} \left(\frac{I^*_{H_2}}{I^*_{D_2}}\right)^{1/2} \left(\frac{V^*_{H_2}}{V^*_{D_2}}\right) \left(\frac{m_{D_2}}{m_{H_2}}\right)^{3/2} \left(\frac{I_{D_2}}{I_{H_2}}\right) e^{+\frac{\Delta E_0}{kT}}$$

Here the m^*, I^*, V^* are respectively the masses, products of moments of inertia, and vibrational partition functions, for the activated complexes. A quantity referring to a complex formed by the union of H_2 with C_2H_4 is denoted by the subscript H_2, and has an asterisk after it; similarly for D_2. m_{D_2} and I_{D_2} are the mass and moment of inertia of the normal deuterium molecule; and similarly for the subscript H_2. If we denote the zero-point energy of a species by E_0, ΔE_0 is defined by $E_0 = E_{0D_2}^* - E_{0H_2}^* + E_{0H_2} - E_{0D_2}$. We know all quantities in the above except for the I^*'s, V^*'s and ΔE_0. Substituting numerical values we find

$$\frac{k_{H_2}}{k_{D_2}} = 2.5 = 5.14 \left(\frac{I^*_{H_2}}{I^*_{D_2}}\right)^{1/2} \left(\frac{V^*_{H_2}}{V^*_{D_2}}\right) e^{\Delta E_0/kT}$$

For the normal ethane molecule in the region 850°K., V, the vibrational partition function, is only about eight,[9] and some, if not most, of the low frequencies contributing to this are associated with motions of the carbon atoms. A reasonable value for $V^*_{H_2}/V^*_{D_2}$ is 0.9. A reasonable value for $(I^*_{H_2}/I^*_{D_2})^{1/2}$ is $^1/_2$. This is equivalent to assuming that each of the three moments of inertia of the activated complex is 60% larger for the deuterium complex than in the light hydrogen complex. This may seem like a large percentage, but it must be remembered that the distended hydrogen atoms are contributing heavily to the moments of inertia, and hence the effect of the heavier deuterium atoms will be considerable.

Putting these values in our expression we get

$$\frac{k_{H_2}}{k_{D_2}} = 2.32\ e^{\frac{\Delta E_0}{kT}} = 2.5 \text{ (observed)}$$

From this it follows that ΔE_0 must be a very small quantity, about 120 calories. Indeed, this is what one would expect. Since the activated complex has seventeen modes of vibration, many of them with high frequencies, it is reasonable to suppose that zero-point energy differences for H_2 and D_2 would almost cancel, and it would not even be surprising if ΔE_0 were negative. In the case of $H_2 + I_2 \longrightarrow 2HI$, and $D_2 + I_2 \longrightarrow 2DI$, calculations by one of us[10] show that zero-point energy differences cancel, even though the activated complex has only five modes of vibration.

II. The Catalytic Reaction.—Reaction was carried out at two temperatures, 0 and 20°, on an active copper catalyst. The results are shown in Table II. In the earlier work[2a] on the light hydrogen reaction, it was shown that the reaction rate is unimolecular with respect to hydrogen and is inhibited by ethylene. It was found in the present experiments that this is also true for deuterium.

TABLE II

Run	Temp., °C.	H_2 or D_2	$k \times 10^{+3}$ (min.$^{-1}$)	$\alpha = \frac{k_{H_2}}{k_{D_2}}$	P^0_{Hyd}, mm.	$P^0_{C_2H_4}$, mm.
30	0	H_2	5.2	2.08	372	372
31	0	D_2	2.5	1.78	352	352
32	0	H_2	4.45	2.07	353	353
33	0	D_2	2.18		345	345
35	20	D_2	9.9	2.1	380	380
36	20	H_2	20.9		378	378
37	0	D_2	2.2	1.83	366	366
38	0	H_2	4.0		366	366

The rate constants in Table II are first order constants, calculated with respect to hydrogen. Pressures are in mm. and times in minutes. Otherwise the quantities in Table II have the same significance as in Table I. The activity of the freshly prepared catalyst was falling consid-

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[7] Sachsse, *Z. physik. Chem.*, **31B**, 79 (1935).

[8] See also Rice and Gershinowitz, *J. Chem. Phys.*, **2**, 857 (1934).

[9] Teller and Topley, *J. Chem. Soc.*, 878 (1935).

[10] Wheeler, Topley and Eyring, *J. Chem. Phys.*, **4**, 178 (1936).

erably, and for this reason the quantity α goes through periodic variations. That is, α for two runs in which the deuterium run followed the hydrogen run is larger than for the inverted case, as one would expect if the catalyst is losing activity. The average value for α at 0° is 1.94. The data at 20° are insufficient to be conclusive, but the 2.1 value of α at 20° must be compared with 2.07 at 0°. Within the experimental error, then, the temperature coefficients (in the range 0–20°) for the hydrogen and deuterium reactions are the same. However, it is to be noted that a difference sufficient to take account of all the difference between the rates of the two reactions in terms of unequal activation energies would have escaped detection.

The observed ratio of two between the rates of the hydrogen and deuterium reactions might be due to any of a number of causes. Collision rates of hydrogen and deuterium with the surface would introduce a factor of 1.4; rates of adsorption may differ by as much as 3.3;[11] different rates of surface reaction may result in rates differing by a factor of 4.4, if the difference in zero-point energies of the Cu–H and Cu–D complexes be taken as 800 cal.[6] It is fairly obvious that we are dealing with something more than a collision frequency. However, extended discussion seems hardly profitable at this time.

Analysis showed no exchange between deuterium and ethylene on the copper catalyst at 0°.

Summary

It has been found that the rate of reaction of hydrogen with ethylene is greater than that of deuterium by a factor of 2.5 in the homogeneous reaction at ~ 500°; and by a factor of 2 in the catalytic reaction over copper at 0°. Exchange reactions are unimportant.

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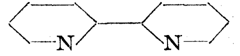
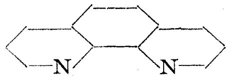
[11] Soller, Goldwasser and Beebe, THIS JOURNAL, **58**, 1703 (1936).

PRINCETON, N. J. RECEIVED MAY 6, 1936

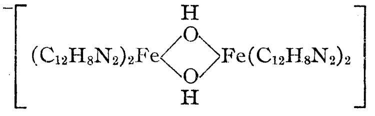
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Structure and Properties of Mononuclear and Polynuclear Phenanthroline-Ferric Complexes[1]

BY ALLISON GAINES, JR., LOUIS P. HAMMETT AND GEORGE H. WALDEN, JR.

The beautifully complete papers in which Blau[2] reported the discovery of the unusually stable complexes which the bases dipyridyl  and *o*-phenanthroline  form with metallic ions propounded, nevertheless, a puzzling problem for valence theory in the existence of two different ferric complexes. One of these, blue in color, is obtained only by oxidation of the ferrous complex. Analysis of the chloroplatinate showed that its formula is $[Fe(C_{12}H_8N_2)_3]^{+++}$ and it would indeed be difficult to reconcile any other composition with the fact that it forms a mobile oxidant–reductant system with the ferrous complex, whose formulation as $[Fe(C_{12}H_8N_2)_3]^{++}$ is well established. By contrast direct reaction of phenanthroline and ferric salts leads to the formation of brown solutions from which Blau isolated no solid compounds. He noted, however, color reactions which suggested the existence of a brown complex with the same ratio, 3:1, of phenanthroline to ferric ion as that which obtains in the blue complex.

We have, however, obtained from these brown solutions a crystalline salt of definite composition whose properties correspond to the formula



$$\left[(C_{12}H_8N_2)_2Fe\overset{H}{\underset{H}{\langle\overset{O}{\underset{O}{}}\rangle}}Fe(C_{12}H_8N_2)_2\right]Cl_4 \qquad (A)$$

of a tetraphenanthroline-diol-diferric chloride. The polynuclear complex ion contained in this salt appears to be the major constituent of the brown solutions. In spite of the fact that the phenanthroline–iron ratio in this complex is 2:1, there is no contradiction between our result and Blau's, which we have indeed confirmed, because in the formation of the bridge hydroxyl or "ol" groups, one hydrogen ion is set free from a water molecule for each ferric ion reacting. The combination of this hydrogen ion with phenanthroline raises to a value considerably above two

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[1] Dissertation submitted by Allison Gaines, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the faculty of Pure Science, Columbia University.

[2] Blau, *Monatsh.*, **19**, 647 (1898).

the proportion of phenanthroline which may become combined as a consequence of the reaction of one ferric ion.

The study of this compound has led to conclusions about the acidity of ol-compounds, about the magnetic properties of polynuclear complexes and about the solubility method of studying complexes which have considerable general interest for problems of complex chemistry.

The Crystalline Brown Chloride, Substance A

Preparation.—This new substance is conveniently prepared by the following method: 50 ml. of a 0.300 molar solution of ferric chloride (0.0150 mole of Fe^{+++}) is added to a well-stirred suspension of 5.400 g. of *o*-phenanthroline hydrate (0.0300 mole of phenanthroline) in 50 ml. of water. The phenanthroline dissolves, and after about an hour a brown crystalline precipitate begins to form. After standing overnight, this is filtered off, washed several times with small quantities of water and dried over sulfuric acid at 2–4 mm. absolute pressure. The yield is from 50 to 60% of the theoretical amount.

We have prepared six different samples from solutions of various compositions as follows.

TABLE I

Sample	Mole ratio phenanthroline/iron	Concn. HCl
a	3	0.00
b, d	3	.04
c, f	2	.00
e	2	.04

Analysis.—Iron was determined by heating the sample in 1 *M* hydrochloric acid to decompose the complex, followed by reduction in the silver reductor[3] and titration with ceric sulfate. The accuracy of this procedure was checked by analyzing aliquots of a ferric chloride solution in the presence and in the absence of two moles of phenanthroline per mole of iron. Three portions in the absence of phenanthroline required an average of 17.42 ml. of ceric sulfate solution with an average deviation of 0.75 part per thousand. Three portions in the presence of phenanthroline required an average of 17.46 ml. with an average deviation of 1.1 parts per thousand.

Phenanthroline was determined by dissolving the sample in about 15 ml. of 6 *M* hydrochloric acid, heating to decompose the complex, and adding saturated mercuric chloride solution slowly from a buret, while the solution was stirred, until the total volume was 192 ml. After standing overnight the precipitate was transferred to a tared crucible with a porous porcelain bottom, washed free from chloride, dried at 110° and weighed. This procedure was verified on amounts of phenanthroline ranging from 0.0500 to 0.3000 g. both in the absence and presence of an equimolar amount of ferric chloride. The average value for the ratio weight phenanthroline/weight precipitate was 0.4001 with an average deviation of 4 parts per thousand in eight determinations. The precipitate is probably $(C_{12}H_8N_2)$-$HgCl_2$[4] for which the above factor is 0.3983. Morgan and Burstall[5] have used the entirely analogous iodide for the quantitative determination of α,α'-dipyridyl.

Chloride was determined by two methods. Method A was a modification of the standard precipitation of silver chloride in which the $[H^+]$ was increased to decompose the complex and the filtration was carried out at 80–90°, to avoid contamination with the silver phenanthroline complex which precipitates from the cold solution. An empirically determined correction was applied for the solubility of silver chloride under the standardized conditions. Method B was the thoroughly tested chromyl chloride distillation method of Robertson.[6] The special all-glass apparatus of Hammett and Lowenheim[7] was used for the analyses.

Results of Analyses.—Samples (a), (b) and (c) were analyzed without intensive drying. They showed the following values of the ratio moles phenanthroline/moles iron, (a) 2.10, (b) 2.078, (c) 2.081, and for moles chloride/moles iron (a) 2.06, (b) 2.013, (c) 1.987. Samples (d), (e) and (f) were analyzed after long-continued drying over 98% sulfuric acid and fresh calcium chloride at 2–4 mm. absolute pressure with the following results.

TABLE II

Sample, found	Iron, %	Phenanthroline, %	Chloride, %
d	11.00	72.24	14.17
e	11.00	72.40	14.31
f	11.07	72.30	14.23
	11.05	72.40	14.16
Calcd. formula (A)	11.06	71.50	14.05

Hydration.—The dried compound is very hygroscopic. Two samples were exposed to the atmosphere until constant weight was reached. One gained 7.47% and the other 7.06%. Assuming formula (A) a tetrahydrate would require 7.16%.

Conductivity.—The specific conductivity of a solution whose concentration, based upon formula (A), was 0.0005023 mole per liter, was found to be 2.5152×10^{-4} mho. The specific conductivity of the water used in preparing the solution was 6.160×10^{-6} mho. The molar conductivity is therefore 488.5 mho, which is an entirely reasonable figure for a salt of this type, provided all of the chloride is ionogen. A consideration of the acidic properties of the compound does not change this conclusion.

Acid–Base Properties.—Twenty-five ml. of a 0.00491 *M* solution of substance (A) (preparation (f)) was titrated with 0.02013 *M* sodium hydroxide using a glass electrode.[8] The titration curve is shown in Fig. 1 in which the points are experimental and the solid curve is calculated for a dibasic acid whose *pK* values are 4.30 and 6.40. The agreement is satisfactory except toward the end of the titration where some other reaction, leading to precipita-

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[3] Walden, Hammett and Edmonds, THIS JOURNAL, **56**, 57 (1934).

[4] Hieber and Mühlbauer, *Ber.*, **61**, 2149 (1928).

[5] Morgan and Burstall, *J. Chem. Soc.*, 2594 (1930).

[6] Robertson, *ibid.*, **107**, 902 (1915).

[7] Hammett and Lowenheim, THIS JOURNAL, **56**, 2620 (1934).

[8] We are indebted to Mr. M. F. Moose for these measurements, which were made on the apparatus described by Kiehl and Ellis, THIS JOURNAL, **57**, 2139 (1935); *Rev. Sci. Inst.*, **4**, 131 (1933).

TABLE III

Substance	Moles Fe per liter	Magnetic pull on soln., F_1, g.	Density of soln., (27°)	Specific susceptibility of anhydrous solute × 10^6	Atomic susceptibility $\chi_{Fe} \times 10^6$	Precision measure, %
$K_3Fe(CN)_6$	0.0400	−0.0258	1.0053	6.76	2350	−3.11
		− .0260				
Substance A preparation (f)	.03995	− .0283	1.0035	1.10	823	−6.71
		− .0283				
$[Fe(C_{12}H_8N_2)_3]_2(SO_4)_3$	.03876	− .025	1.0442	3.34	2860	...

tion at the point marked by the arrow, overlaps the simple neutralization process.

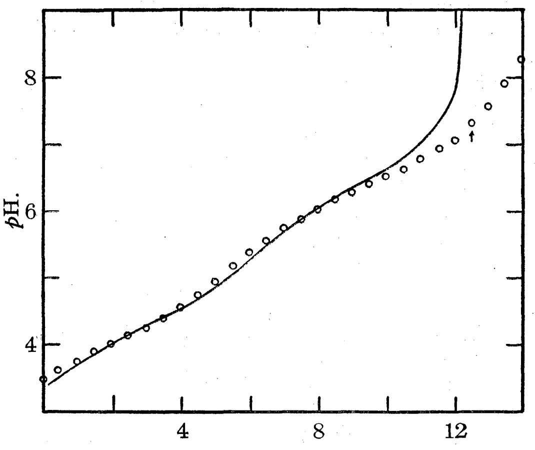

Fig. 1.—Titration of tetraphenanthroline-diol-diferric chloride solution with sodium hydroxide.

Magnetic Properties.—The magnetic susceptibilities of solutions of several ferric phenanthroline and other iron complexes were determined by the Gouy method.[9] Essentially, a definite volume of a solution of the substance to be investigated was placed in a glass tube which was suspended from one arm of an analytical balance so that the plane bottom of the tube was symmetrically placed in the magnetic field between the poles of a powerful electromagnet (*ca.* 20,000 gausses). The force exerted on the tube and contents was determined by weighing. Deducting the force exerted on the empty tube by the standardized field gives the force exerted on the solution. The equation relating the force on the solution with its susceptibility is $F = {}^1/_2A(\kappa_1 - \kappa_2)(H_1^2 - H_0^2)$ where

A = cross-sectional area of the column
κ_1 = volume susceptibility of the solution
κ_2 = volume susceptibility of air
H_1 = field at plane bottom of the tube
H_0 = field at upper level of liquid

For the tube used and the constant field which was maintained the force exerted when the tube was filled with water to the constant level which was also used for the solutions was −0.0296 g. Using Brant's[10] values obtained at 20° for the volume susceptibility of water, -0.71798×10^{-6}, and for that of air, $+0.0288 \times 10^{-6}$, this gave a value for the quantity ${}^1/_2A(H_1^2 - H_0^2)$, by means of which, together with the measured force when the tube was filled with the solution, the volume susceptibility of the latter can be calculated. Division of this figure by the density, which was determined at 27°, the average temperature of the experiments, gives the mass susceptibility of the solution, χ_1.

By Wiedeman's law of the additivity of susceptibilities the value for the solute may be calculated from the relation

$$m_1\chi_1 = m_s\chi_s + m_w\chi_w$$

in which m is mass in grams, χ is specific susceptibility, and the subscripts 1, s and w refer to solution, solute, and water, respectively.

Multiplication of χ_s by the formula weight associated with one gram atom of iron in the compound, and subtraction from the resulting figures of the sum of the Pascal additive values for the susceptibilities of the various atoms of carbon, nitrogen, etc., present gives a quantity which should be a good approximation (in spite of the constitutive effects and other inaccuracies of the Pascal relationship) to the atomic susceptibility of the iron atoms present in the compound. It is so listed in column 6 of Table III, which gives the results on solutions of the brown chloride (preparation (f)), of potassium ferricyanide, and of the blue triphenanthroline ferric sulfate. The latter solution was prepared by oxidizing a solution of phenanthroline ferrous sulfate in 0.7 molar sulfuric acid with lead dioxide, and filtering through porous porcelain. The susceptibility was determined immediately. The value of the magnetic pull in the table was obtained by graphical extrapolation to the time when filtration was started of the following values: 20 min., −0.0217; 40 min., −0.0187; 75 min., −0.0143; 125 min., −0.0117 g. The volume susceptibility of the 0.7 molar sulfuric acid was found to be identical with that of water, and its density was 1.0451.

Our value for the atomic susceptibility of the iron in potassium ferricyanide is in approximate agreement with the value of Gray and Birse[11] obtained from measurements on solution, and with that of Ishiwara[12] from measurements on the solid salt. The value for the susceptibility of the iron in the blue complex is nearly the same as that which it has in ferricyanide, which emphasizes the probability that this value is typical for ferric iron in complexes which involve electron sharing. The values of magnetic moment in Bohr magnetons (P_B) calculated from these susceptibilities by the equation

$$P_B = \sqrt{3RT\chi_{Fe}}/5593$$

are 2.4 for ferricyanide, 2.6 for the blue triphenanthroline ferric ion. These are considerably higher than the

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(9) Stoner, "Magnetism and Atomic Structure," E. P. Dutton Co., New York, 1926, p. 40.

(10) Brant, *Phys. Rev.*, **17**, 678 (1921).

(11) Gray and Birse, *J. Chem. Soc.*, **105**, 2707 (1914).

(12) Ishiwara, *Science Reports of the Tôhoku Imperial University*, **3**, 310 (1914).

theoretical value of 1.73 of the spin moment of a single unshared electron, but this excess is also observed with other ions containing a single unshared electron, and is generally attributed to incomplete quenching of the orbital moment.[13]

The magnetic moment of the iron atom in the brown ferric complex is, however, only 1.4 Bohr magnetons. It is therefore much smaller than the moment of ferric ion in other stable ferric complexes. It is even considerably smaller than the theoretical minimum value of 1.73, which corresponds to the spin moment only. This result is extremely important in connection with the question of the molecular weight of the complex ion.

Diffusibility.—Measurements of diffusibility offer one of the most promising means of studying the molecular dimensions of ions in solution, although their quantitative interpretation is still open to considerable question.[14]

Qualitative diffusion experiments were made with collodion bags, gelatin test-tubes and a fritted glass membrane. A solution initially 0.02 *M* in tri-*o*-phenanthroline ferrous chloride required some four hours to reach equilibrium by diffusion through a collodion membrane, while a comparable set-up for the brown phenanthroline ferric complex salt did not reach equilibrium on standing overnight.

The same solutions poured on gelatin gels in test-tubes showed about a 3:2 penetration ratio in an overnight test with the ferrous complex having the higher diffusion rate.

The technique of McBain and Liu,[15] using a 0.2-cm. membrane of G-4 fritted glass, was applied to the two solutions. The *KD* value obtained for the ferric complex salt was 0.0035 and for the ferrous complex salt 0.0042. Flushing the cell with distilled water effectively removed all coloration due to the ferric salt prior to the diffusion of the ferrous salt, but the ferrous complex stained the membrane so that a treatment with chromic acid mixture was required to clean it. A subsequent pair of diffusion runs gave a *KD* value of 0.0048 for the ferric salt and of 0.0055 for ferrous. The changed values, showing an increased membrane porosity, are nevertheless in the same direction, and support the conclusion that the ferric complex has a higher average molecular weight than has the ferrous complex, whereas the empirical formulas have the reverse relation.

We were unable to make diffusion measurements in the presence of a large concentration of another electrolyte, as is necessary if the diffusibility of the complex ion alone is to be obtained,[16] because the brown salt is so easily salted out by other electrolytes.

Particle Size.—An unfiltered solution of sample (f) showed a bright field in the ultramicroscope. However, a freshly prepared solution and the filtrate from the above solution were optically void. The substance must polymerize on standing in solution, a fact corroborated by visible precipitates formed in 0.01 *M* solutions after standing for a week, but the freshly prepared solution is probably a true solution, rather than a colloidal one. Because of this aging of the solutions all measurements reported in this article were made not more than three hours after the preparation of the solution.

Composition and Structure.—The substance is unquestionably a definite compound. It forms crystals of visible dimensions; its composition is independent of the composition of the solution from which it is prepared within a considerable range of variation of acidity and phenanthroline concentration (see Table I); and the analysis agrees closely with the simple proportion of 1 Fe to 2 Cl to 2 phenanthroline.

The composition is necessarily that represented by the formula $Fe(C_{12}H_8N_2)_2(OH)Cl_2$, because some negatively charged constituent other than the two chloride ions must be present to balance the three positive charges of the ferric ion, and hydroxyl ion is the only possibility. As Table II shows, the actual proportions of iron, chlorine and phenanthroline in the dried compound agree excellently with this composition.

While the interpretation of the conductivity results is complicated by the hydrolysis reaction, they demonstrate beyond question that the chlorine atoms are free chloride ions, and not non-ionogen chlorine in the complex.

Here as always with polynuclear complex ions, the molecular weight is difficult to establish. That we have to do with a polynuclear complex seems beyond doubt. The low diffusibility by comparison with the similar but mononuclear phenanthroline ferrous ion is practically conclusive evidence; moreover, the magnetic properties and the nature of the acid–base titration curve strongly support the conclusion. There is no physical picture to account for the existence in a mononuclear ferric complex of a magnetic moment less than the 1.73 Bohr magnetons which correspond to the spin moment of a single unpaired electron, and no moment less than this has in fact been observed in a substance containing an odd number of electrons. It is therefore extremely probable on this basis alone that we have to do with a polynuclear complex in which two or more ferric ions are rigidly bound together in such a way that their individual magnetic moments partially neutralize each other. The existence of such a phenomenon as this has been several times suggested, but it has not previously been observed with certainty.

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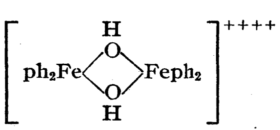
[13] This question has been discussed by Noyes, Pitzer and Dunn, THIS JOURNAL, **57**, 1234 (1935), in connection with the susceptibility of argentic ion.

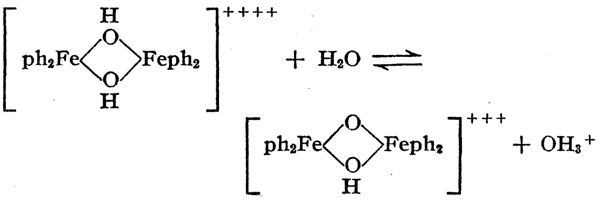
[14] (a) Jander and Jahr, *Kolloid Beihefte*, **41**, 1, 297 (1935); (b) Brintzinger, *et al.*, *Z. anorg. Chem.*, **220**, 201 (1934), and others.

[15] McBain and Liu, THIS JOURNAL, **53**, 59 (1931).

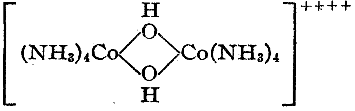
[16] Jander and Winkel, *Z. physik. Chem.*, **149A**, 102 (1930).

The binuclear structure  $\left[\text{ph}_2\text{Fe}\overset{\text{H}}{\underset{\text{H}}{\langle\text{O}_2\rangle}}\text{Feph}_2\right]^{++++}$ which we have proposed is consistent with the general principles of complex chemistry developed by Werner. The coördination number of the iron atoms is six, as it is in other stable ferric complexes (each phenanthroline molecule with its two nitrogen atoms counts of course two in reckoning this value). The ease of formation and stability of the double ol bridge are well established with cobaltic and chromic ammines and are basic features of those important theories of colloidal oxides which Stiasny[17] and Thomas[18] have developed.

The acidic properties of the substance (the *p*H of 0.00491 *M* aqueous solution is 3.5) might seem inconsistent with this structure but they are not so in reality. The only way in which a substance with the structure suggested can react acid is by loss of hydrogen ions from an ol bridge, forming an oxo bridge

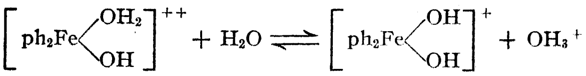


$$\left[\text{ph}_2\text{Fe}\overset{\text{H}}{\underset{\text{H}}{\langle\text{O}_2\rangle}}\text{Feph}_2\right]^{++++} + H_2O \rightleftharpoons \left[\text{ph}_2\text{Fe}\underset{\text{H}}{\langle\text{O}_2\rangle}\text{Feph}_2\right]^{+++} + OH_3^+$$

and it is true that this process does not occur to a significant extent with the cobalt derivatives, which are the most thoroughly studied examples of substances containing these bridges. Such substances as  $\left[(NH_3)_4\text{Co}\overset{\text{H}}{\underset{\text{H}}{\langle\text{O}_2\rangle}}\text{Co}(NH_3)_4\right]^{++++}$ are reported as giving neutral aqueous solutions. There is, however, every reason to expect that the hydrogen ions should be much less firmly bound in the iron compound than in the cobaltic compound.

Both the ol compounds and the simple aquo compounds are derivatives of oxonium ion, OH_3^+, in which one hydrogen ion in the case of an aquo compound (such as $[Co(NH_3)_5OH_2]^{+++}$), and two hydrogen ions in the case of ol compounds, have been replaced by a metallic ion. This substitution decreases the acidity cumulatively; in the cobalt case $[Co(NH_3)_5OH_2]^{+++}$ has an acidity constant of 2×10^{-6}, while the ol compounds are so weakly acid that their aqueous solutions are neutral. The work of Uémura and Suéda[19] shows, however, that aquo chromic ions are considerably more acid than are analogous aquo cobaltic ions, while the work of Brönsted and Volqvartz[20] shows that aquo ferric ions are more acid than are analogous chromic ions. That is to say, the introduction of one ferric ion into oxonium ion decreases the acidity much less than the introduction of one cobaltic ion; the second ferric ion likewise should have a smaller effect than the second cobaltic ion. It is therefore extremely probable that ol-ferric compounds will be more acidic and have less firmly bound hydrogen ions than do ol-cobaltic compounds.

On titration with alkali the behavior of the substance agrees with that to be expected of a dibasic acid, except when nearly two moles of hydroxyl ion have been added (for two iron atoms) when some other process which leads to a precipitation is superimposed. This is shown in Fig. 1 in which the points are experimental and the solid curve is calculated for a dibasic acid. The behavior is consistent with the proposed formula, which contains two dissociable hydrogen ions, one on each of the ol bridges. It does not serve to eliminate the possibility of a more highly polymerized ion, because the experimental curve also agrees with predicted ones for acids of higher basicity than two, but it does furnish another proof of the impossibility of a mononuclear formula. The only possible structure of the latter type is that of an aquohydroxo ion which must titrate as a monobasic acid



$$\left[\text{ph}_2\text{Fe}\begin{smallmatrix}OH_2\\OH\end{smallmatrix}\right]^{++} + H_2O \rightleftharpoons \left[\text{ph}_2\text{Fe}\begin{smallmatrix}OH\\OH\end{smallmatrix}\right]^{+} + OH_3^+$$

It is completely impossible to fit our experimental results to such a process.

On Solutions Containing Ferric Salts and Phenanthroline

The high yields obtained in the preparation of the crystalline brown chloride (A) suggest strongly that it is a major constituent of the solutions obtained by mixing ferric chloride and phenanthroline. It is not the sole constituent, as several kinds of evidence demonstrate.

The Magnetic Titration of Ferric Chloride with Phenanthroline.—We have determined the magnetic susceptibilities of a series of solutions con-

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[17] Stiasny *et al.*, *Colegium*, **752**, 902 (1932), and others.

[18] Thomas *et al.*, THIS JOURNAL, **56**, 794 (1934), and others.

[19] Uémura and Suéda, *Bull. Chem. Soc. Japan*, **10**, 50, 267 (1935); *Bull. faculté arts métiers Tokyo*, **4**, 29 (1935).

[20] Brönsted and Volqvartz, *Z. physik. Chem.*, **134**, 97 (1928).

taining a constant concentration of ferric chloride and varying proportions of phenanthroline with the results shown in Table IV and Fig. 2. Except for the last point, each one represents the mean of two or more measurements with a maximum deviation of 0.0002 g. There are several points of interest about this "magnetic titration curve."

TABLE IV

Ferric chloride (mole/liter)	*o*-Phenanthroline (mole/liter)	Magnetic pull on soln., F_1, g.	Density of soln. (27°)	Atomic susceptibility of ferric ion × 10^6	Precision measure, %
0.03870	0.00	−0.0084	0.9965	13,760	..
.03867	.01935	− .01700	.9974	8,140	0.49
.03865	.03870	− .02337	.9997	4,020	.99
.03865	.05800	− .02630	1.0011	2,120	2.21
.03865	.07740	− .02765	1.0028	1,270	3.81
.03865	.1160	− .02715	1.0052	1,620	2.94
.03872	.1560	− .02425	1.0087	3,550	1.31
.03864	.2320	− .02340	1.0119	4,140	3.81

The gradual curvature shows that several overlapping equilibria are present. Because of the well-verified additivity of magnetic susceptibilities, the curve would consist of two intersecting straight lines if the solutions contained only mixtures of hydrated ferric ion and one phenanthroline complex.

The curve has a pronounced minimum in the neighborhood of the proportion of 2 phenanthroline to 1 iron, the ratio present in the crystalline salt. This is consistent with the hypothesis that the tetraphenanthroline diol diferric ion is a preponderant constituent of solutions containing this proportion of phenanthroline and iron. The rise on both sides, together with the curvature, demonstrates, however, that other compounds of phenanthroline and ferric iron of higher susceptibility are formed in which the ratio may be either greater or smaller than two.

The difference in susceptibility between solutions of the pure crystalline salt and solutions made by adding two moles of phenanthroline to one of ferric chloride is outside of the probable experimental error and indicates the presence in the latter solution of a certain amount of these complexes of higher susceptibility.

Colorimetric Work.—Tests were made in a colorimeter of the intensity of color developed by the addition of ferrous sulfate to solutions containing various proportions of phenanthroline and ferric chloride, the brown color of the ferric complex being compensated in the usual way. In all cases, the intensity of the color increased with time, the more rapidly the greater the proportion of phenanthroline. Extrapolation to zero time showed that solutions containing phenanthroline and ferric iron in the proportion of 1:1 or 2:1 contain no phenanthroline in a form which reacts immediately with ferrous iron, whereas solutions containing proportions of 3:1, of 4:1, and of 9.16:1 contain about two-thirds of the phenanthroline present above the ratio of 2:1 in a form which does not react immediately with ferrous ion. A part but certainly not all of this unreactive phenanthroline is in the form of phenanthrolinium ion. Further interpretation of these experiments must await a knowledge of the equilibrium and kinetics of the ferrous phenanthroline reaction which is now being sought in another research in this Laboratory.

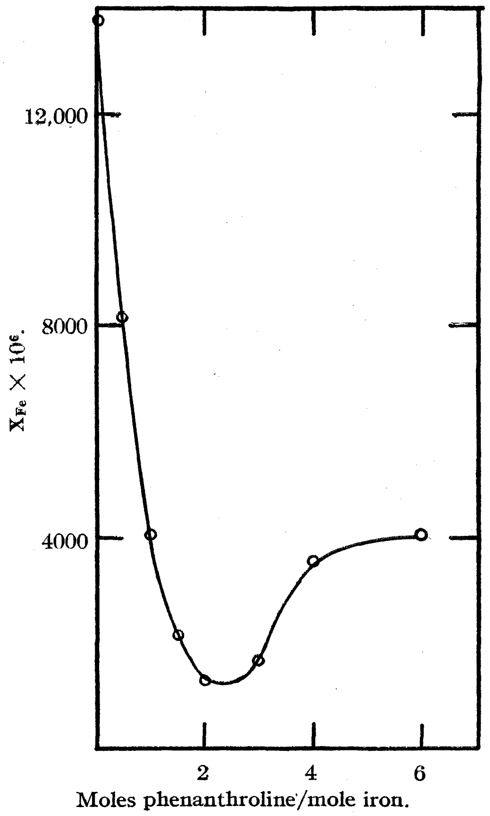


Fig. 2.—Magnetic titration curve.

Solubility Effects.—Attempts to investigate the nature of the phenanthroline complexes by the solubility method which has been so often applied to the investigation of complex compounds gave a most surprising result which led us to determine the solubility of phenanthroline in the various media shown in Table V. All measurements were made at 25° by rotating an excess of phenanthroline with the solution named in a thermostat until analyses made on two successive days showed no further change. Phenanthroline was determined by the mercuric chloride precipitation method previously described. Each figure shown in the table is the average of at least two determinations with a probable error of about 1%.

TABLE V

Soln.	Concn. of soln., moles per liter	Concn. of *o*-phenanthroline, moles per liter	Concn. of *o*-phenanthroline less water soly. of *o*-phenanthroline, moles per liter	Moles of *o*-phenanthroline per mole of other component
Pure water		0.01627		
$FeCl_3$	0.003640	.03834	0.02207	6.07
$FeCl_3$	.007240	.06567	.04450	6.04
HCl	.009953	.03824	.02197	2.21
NaCl	.002014	.01604	−.00023	..
$FeCl_2$	.009390	.06510	.04883	5.20
$NiCl_2$	.005614	.03937	.02310	4.11
H_2SO_4	.004898	.03762	.02135	4.36

There will be noted in every case except that of sodium chloride a large increase in solubility over that in water. Even in the case of the acids, where one would expect one equivalent of acid to dissolve at the most one mole of base, we find an increase in solubility which is of the order of 2.2 moles of base per equivalent of acid. Ferrous ion and nickel ion form extremely stable complexes in which the proportion of phenanthroline to metallic ion is three. There is no evidence whatsoever from the composition of solid salts of the existence of complexes in which the proportion is greater than three. Yet one mole of ferrous chloride dissolves 5.2 moles more of the base than does water; one mole of nickel ion increases the solubility by 4.1 moles. Evidently, then, the presence in a solution of phenanthroline combined either with hydrogen ion or with a metallic ion leads to a considerably increased solubility of phenanthroline in the solution, presumably as a result of the formation of some secondary complex of low stability. The quantity of this excess dissolved phenanthroline bears no simple ratio either to the quantity of combined phenanthroline or to the ionic charge of the complex in which it is present. This peculiar phenomenon may be confined to phenanthroline and bases of similar structure or it may not; it obviously must be reckoned with in any future studies on complex ions by the solubility method.

Of the somewhat over six moles of phenanthroline dissolved by ferric chloride, two can be assigned to the formation of the complex of structure A, about two more to the hydrogen ion liberated in the formation of that compound. The remainder may be due to the loose kind of combination which produces the excess solubility in the case of the other metallic ions, but it is difficult to see how this kind of combination could account for the increase in magnetic susceptibility which we have observed when the proportion of phenanthroline to iron is greater than two.

We wish to acknowledge the kindness of Professors Samuel J. Kiehl, Victor K. La Mer and Arthur W. Thomas in lending special apparatus and of Henry A. Boorse, in making preliminary magnetic susceptibility measurements.

Summary

A brown crystalline substance has been prepared by the direct reaction of phenanthroline and ferric chloride solution. The properties of this substance are consistent with the assumption that it is a tetraphenanthroline-diol-diferric chloride.

Evidence is presented showing the probable existence of other compounds in the mother liquor.

The acid–base properties of the polynuclear complex extend the knowledge of this characteristic of the ol bridge as established with cobaltic and chromic compounds.

The unusually low magnetic susceptibility of the new complex suggests the partial neutralization of the magnetic moments of the two iron atoms, and is additional evidence of a polynuclear structure.

The magnetic susceptibility of the blue triphenanthroline–ferric complex ion approximates that of the ferricyanide ion.

Evidence is presented showing that stable phenanthroline complexes whose composition has been established in the solid state may, in solution, add more phenanthroline, forming secondary complexes of lower stability.

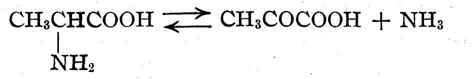
NEW YORK, N. Y. RECEIVED JUNE 1, 1936

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

The Photochemical Deamination of Amino Acids in Water Solution. Part I

BY CH. WEIZMANN, E. BERGMANN AND Y. HIRSHBERG

The only method of de-amination of amino acids under physiological conditions is the oxidative de-amination, *e. g.*



$$\underset{\displaystyle NH_2}{CH_3CHCOOH} \rightleftarrows CH_3COCOOH + NH_3$$

which has been thoroughly investigated by many authors. The ordinary hydrolysis of amino acids

$$\underset{\displaystyle NH_2}{CH_3CHCOOH} + H_2O \qquad \underset{\displaystyle OH}{CH_3CHCOOH} + NH_3$$

has never been observed in biological systems and even against treatment with acid or alkali, the amino acids exhibit such a marked resistance that occasionally the view has been expressed that the occurrence of ammonia in the hydrolysis of proteins is not due to hydrolysis of amino, but rather of amide groups. (That this view is not correct has been demonstrated by Melville[1] in the case of glutamine containing peptides.)

Therefore, an observation made by Henri, Weizmann and Hirshberg[2] seemed to be worthy of further study. These authors reported that in aqueous solution glycine is hydrolyzed under the influence of ultraviolet rays according to the above scheme. The experiments have been extended to include alanine, betaine and aspartic acid. In all these cases the photolysis occurred markedly. The kinetics of the reactions could be studied easily, using the conductivity change or the *p*H change accompanying the photolysis, or, in a more accurate way, determining the amount of ammonia formed during the reaction. As a qualitative test showing whether the desired reaction has occurred or not, the color reaction with 2,7-dioxynaphthalene proved useful; it may be mentioned that the reaction is by no means specific for glycolic acid, as was assumed by Eegriwe,[3] but is a group test for α-hydroxy acids.

The attempt to become familiar with the details of the photolytic reaction meets with one main difficulty: one does not know, *a priori*, which is the reactive form of the amino acid molecules. In this connection, the observation of Henri, Weizmann and Hirshberg[4] is noteworthy that the effective radiation in the case of glycine has a wave length of $\lambda < 2265$ Å. Since, according to a recent paper of Henri and Lasareff,[5] methylamine shows an ultraviolet absorption between 2529 and 1986 Å., the most intense bands lying between 2320 and 2100 Å. the conclusion seems justified that the radiation effective in our photolysis is that absorbed by the C–N linkage, in other words, the photochemical primary process involves that linkage. Two arguments appear to show that the photolysis does not occur or, at least, does not occur markedly on the "Zwitterions." (1) The speed of the photolysis depends on the *p*H of the medium; at neutral reaction, the reaction velocity has a minimum; it increases both to the acid and to the alkaline side, giving a graph (Fig. 1) very similar to those obtained for the hydrolysis of certain esters[6] or the bromination of certain aliphatic ketones.[7] Since one knows[8] that at the neutral point the relative amount of

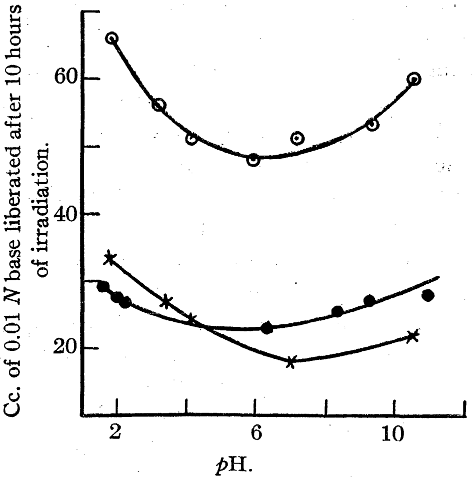


Fig. 1.—Photolysis of alanine 0.05 *N*, ⊙; betaine, 0.05 *N*, ●; aspartic acid, 0.01 *N*, ×.

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(1) Melville, *Biochem. J.*, **29**, 178 (1935).

(2) Henri, Weizmann and Hirshberg, *Compt. rend.*, **198**, 168 (1934).

(3) Eegriwe, *Z. anal. Chem.*, **89**, 121 (1932).

(4) Henri, Weizmann and Hirshberg, *Compt. rend.*, **199**, 1205 (1934).

(5) Henri and Lasareff, *ibid.*, **200**, 829 (1935). Compare also Herzberg and Koelsch, *Z. Elektrochem.* **39**, 572 (1933); Woo and Liu, *J. Chem. Physics*, **3**, 544 (1935); Emeléus and Jolley, *J. Chem. Soc.*, 1612 (1935).

(6) Ingold, *et al.*, *J. Chem. Soc.*, 1039 (1930); 2035 (1931).

(7) Watson and Yates, *ibid.*, 1207 (1932).

(8) Compare Schlenk and Bergmann, "Textbook," p. 450.

molecules occurring in the "Zwitter-ion" form is highest, that form cannot be the carrier of the photolysis reaction. (2) If one compares the photolysis of betaine with that of the unmethylated amino acids we have investigated, one will find that the photolysis of betaine is markedly slower (see *e. g.*, Fig. 1, where a 0.1 *N* solution of betaine is compared with a 0.01 *N* solution of aspartic acid).

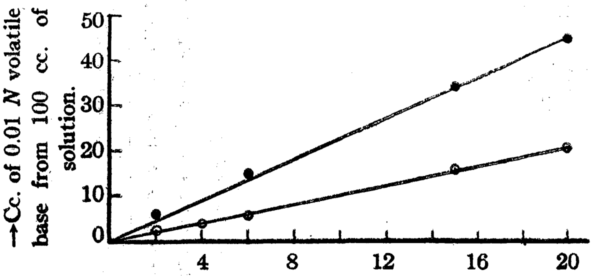

Fig. 2.—Speed of the photolysis of 0.01 *N* betaine (lower curve); 0.01 *N* aspartic acid (upper curve).

We suggest that the normal form of the amino acid molecule is "photo-active"; its C–N bond is split not by water molecules, but by H^+ and OH^-.

The quantum yield of the photolysis has been determined in several experiments by comparison with the photochemical decomposition of monochloroacetic acid. For glycine and alanine the quantum yield has been found to be about equal to unity, which corresponds to the case of, say, monochloroacetic acid.[9] It is surprising that the quantum yield for betaine under the same conditions is only 0.5. It is rather difficult to explain that figure definitely, but it may be due to the fact that in betaine there are two different kinds of C–N bonds absorbing the "active" light, one representing the CH_3N groups, one connecting the nitrogen with the trunk of the acetic acid molecule, and that only the latter one by absorption of light can lead to the desired photolytic process, the other one causing just a dissipation of the absorbed light energy.[9a]

As regards the various amino acids investigated, the details will be given in the experimental part of the paper, but a few remarks may be added here. In the case of alanine, the lactic acid formed has been isolated as zinc salt, in the case of betaine the trimethylamine as the chloroaurate. From aspartic acid, crystalline malic acid has been obtained. A few preliminary experiments were made with *l*-tyrosine, but without success, since the alkaline solution immediately turned yellow, afterward brown; the acid solution behaved similarly after a short period of irradiation. (At the neutral point, tyrosine is known to be insoluble in water.) We thought the color may be due to melanine formation, caused by unavoidable traces of oxygen, but the absorption spectrum of our solution was quite different from the absorption spectrum exhibited by tyrosine after treatment with tyrosinase.[10] Therefore, no conclusion can be drawn regarding the color change of our tyrosine solutions.

The experiments with aspartic acid were made on an optically active (levorotatory) preparation which gave us the opportunity of dealing with the question of the configurational relationship between the starting material and the end-product of the photolysis. The malic acid obtained was nearly completely racemic and only a negligible levorotation could be observed. According to the view of Polanyi and co-workers,[11] racemization can only occur in substitution reactions of the type suggested above when the trunk of the molecule passes a stage where it exists as a positively charged ion or a free radical. Obviously, we cannot decide definitely between these alternatives, but in view of the above conclusion that in this reaction hydrogen and hydroxyl *ions* take part, the former possibility seems more reasonable. The photochemical stretching of the C–N bond leads to the formation of ions RCH^+COOH and NH_2^-, which stabilize by the reactions

$$RCH^+COOH + OH' \longrightarrow RCH(OH)COOH$$
$$NH_2^- + H^+ \longrightarrow NH_3$$

Experimental Part

The preparations used were commercial samples which were purified by the usual methods. Betaine was prepared from its hydrochloride according to Husemann and Marmé.[12] The solutions of the amino acids in doubly distilled water were irradiated in two ways: (1) the quartz lamp was surrounded by two jackets, the first containing running water, the second the solution; (2) the solution was filled into a quartz cell which was irradiated by the direct light of a horizontal mercury arc (without any light filters) at a certain distance. After definite times, the am-

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[9] L. Farkas and O. H. Wansbrough-Jones, *Z. physik. Chem.*, **18B**, 124 (1932).

[9a] For theoretical discussion of low quantum efficiency, see Thompson and Linnett, *J. Chem. Soc.*, 1453 (1935).

[10] Florence, Enselme and Pozzi, *Bull. soc. chim. biol.*, **17**, 290 (1935). Compare also Lignad, *Strahlentherapie*, **34**, 605 (1921).

[11] Polanyi and Meer, *Z. physik. Chem.*, **19B**, 164 (1932); Bergmann, Polanyi and Szabo, *ibid.*, **20B**, 161 (1933); *Trans. Faraday Soc.*, **32**, 843 (1936); Bergmann and Polanyi, *Naturwiss.*, **21**, 378 (1933); see also Ingold and Hughes, *J. Chem. Soc.*, 244 (1935); Hughes, *ibid.*, 255 (1935).

[12] Husemann and Marmé, *Ann.*, Suppl., **3**, 246 (1864).

monia formed was determined in the usual way; the conductivity and the *p*H were measured, the latter with a glass electrode.

An absolute determination of the **quantum yield** proved tedious, since the reactions are relatively slow. Therefore, the reaction was compared in a rather crude way with the photo-decomposition of monochloroacetic acid for which the quantum yield is equal to unity. A parallel ultraviolet light beam was obtained from the light of an ordinary mercury lamp (Heraeus lamp) through a quartz lens of f = 10 cm. At a constant distance a quartz cell of 10 cm. length and 46 cc. volume was placed in the path of the light beam. The lamp worked constantly at 220 volts and 4 amperes.

We compared the amount of monochloroacetic acid decomposed in a second cell after passing (a) water, (b) the investigated solution. The difference between the two figures gave the quantity of energy absorbed in the photodecomposition of the solution investigated. The following results were obtained:

Glycine	0.93	0.88	0.86	0.85	0.82
Alanine	1.02	.98	.95	1.00	
Betaine	0.46	.49	.52		

In order to demonstrate our procedure in the **kinetic** experiments, the data obtained in some experiments may be given here.

TABLE I

BETAINE

100 cc. of a 0.1 *N* solution was irradiated with the horizontal mercury lamp (220 v., 9 amp.). The distance between the lamp and the cell was 13 cm.

Time, hours	Conductivity, measured at 30°	*p*H	0.01 *N* trimethylamine, cc.
0	3.24×10^{-5}	6.2	0
2	7.43×10^{-5}	6.4	2.2
4	9.2×10^{-5}	6.62	4.2
6	11.2×10^{-5}	6.9	6.0
8	14.9×10^{-5}	7.1	8.2
10	18.3×10^{-5}	7.25	10.5
15	30.4×10^{-5}	7.55	16.0
20	40.0×10^{-5}	7.8	21.2

A part of the same solution was not irradiated; during the same period no change in conductivity or *p*H occurred.

TABLE II

(2) ALANINE

100 cc. of a 0.1 *N* solution was irradiated as above

Time, hours	Conductivity, measured at 30°	*p*H	NH_3, mg.	NH_3, %
0	3.38×10^{-5}	6.4	0	0
1	7.17×10^{-5}	6.85	0.017	0.20
2	9.14×10^{-5}	7.10	.034	.40
4	19.7×10^{-5}	7.50	.072	.75
6	23.8×10^{-5}	7.75	.10	1.2
15	44.6×10^{-5}	7.95	.27	3.2

100 cc. of a 0.05 *N* solution as above, but with a stronger lamp.

0	7.33×10^{-6}	5.65	0	0
1	28.6×10^{-6}	6.0	...	...
4	71.1×10^{-6}	6.65	0.61	4.5
6	103.0×10^{-6}	7.25	1.1	8.0
8	200.0	7.65	1.5	11.0

100 cc. of a 0.02 solution as before

0	7.37×10^{-6}	5.5	0	0
2	24.3×10^{-6}	6.7	0.2	1.49
3	33.2×10^{-6}	6.9	.29	2.12
6	73.6	7.2	.61	4.5
10	148.0×10^{-6}	7.5	1.3	10.0

TABLE III

(3) ASPARTIC ACID

100 cc. of a 0.01 *N* solution was irradiated as above; distance 10 cm.

Time, hours	*p*H	0.01 *N* NH_3, cc.
0	3.2	0
2	3.5	5.5
6	3.9	15.2
9	4.1	19.5
15	4.5	33.5
20	5.1	45.0

TABLE IV

Change of absorption during irradiation of alanine

(a) 0.02 *N* SOLUTION

λ, Å.	ε before irradiation	ε after 10 hours of irradiation
2150	17.5	17.5
2225	8.74	13.5
2240	6.72	8.74
2264	4.40	5.85
2280	3.36	4.40

(b) 0.05 *N* SOLUTION

		ε after 8 hours of irradiation
2144	28.08	28.08
2195	10.80	21.6
2240	6.92	10.8
2260	5.40	6.92
2328	1.58	2.81
2350	...	2.16
2360	...	2.05
2370	...	1.58

Isolation of the Irradiation Products.—The solution obtained by photolysis of *alanine* was concentrated, acidified with sulfuric acid, then extracted several times with ether. The ether was distilled off and the residue taken up with water and heated with zinc carbonate on the water-bath. The excess of the carbonate was filtered off and the solution evaporated in a desiccator. The residue was identified by micro-analysis. Calcd. for $C_6H_{10}O_6Zn \cdot 3H_2O$: C, 24.2; H, 5.4; Zn, 22.0. Found: C, 24.7; H, 5.4; Zn, 22.9.

The trimethylamine formed by irradiation of a *betaine* solution was distilled off—after addition of a few drops of alkali—into dilute hydrochloric acid. The acid solution was concentrated on the water-bath and a solution of gold chloride added. The precipitate was filtered off, washed with distilled water, dried to constant weight and analyzed. Calcd. for $C_3H_9NCl_4Au$: C, 9.0; H, 2.3; N, 3.5; Au, 49.4. Found: C, 9.5; H, 2.6; N, 3.7; Au, 49.2. The malic acid obtained from *aspartic acid* by irradiation was isolated in the same way as lactic acid. The crystalline product was recrystallized from a mixture of acetone and carbon tetrachloride; m. p. 121°. The analysis did not agree very well with theory (hygroscopicity?): Calcd. for $C_4H_6O_5$; C, 35.8; H, 4.5. Found: C, 36.2; H, 5.5.

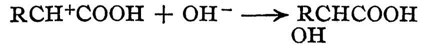
Summary

1. In water solution glycine, alanine, betaine and aspartic acid are hydrolyzed under the influence of ultraviolet light, giving the corresponding hydroxy acids.

2. The kinetics and quantum yields of these reactions have been measured.

3. The following mechanism has been suggested.

(a) $\underset{NH_2}{RCHCOOH} \longrightarrow RCH^+COOH + NH_2^-$



(b) $RCH^+COOH + OH^- \longrightarrow \underset{OH}{RCHCOOH}$

(c) $NH_2^- + H^+ \longrightarrow NH_3$

4. The hydrolysis of optically active aspartic acid is accompanied by racemization, which is in accordance with the above mechanism.

5. The behavior of tyrosine has been studied qualitatively.

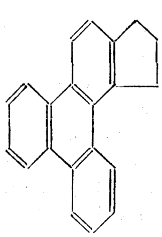
REHOVOTH, PALESTINE RECEIVED APRIL 9, 1936

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

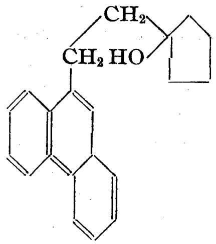
Cyclopentenotriphenylene

BY ERNST BERGMANN AND OTTILIE BLUM-BERGMANN

Jacobs and Elderfield[1] obtained by dehydrogenation of strophanthidin, *inter alia*, a hydrocarbon, the analysis of which gave figures corresponding to the formula $C_{21}H_{16}$. On the basis of a strophantidine formula which has since been abandoned, the authors suggested the structure of cyclopentenotriphenylene (I). In connection with other experiments we thought it interesting to synthesize the above hydrocarbon; its properties were quite different from those of the hydrocarbon obtained by the American authors. Our synthesis parallels the preparation of cyclopentenophenanthrene by Cook and co-workers.[2] Their work gave us some valuable information about the formation and structure of various by-products.



I



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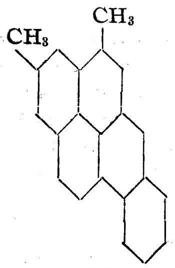

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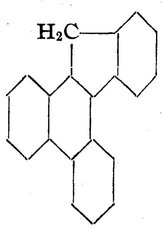

IV

β-(9-Phenanthryl)-ethanol was easily prepared from 9-phenanthrylmagnesium bromide and ethylene oxide or ethylene chlorohydrin and converted into the corresponding chloride. Its magnesium derivative reacted with cyclopentanone to give (9-phenanthrylethyl)-cyclopentanol (II). In accordance with the observations of Cook, we tried to convert (II) directly into (I) with glacial acetic acid and concentrated sulfuric acid, but without success, and also none of the two crystalline hydrocarbons resulting from the crude reaction product by subsequent dehydrogenation was the desired product (I). The first had the formula $C_{21}H_{14}$ and was characterized by a vermillion picrate. It is most probable that it corresponds to 2-methylpyrene[2a] obtained by Cook in the corresponding experiment in the naphthalene series, and therefore is 7-methyl-1,2-benzpyrene (III). We hope to confirm this suggestion, by spectroscopic comparison of our product with benzpyrenes of known structure, as 1,2- and 4,5-benzpyrene recently described by Cook and Hewett[3] and Fieser and Fieser,[4] respectively. The second isolated hydrocarbon, which occurred only in minor quantities, turned yellow on keeping. It resembles in this respect the complex fluorene derivatives prepared by Cook and Hewett;[2b] we therefore assume that it has the structure of 1,2,3,4-dibenzofluorene (IV) and is analogous to chrysofluorene isolated by Cook in his experiments in the naphthalene series. The corresponding fluorenone has recently

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(1) Jacobs and Elderfield, *J. Biol. Chem.*, **107**, 143 (1934).

(2) Cook, *et al.*, *J. Chem. Soc.*, (a) 1098 (1933); (b) 365 (1934).

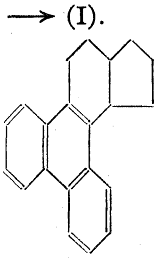
(2a) Barry, Cook, *et al.*, *Proc. Roy. Soc.* (London), **B117**, 321 (1935).

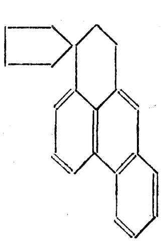
(3) Cook and Hewett, *J. Chem. Soc.*, **398** (1933).

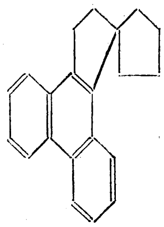
(4) Fieser and Fieser, THIS JOURNAL, **57**, 782 (1935).

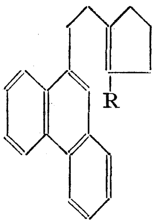
been described by Koelsch.[5] These hydrocarbons cannot be formed by dehydrogenation of the normal compound (V) which we expected from the treatment of II with concentrated sulfuric acid, as an intermediate product; they must derive from the two spirans (VI) and (VII), respectively, by thermal rearrangement and subsequent dehydrogenation.[5a] As a matter of fact we succeeded in isolating, from the crude product of the above treatment of (II), a crystalline substance $C_{21}H_{20}$ which was not identical with (V) and, since under our experimental conditions the *cis* isomer of (V) would not be stable,[6] must be one of the spirans (VI) or (VII).

After this failure, we had to proceed by the way suggested by the formulas (II) ⟶ (VIII) ⟶ (V) ⟶ (I).


V


VI


VII



VIII

The dehydration of (II) was effected easily by heating with potassium bisulfate and the conversion of (VIII, R = H) into (V) by means of aluminum chloride. We prefer the olefinic double bond in (VIII, R = H) in the five-membered ring, rather than in the semicyclic position; but that question is of no importance for the course of the reaction.

Cook and his co-workers observed in several cases that 2-methylcyclopentanone is more suitable for syntheses of this kind, since the condensation with Grignard compound and subsequent dehydration and dehydrogenation gives more uniform products.[7] A series of experiments starting with the methylated ketone was unsuccessful, since 9-ethylphenanthrene formed prevented the easy isolation of the expected ethylene (VIII, R = CH_3).

The cyclopentenotriphenylene obtained by dehydrogenation of (V) is a well-crystallized compound characterized by its dark brown-red picrate. It is isomeric with methylcholanthrene and the melting points and those of their picrates show a striking resemblance; but the mixtures show a depression of the m. p. Obviously, methylcholanthrene could not be formed in our synthetical process. The spectroscopic analysis of cyclopentenotriphenylene and its comparison with similar hydrocarbons is now in progress.

Experimental

β-(9-Phenanthryl)-ethanol.—(a) An ethereal solution of ethylene oxide (10 g.) was added to 9-phenanthrylmagnesium bromide, prepared according to Bachmann[8] from magnesium (5 g.), 9-bromophenanthrene (48.5 g.) in a mixture of benzene (120 cc.) and ether (120 cc.). The rather violent reaction was completed by boiling for two hours; the reaction mixture was decomposed with ice and acid, washed with soda solution, dried and evaporated. The oily residue crystallized, on trituration with light petroleum and acetone; from benzine clusters of needles; m. p. 92°; yield 15–21 g. Calcd. for $C_{16}H_{14}O$: C, 86.5; H, 6.3. Found: C, 86.7, 86.7; H, 6.7, 6.6.

(b) According to Grignard[9] an ethereal solution of 9-phenanthrylmagnesium bromide (from 102 g. of bromophenanthrene and 11 g. of magnesium) was added to a solution obtained by addition of ethylene chlorohydrin (22.4 cc.) to ethylmagnesium bromide (8.1 g. of magnesium and 25.4 cc. of ethyl bromide). Since no reaction took place, the solvents were distilled off; at the end of the distillation reaction occurred, causing the mass to foam and swell violently. After addition of fresh ether the mass was treated as above and the product isolated by distillation (1 mm.). At 145–170° some phenanthrene passed over, then at 200° the reaction product, which crystallized quickly (40–50 g.).

β-(9-Phenanthryl)-ethyl Chloride.—The above alcohol (20 g.) was mixed with dimethylaniline (11.7 cc.) and benzene (24 cc.) and the mixture cooled with ice water. Then thionyl chloride (7.6 cc.) was added drop by drop and the dark red solution heated until the evolution of sulfur dioxide ceased. On addition of water a dark oil separated and was isolated with ether. The residue crystallized at once and was triturated with ethyl acetate and recrystallized from benzine mixed with a little benzene; m. p. 82–84°; yield, 15–17 g. Calcd. for $C_{16}H_{13}Cl$: C, 79.7; H, 5.4. Found: C, 79.9; H, 5.4.

(9-Phenanthryl-ethyl)-cyclopentanol (II).—The above chloride (29.6 g.) reacted smoothly with magnesium (3.2 g.) when activated with iodine and methyl iodide. After

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[5] Koelsch, This Journal, **56**, 480 (1934).

[5a] See Fieser, "Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1936, p. 162.

[6] Zelinsky and Turowa-Pollak, *Ber.*, **65**, 1299 (1932).

[7] Compare Bergmann and Weiss, *Ann.*, **480**, 65 (1930).

[8] Bachmann, This Journal, **56**, 1363 (1934).

[9] Grignard, *Ann. chim.*, [8] **10**, 23 (1907). Compare Schlenk, O. Bergmann and E. Bergmann, *J. Soc. Chem. Ind.*, **52**, 209T (1933).

two hours of boiling, cyclopentanone (10.8 cc.) was added; it reacted markedly and gave a crystalline precipitate. The mass was boiled for a further two hours and then decomposed with ice and ammonium chloride or ice and acid. An insoluble compound separated and was filtered off after some time (1.75 g.); it was recrystallized from xylene. The yellowish leaflets, m. p. 214–216°, exhibit a strong violet fluorescence and consist, according to the analysis, of α,δ-di-(9-phenanthryl)-butane, $C_{14}H_9CH_2CH_2CH_2CH_2$-$C_{14}H_9$. Calcd. for $C_{32}H_{26}$: C, 93.7; H, 6.3. Found: C, 93.8, 94.1; H, 6.1, 6.5. The residue of the ethereal filtrate crystallized on trituration with benzine. This carbinol was recrystallized from benzine and cyclohexane as transparent prisms, m. p. 108–109°; yield, 17.1 g. Calcd. for $C_{21}H_{22}O$: C, 86.9; H, 7.6. Found: C, 86.5; H, 7.6.

Reactions with Concentrated Sulfuric Acid.—(a) The carbinol (II) (4 g.) was heated for two hours on the water-bath with glacial acetic acid (40 cc.) and concd. sulfuric acid (4 cc.); a violet color and smell of sulfur dioxide was observed. Then water was added and the oily product, after isolation with ether, directly heated with selenium (10 g.) to 320–340° for sixteen hours. The mass was extracted with benzene and ethyl acetate and purified by distillation at 0.8 mm. (bath temperature 240–280°). The reddish oil (1.2 g.), on trituration with benzine, gave a crystalline powder (0.5 g.) melting at 132–142°; from propyl alcohol, then from glacial acetic acid, silky needles, m. p. 157.5–159.5°. Calcd. for $C_{21}H_{14}$ (III): C, 94.7; H, 5.3. Found: C, 94.3, 94.3, 94.6, 95.0, 94.6; H, 5.3, 5.6, 5.4, 5.6, 5.3. The picrate, prepared from equivalent amounts of the components in benzene and isolated by evaporation of the solvent, was recrystallized from alcohol, containing picric acid, as beautiful vermilion needles of m. p. 153–155°. Calcd. for $C_{27}H_{17}O_7N_3$: C, 65.5; H, 3.4; N, 8.5. Found: C, 66.0, 66.0; H, 4.1, 3.6; N, 7.6. From the benzine mother liquors of the above hydrocarbon (III), there separated, on standing, a second hydrocarbon (0.2 g.), which melted at 115–116°, after repeated recrystallization from benzine, and after purification through the picrate; needles turning yellow on exposure to air and light. The picrate prepared in hot alcohol, crystallized on cooling as orange-yellow needles, m. p. 165–167°. Calcd. for $C_{27}H_{19}N_3O_7 = C_{21}H_{16}$ (IV) + $C_6H_3N_3O_7$: C, 65.2; H, 3.8; N, 8.4. Found: C, 65.4; H, 4.2; N 8.0.

(b) The experiment was repeated as before but the crude oily product left for some time. A small amount of a crystalline powder separated which was triturated with ethyl acetate, filtered, washed with alcohol and recrystallized from the same solvent as leaflets of m. p. 117–120°. Undoubtedly, the substance is one of the spirans (VI) or (VII). Calcd. for $C_{21}H_{20}$: C, 92.6; H, 7.4. Found: C, 92.3; H, 8.2.

1′-β-(9-Phenanthryl)-ethyl-cyclopentene-(1) (VIII).—The carbinol (17 g.) and potassium bisulfate (25.5 g.) were heated at 160–170° for one hour; the mixture was poured into water, the product extracted with ether and distilled; b. p. 206–207° (1.3 mm.). The distillate (14.3 g.) was a viscous oil unsaturated toward bromine, which crystallized immediately; it melted at 50–54.5°, but it was impossible to recrystallize it and therefore it was converted into tetrahydro-cyclopenteno-triphenylene (V) by dissolving in carbon disulfide and adding finely powdered aluminum chloride (14 g.), at room temperature. After twelve hours the violet mass was decomposed with ice and hydrochloric acid and the product distilled; b. p. 210–215° (1 mm.). The oil crystallized spontaneously; on recrystallization from ethyl or propyl alcohol it gave beautiful prisms (6.9 g.) m. p. 105.5–107°. Calcd. for $C_{21}H_{20}$: C, 92.6; H, 7.4. Found: C, 92.6; H, 7.6. (Picrate, see below.)

Cyclopentenotriphenylene (I).—The tetrahydro compound (5 g.) was mixed with selenium (12 g.) and heated for twenty hours at 330–340°. The mass was powdered and extracted with ether in a Soxhlet apparatus. The solution was evaporated and the residue distilled at 1 mm. The yellow oil (2.5 g.) on trituration with acetone and benzene gave 0.4 g. of cyclopentenotriphenylene as a yellow powder which was recrystallized several times from glacial acetic acid and propyl alcohol as yellowish, small needles, m. p. 171–172.5°. Calcd. for $C_{21}H_{16}$: C, 94.0; H, 6.0. Found: C, 94.2, 94.1; H, 5.7, 5.8. The picrate, prepared in propyl alcohol, was recrystallized from a mixture of benzene and propyl alcohol, containing picric acid; it formed brownish-red needles; m. p. 172–173°. Calcd. for $C_{27}H_{19}O_7N_3$: C, 65.2; H, 3.8. Found: C, 65.4, 65.7; H, 4.1, 4.1. The mother liquor of the cyclopentenotriphenylene was treated with picric acid in benzene solution. The precipitate consisted of the above dark picrate and a small proportion of a yellow picrate which, after recrystallization from alcohol containing picric acid, proved to be the picrate of some unchanged tetrahydro compound (V); needles, m. p. 161–162°. Calcd. for $C_{27}H_{23}O_7N_3$: C, 64.7; H, 4.6. Found: C, 64.1, 64.1, 64.4; H, 4.7, 4.4, 5.0.

Experiments with 2-Methylcyclopentanone.—Methylcyclopentanone (7.6 g.; b. p. 135–136°; prepared according to Cornubert and Borrell,[10] was added to phenanthrylethylmagnesium chloride (from magnesium (2.1 g.) and the chloride (19.2 g.)); during the vigorous reaction a white product crystallized. After boiling for one hour, the mass was decomposed with ice and ammonium chloride (or ice and dilute sulfuric acid), the precipitate of 1,4-di-(9-phenanthryl)-butane (1.2 g.) filtered off and the reaction product isolated as usual. It could not be obtained in a crystalline state and free of 9-ethylphenanthrene and was therefore heated with twice its weight of potassium bisulfate at 160–170° for one hour. The product isolated as above was fractionated at 1.5 mm. The *first fraction*, b. p. 162–170°, crystallized spontaneously and was recrystallized from alcohol, containing a little light petroleum as white, silky prismatic needles, m. p. 62–64°. The melting point and the analysis showed that the substance was 9-ethylphenanthrene. Calcd. for $C_{16}H_{14}$: C, 93.2; H, 6.8. Found: C, 93.4, 93.3; H, 7.1, 7.0. The *second fraction*, b. p. 180–195° (0.8 mm.) was an unsaturated (bromine) yellow oil, n_D 1.6499, which crystallized after some time; from alcohol as needles, exhibiting blue fluorescence, m. p. 73–75°. The analysis showed that the desired 1-(phenanthryl-ethyl)-2-methyl-cyclopentene-(1) (IX) had been formed but the yield was so poor that further experiments with this substance had to be abandoned.

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[10] Cornubert and Borrell, *Bull. soc. chim.* (IV), **47**, 304 (1930).

Calcd. for $C_{22}H_{22}$: C, 92.3; H, 7.7. Found: C, 92.3; H, 8.2. In view of the violence of the Grignard reaction, it is improbable that the ethylphenanthrene derives from unchanged Grignard compound. It could have been formed by dismutation of the expected carbinol, or when methylcyclopentanone inclines to react in an enolic form.[11]

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(11) Compare Grignard and Savard, *Bull. soc. chim. Belg.*, **36**, 97 (1927).

Summary

1. Cyclopentenotriphenylene has been prepared, starting with β-(9-phenanthryl)-ethyl chloride and cyclopentanone.
2. The nature of several by-products has been discussed.

REHOVOTH, PALESTINE RECEIVED APRIL 9, 1936

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

Cerin and Friedelin. III. A Study of the Oxidative Degradation of Friedelin[1]

BY NATHAN L. DRAKE AND WILLIAM P. CAMPBELL

Our previous study of cerin and friedelin[2] has shown that these substances are polycyclic in nature, the former a hydroxy ketone, the latter a ketone, both derived from the same nucleus. From evidence now available[3] it is apparent that this polycyclic nucleus contains five fused rings, and that cerin and friedelin are derived from a completely hydrogenated picene, and should be classed as derivatives of a triterpene.

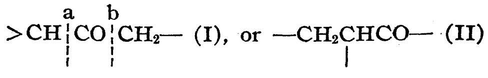
It is the purpose of this communication to describe certain degradation experiments in which the attack on the friedelin molecule is at the carbonyl group.

Sodium and amyl alcohol reduce friedelin to the corresponding alcohol, friedelinol, whose benzoate can be prepared readily by the action of benzoyl chloride on the alcohol in pyridine solution. This benzoate, when heated in an atmosphere of nitrogen to 300°, is converted into a hydrocarbon friedelene, $C_{30}H_{50}$, and benzoic acid. Similar unsaturated hydrocarbons with alkyl or aryl groups attached to the carbon which, in the original friedelin molecule, held the carbonyl oxygen, can be prepared by the action of the Grignard reagent on friedelin. Phenylmagnesium bromide yields such a hydrocarbon directly; the tertiary alcohol first produced undergoes spontaneous dehydration. Two products are obtained when methylmagnesium iodide reacts with friedelin. One is the expected methyl-substituted tertiary alcohol, the other methylfriedelene. The tertiary alcohol is readily dehydrated by acetic anhydride to methylfriedelene. All of these unsaturated substances give a pronounced yellow color with tetranitromethane, but the *purest* friedelin gives no color.

The ready dehydration which these alcohols undergo, and the formation of benzoic acid from the benzoate, prove the presence of a hydrogen atom adjacent the carbonyl group of friedelin, and indicate that this hydrogen is probably tertiary.

Because friedelene is so easily accessible it was chosen for further study. Oxidation of friedelene by chromic anhydride in glacial acetic acid yields a neutral substance, $C_{30}H_{48}O$. This compound gives a color with tetranitromethane and yields no methane when treated with methylmagnesium iodide. The substance $C_{30}H_{48}O$ must, therefore, be an unsaturated ketone, and since no methylene group of friedelin behaves in a similar fashion during oxidative degradations, it is reasonable to assume that the ketone $C_{30}H_{48}O$, which we have called friedelenone, owes its formation to the activating effect of the double bond on the hydrogens of an adjacent methylene group. The formation of α,β-unsaturated ketones by oxidation is a common reaction in the terpene series. Pinene can be oxidized to verbenone by treatment with chromic acid[4] and cedrin[4] and limonene can also be converted to α,β-unsaturated ketones by oxidation.[5] Similarly cholestene is converted to cholestenone under the influence of chromic anhydride.[6]

On the basis of this evidence the existence of the grouping



$$>CH\overset{a}{\vdots}CO\overset{b}{\vdots}CH_2\text{— (I), or —}CH_2\underset{|}{C}HCO\text{— (II)}$$

in friedelin is postulated. Evidence obtained from the oxidation of friedelin makes it possible

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(1) From the Ph.D. dissertation of William P. Campbell.

(2) Drake and Jacobsen, THIS JOURNAL, **57**, 1570; Drake and Shrader, *ibid.*, 1854 (1935).

(3) *Cf.* the fourth article in this series, *ibid.*, **58**, 1684 (1936).

(4) Semmler and Jakubowicz, *Ber.*, **47**, 1143 (1914).

(5) Blumann and Zeitschel, *ibid.*, **47**, 2624 (1914).

(6) Windaus, *ibid.*, **53**, 488 (1920).

to assign the partial structure (I) to one ring of the friedelin molecule.

Friedelin is oxidized by chromic anhydride in glacial acetic acid mainly to a keto acid containing thirty carbon atoms $C_{30}H_{50}O_3$, for which we propose the name friedonic acid. The neutralization equivalent of the acid, the saponification equivalent of its methyl ester, and determination of its carbon and hydrogen content are all in accord with the formula written. It is obvious, therefore, that friedonic acid is produced by the opening of a hydroaromatic ring which holds some substituent on the carbon adjacent to the carbonyl group. Although it has not proved possible to obtain from this acid any derivatives by replacement of the carbonyl oxygen, it is possible to reduce friedonic acid to a neutral substance, $C_{30}H_{50}O_2$, the lactone of an hydroxy acid. In accord with this interpretation are the neutrality of the reduction product, the fact that it gives no color with tetranitromethane, thus excluding simple dehydration of an hydroxy acid with formation of an unsaturation, and its saponification equivalent. We propose to call this substance the lactone of friedolic acid.

In addition to friedonic acid, a keto acid containing twenty-nine carbon atoms is produced by the oxidation of friedelin.

It has proved impossible thus far to separate the more soluble C_{29} keto acid as such from the C_{30} acid, for both crystallize very poorly, but reduction of the more soluble fractions obtained during purification of the C_{30} acid yields a mixture of lactones from which that of the C_{29} acid can be separated. Analyses and determinations of saponification equivalent demonstrate the formula of this lactone to be $C_{29}H_{48}O_2$; it is therefore norfriedolo lactone.

The simplest interpretation of these reactions considered in conjunction with the oxidation of friedelene to friedelenone is that during the oxidation of friedelin the structure (I) is cleaved at (a) and at (b) forming, respectively, friedonic acid and a dibasic acid which, because it contains the grouping $>CH-$ adjacent to the carboxyl is very easily degraded further, yielding norfriedonic acid.

There is ample justification in the literature for the assumption that the intermediate dibasic acid would readily undergo further degradation, for isobutyric acid yields acetone when treated with hydrogen peroxide or chromic acid,[7] and methylheptylacetic acid is degraded by chromic acid to methyl heptyl ketone.

Oxidation of friedelene produces a very small acidic fraction, from which by reduction with sodium and alcohol norfriedolo lactone, identical with the compound obtained by oxidation of friedelin, is obtained. It should be stated that the evidence on which the identity of this acidic oxidation product of friedelene is based consists of a determination of the melting point of the compound mixed with norfriedolo lactone obtained from friedelin. This sort of evidence appears to be admissible in the light of our experience with other degradation products of friedelin.

Norfriedonic acid is formed, then, from friedelenone by cleavage of the ketone at the double linkage and further degradation of the α-keto acid so produced. The formation of norfriedonic acid in this reaction proves that the methylene group in friedelin must be adjacent to the carbonyl and not as represented in (II). Thus it is clear that the carbon which is lost in the formation of norfriedonic acid is the one which held the carbonyl oxygen in friedelin.

Experimental

Friedelinol.—To 1 g. of friedelin dissolved in 100 ml. of boiling *n*-amyl alcohol was added 2 g. of sodium. Refluxing was continued until the sodium had dissolved, whereupon the solvent was removed by distillation with steam, and the product crystallized from benzene–ethyl acetate or from amyl alcohol. Friedelinol crystallizes in hexagonal plates which melt 301–304°. The yield of friedelinol prepared from pure friedelin was 90%. When so called "friedelin-rich"[8] material is reduced, the yield is 50–65%, but this lower yield actually represents a larger friedelinol yield based on "friedelin-rich" substance, for a considerable loss is entailed in purifying friedelin through its enol ester.

Anal. Calcd. for $C_{30}H_{52}O$: C, 84.03; H, 12.23. Found: C, 83.81, 83.75; H, 12.10, 12.08.

Friedelinyl Iodide.—Friedelinol (0.5 g.), red phosphorus (0.2 g.), and iodine (1.3 g.) were heated in dry benzene under reflux for three hours. The warm solution was shaken with mercury to remove excess iodine and evaporated to 5 ml. *in vacuo*. Water was added, the benzene removed *in vacuo*, and the product recrystallized from benzene. Leaching with a small quantity of benzene removed contaminating mercuric iodide, whereupon recrystallization from benzene–ethyl acetate resulted in a product which melted with decomposition at 224–226°.

Anal. Calcd. for $C_{30}H_{51}I$: I, 23.57. Found: I, 23.59, 23.36.

The molecular weights of friedelin calculated from these analyses are 426 and 432, respectively. These values

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[7] Schmidt, *Ber.*, **7**, 1363 (1874).

[8] *Cf.* paper I, THIS JOURNAL, **57**, 1571 (1935).

are in excellent agreement with those obtained from the saponification equivalents of certain enol esters of friedelin (*cf.* paper I).[8] The calculated molecular weight for $C_{30}H_{50}O$ is 426.

Friedelinyl Methyl Ether.—Friedelinol (0.04 g.) in methyl iodide (20 ml.) was heated under reflux for several hours with silver oxide. The solution was filtered, and the ether obtained by evaporation of the methyl iodide. After recrystallizations from ethyl acetate, from which the ether crystallizes in plates, the product melted at 265–267°.

Anal. Calcd. for $C_{31}H_{54}O$: C, 84.09; H, 12.30. Found: C, 84.04; H, 12.25.

Friedelinyl Acetate.—Friedelinol (1 g.) was heated for two hours under reflux in 100 ml. of acetic anhydride. The acetate which separated in long lath-like plates when the solution was cooled, was recrystallized from benzene. The product melted at 315–316°.

Anal. Calcd. for $C_{32}H_{54}O_2$: C, 81.63; H, 11.57. Found: C, 81.46, 81.55; H, 11.65, 11.55.

Friedelinyl Benzoate.—To a boiling solution of friedelinol (2.8 g.) in dry pyridine (125 ml.) was added benzoyl chloride (15 ml.). After the solution had been heated under reflux for one-half hour, 300 ml. of 95% ethanol was added and the solution allowed to cool to room temperature. The substance which separated was recrystallized from a benzene–alcohol mixture. Friedelinyl benzoate crystallizes in long laths which melt at 250–251°.

Anal. Calcd. for $C_{37}H_{56}O_2$: C, 83.39; H, 10.59. Found: C, 83.43, 83.29; H, 10.56, 10.71.

Friedelene.—Friedelinyl benzoate (5 g.) was heated in an atmosphere of nitrogen at 280–320° for three and one-half hours. The benzoic acid was removed from the product by 10% aqueous sodium hydroxide. After purification by crystallization from ethyl acetate–benzene the substance melted at 257–258°. It crystallizes in lath-like plates, and gives a yellow color with tetranitromethane.

Anal. Calcd. for $C_{30}H_{50}$: C, 87.72; H, 12.28. Found: C, 87.89, 87.98; H, 12.37, 12.26.

Attempts to dehydrate friedelinol directly by use of sulfuric acid, oxalic acid, sodium bisulfate, phosphorus pentachloride and thionyl chloride yielded products which would not crystallize.

Phenylfriedelene.—To a solution of phenylmagnesium bromide, prepared in ethyl ether from 25 ml. of bromobenzene and 6 g. of magnesium, was added an equal volume of dry benzene. This solution of Grignard reagent was then mixed at room temperature with a solution of 5 g. of friedelin in 500 ml. of dry benzene. To complete the reaction the mixture was heated under reflux for one-half hour. The crude product, obtained by pouring the solution into dilute acid and removing the benzene by steam distillation, was recrystallized several times from ethyl acetate from which it separated in the form of thin plates, which melted at 269–271°.

Anal. Calcd. for $C_{36}H_{54}$: C, 88.82; H, 11.18. Found: C, 88.84, 88.97; H, 11.26, 11.30.

Only 0.3 g. of phenylfriedelene was obtained; the balance of the reaction products was a gum which would not crystallize, and would not react with acetic anhydride to yield a crystalline product.

Methylfriedelinol.—This compound was prepared from 5 g. of friedelin by a method quite similar to that described directly above. The crude solid product was leached with 250 ml. of a boiling ethyl acetate–benzene mixture (2:1). Methylfriedelinol crystallized from the leachings, and after further purification by crystallization from benzene a product which crystallized in lath-like hexagonal plates, and melted at 316–319°, was obtained.

Anal. Calcd. for $C_{31}H_{54}O$: C, 84.09; H, 12.30. Found: C, 83.98, 84.19; H, 12.43, 12.42.

A small quantity of methylfriedelene was obtained from the residue left by the leaching process described above.

Methylfriedelene.—Methylfriedelinol was dehydrated by heating it under reflux in an acetic anhydride solution containing a little xylene to render the alcohol more soluble. After about two hours, a part of the solvent was removed by distillation, and the product which separated on cooling was recrystallized from benzene and ethyl acetate to constant melting point. Methylfriedelene crystallizes in hexagonal plates which melt at 272–274°.

Anal. Calcd. for $C_{31}H_{52}$: C, 87.65; H, 12.35. Found: C, 87.65, 87.70; H, 12.36, 12.47.

Oxidation of Friedelene to Friedelenone.—Friedelene (3.6 g.) dissolved in acetic acid (900 ml.) was oxidized at 97° by chromic anhydride (2.4 g.). After six hours 500 ml. of water and a little methanol were added, the mixture boiled for a few minutes and filtered; 3.5 g. of light green solid separated on cooling. This substance was dissolved in ether and shaken with 10% sodium hydroxide solution to remove any acidic fraction. The ether layer was separated and evaporated until crystallization started. The substance so obtained melted at 290–291° after one recrystallization from ether. Friedelenone crystallizes from ether in lath-like plates apparently monoclinic, which are easily differentiated under a petrographic microscope from all of the other oxidation products herein described. Friedelenone is the only oxidation product thus far examined which shows oblique extinction; the extinction angle measured from the long side of the crystal is approximately 24°.

Anal. Calcd. for $C_{30}H_{48}O$: C, 84.83; H, 11.40. Found: C, 84.83, 84.83; H, 11.32, 11.36.

Friedelenone gave a pronounced yellow color with tetranitromethane, and when treated with methylmagnesium iodide in amyl ether evolved no methane.

Acidification of the alkaline extract mentioned above produced 1.5 g. of amorphous solid. To this solid, dissolved in 50 ml. of boiling *n*-propyl alcohol, was added 3 g. of sodium cut in small pieces. When all of the sodium had dissolved, the solution was diluted with 500 ml. of water and acidified. The substance which separated was crystallized from ethyl acetate to yield a very small quantity of a compound which melted 287–289°. A mixture of this substance with norfriedolo lactone obtained from friedelin (m. p. 289–291°) melted at 288–289°.

Oxidation of Friedelin to Friedonic Acid.—Chromic anhydride (2.4 g.) dissolved in glacial acetic acid (125 ml.) was added slowly over a period of about four hours to a suspension of 5 g. of friedelin in 600 ml. of boiling glacial acetic acid. The mixture was heated under reflux for an additional eleven hours, during which time the friedelin gradually dissolved. After about two-thirds of the solvent had been removed by distillation, 500 ml. of water was added to the hot solution. After cooling and filtering, the solid was dissolved in ether, and shaken with 10% sodium hydroxide. Sodium salts precipitated in the aqueous layer and were rendered compact at the ether-water interface by the use of a centrifuge. The ether solution was separated and the mixture extracted with a fresh portion of ether. From the combined ether extracts was obtained 0.8 g. of friedelin and 0.2 g. of a resinous material.

The aqueous layer was made acid to Congo red paper, warmed to coagulate the acids and filtered. By recrystallization from aqueous alcohol and finally from 95% alcohol 1.3 g. of a product, which crystallized in narrow laths and melted 206–207°, was obtained.

Anal. Calcd. for $C_{30}H_{50}O_3$: C, 78.54; H, 11.00. Found: C, 78.83, 78.75; H, 10.91, 11.02. *Neutral Equiv.* Calcd. for $C_{28}H_{49}(CO)(COOH)$: 458. Found: 463, 461.

Methyl Friedonate.—This ester was prepared from the crude acid fraction obtained by oxidation of friedelin as above. Esterification was accomplished by heating the sodium salt in absolute ethanol with excess methyl iodide. Methyl friedonate crystallizes from methyl alcohol in narrow laths which melt at 249–251°.

Anal. Calcd. for $C_{31}H_{52}O_3$: C, 78.75; H, 11.09. Found: C, 78.60, 78.85; H, 11.21, 11.42. *Sapon. Equiv.* Calcd. for $C_{29}H_{49}(CO)(COOCH_3)$: 472. Found: 473, 471.

Friedolo Lactone and Norfriedolo Lactone.—Two and four-tenths grams of the lower melting crude acid fraction obtained from the oxidation of friedelin was dissolved in 140 ml. of *n*-propyl alcohol. This solution was heated under reflux and 6 g. of sodium cut in small pieces was added. When all the sodium had dissolved, the solution was diluted with 500 ml. of water, cooled and filtered. The resulting solid was crystallized from ethyl alcohol (160 ml.) and then several times from ethyl acetate. Friedolo lactone crystallizes from ethyl acetate in rods, which melt 309–312°.

Anal. Calcd. for $C_{30}H_{50}O_2$: C, 81.37; H, 11.39. Found: C, 81.24, 81.12; H, 11.26, 11.25.

The alcoholic filtrate from the first crystallization mentioned above was evaporated to half its volume, cooled and filtered. The crystals which separated were purified by further recrystallization from ethyl acetate. The compound norfriedolo lactone crystallizes from ethyl acetate in long needle-like laths, and melts 289–291°. This melting point is considerably depressed by admixture of friedolo lactone.

Anal. Calcd. for $C_{29}H_{48}O_2$: C, 81.24; H, 11.30; sapon. equiv., 428. Found: C, 81.09, 81.29; H, 11.29, 11.34; sapon. equiv., 431, 429.

We should like to acknowledge our indebtedness to R. P. Jacobsen for his analyses of friedelinyl iodide, and to J. R. Spies for analyses of friedelinol and friedelinyl methyl ether.

Summary

1. The oxidation of friedelin and friedelene by chromic anhydride in glacial acetic acid has been studied, and from evidence so obtained the structure $CHCOCH_2$- in the friedelin molecule is deduced.

2. The preparation of friedelinol and of several of its derivatives is described.

3. Several acidic and neutral degradation products of friedelene and friedelin have been prepared.

COLLEGE PARK, MD. RECEIVED JUNE 25, 1936

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

Cerin and Friedelin. IV. The Dehydrogenation of Friedelinol[1]

BY NATHAN L. DRAKE AND WILLARD T. HASKINS

In continuation of our studies on the structure of cerin and friedelin, we have subjected friedelinol to dehydrogenation by selenium in order to determine the type of aromatic nucleus to which friedelin is related. Friedelinol rather than friedelin was chosen for study because previous investigation had shown that friedelin, like most ketones whose carbonyl forms a part of a ring system, yielded products too complex and too far removed from the original nuclear structure to be a satisfactory substance for dehydrogenation studies.

The products obtained from friedelinol by dehydrogenation are 1,2,7-trimethylnaphthalene (sapotalene), 1,2,8-trimethylphenanthrene, a hydrocarbon $C_{25}H_{20}$, apparently identical with a polymethyl picene isolated by Ruzicka and coworkers from the dehydrogenation products of a number of triterpenes,[2] and a liquid hydrocarbon, $C_{11}H_{20}$, which has the properties of an alkyl substituted cyclohexene.

The evidence advanced by Ruzicka[3] in support of a picene nucleus in the hydrocarbon $C_{25}H_{20}$ is quite conclusive; consequently there must be in cerin and friedelin a pentacyclic nucleus of the

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(1) From the Ph.D. dissertation of W. T. Haskins.

(2) Ruzicka, Frame, Leicester, Liguori and Brüngger, *Helv. Chim. Acta*, **17**, 426 (1934).

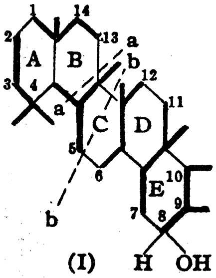
(3) Ruzicka, Hösli and Ehmann, *ibid.*, **17**, 445 (1934).

hydrogenated picene type. The formation of new rings during dehydrogenation is a reaction known to occur, but at the temperatures of our dehydrogenations such ring formation is highly unlikely. Extra cycle formation is most probable at temperatures above 350°,[4] and our dehydrogenations were carried out at temperatures from 315 to 325° (bath temp.).

It seems unlikely that alkyl group rearrangement occasioned by the dehydration of friedelinol occurred prior to the actual dehydrogenation, for both friedelin and friedelene gave the same product, norfriedonic acid[5] on oxidation, and friedelene was prepared at temperatures approximating those employed during the dehydrogenations. It seems logical to conclude, therefore, that the locations of the alkyl groups in the polymethylpicene actually represent the original structure. There is considerable doubt as to the exact number of these methyl groups. Ruzicka has synthesized 3,9,10-trimethylpicene and 3,8-dimethylpicene, neither of which[6] is identical with the product obtained by dehydrogenation, although the absorption bands of the trimethylpicene in the ultraviolet were very much like those of the unknown. All of our analyses on the hydrocarbon obtained from friedelinol and the same substance obtained from ursolic acid are better in accord with $C_{24}H_{18}$ than $C_{25}H_{20}$. Furthermore, our determinations of molecular weight on different specimens of the hydrocarbon from the sources mentioned above are considerably too low for the $C_{25}H_{20}$ formula and check the $C_{24}H_{18}$ formula almost exactly. The concordance of these two sets of determinations carried out by different operators on material from different sources might possibly be fortuitous, but we believe that our findings emphasize the necessity of considering the dimethylpicenes in any attempt to identify the unknown polymethylpicene.

Ruzicka has concluded as a result of certain degradation reactions of hederagenin[7] that the hydroxyl group of the triterpenes must be considered to be adjacent to a carbon atom holding two methyl groups. It is apparent from the behavior of friedelin on oxidation that this structure does not exist in friedelinol.[5]

We suggest as a tentative formula for friedelinol the following (I)



(I)

in which the heavy lines represent isoprene nuclei. This structure corresponds closely to one suggested by Ruzicka for certain triterpenoids,[7b] (p. 391) but differs in the location of the hydroxyl group, and in the absence of the Δ^8 unsaturation. It is entirely possible that the hydroxyl group of cerin corresponds in location to the hydroxyl of those triterpenoids which Ruzicka has studied and should be placed at 3 in Ring A.

Cleavage of the molecule at (a)------(a) would result in the formation of 1,2,8-trimethylphenanthrene and another substance containing eleven carbon atoms, corresponding to the compound $C_{11}H_{20}$, which apparently is a polyalkylcyclohexene. This substance was obtained in small quantity, but possessed properties which were in accord with the suggested structure. It had a refractive index like other known polyalkylcyclohexenes containing eleven carbons, absorbed bromine in cold carbon tetrachloride but yielded no solid bromide, and had a molecular weight and percentage composition which were excellently in accord with the formula $C_{11}H_{20}$. It was distilled several times over platinized asbestos at 300° and later at 420° without being further dehydrogenated. It was possible, however, by heating the substance in a sealed tube with selenium for twenty-four hours at 320° to accomplish further dehydrogenation as evidenced by the escape of hydrogen selenide when the tube was opened. The resulting substance possessed a considerably higher refractive index than the original material and was converted at 0° by the action of bromine in the presence of a bit of aluminum chloride into a solid bromide. The melting point of the bromide did not, however, correspond to that of any of the known derivatives of polyalkylbenzenes. The difficulty of dehydrogenating this material by platinum black is in accord with the findings of Zelinsky,[8] who has examined the

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[4] *Cf.* Diels, *Ann.*, **459**, 1 (1927); *Ber.*, **66**, 487, 1122 (1933); Ruzicka, Thomann, Brandenberger, Furter and Goldberg, *Helv. Chim. Acta*, **17**, 200 (1934).

[5] *Cf.* paper III, THIS JOURNAL, **58**, 1681 (1936).

[6] Ruzicka and Mörgeli, *Helv. Chim. Acta*, **19**, 377 (1936).

[7] (a) Ruzicka and Hofmann, *ibid.*, **19**, 121, 122 (1936); (b) Ruzicka, Hofmann and Frei, *ibid.*, **19**, 387 (1936).

[8] Zelinsky, *Ber.*, **44**, 3121 (1911); **45**, 3678 (1912); **56**, 1716 (1923).

behavior of a number of hydroaromatic rings when subjected to the dehydrogenating influence of platinum at elevated temperatures. Only those rings containing no quaternary carbon atom were aromaticized at temperatures up to 300°.

Cleavage of (I) at (b)----(b) and migration of a methyl group from 4 to 3 would result in the formation of sapotalene. The migration of the alkyl group is certainly within the bounds of reason, for Mayer and Schiffner have shown[9] that α-methylnaphthalenes have a pronounced tendency to rearrange to β-derivatives when distilled over silica gel at temperatures above 400°, and α-phenylnaphthalene rearranges at about 350°.

The location of the hydroxyl group at the 8-position in (I) is based on results obtained in oxidation studies.[5] It is apparent from this work that the secondary hydroxyl of friedelinol must be present in a cycle which contains the unit of structure $CHCHOHCH_2$-; furthermore, we have isolated a lower oxidation product of friedonic acid which apparently is a keto acid containing twenty-seven carbon atoms.[10]

Experimental

Apparatus.—The dehydrogenations were carried out in a 200-ml. Pyrex flask to which was sealed a broad U-tube of 20 mm. tubing. One arm of the U, about a meter long, served as a reflux condenser, the other arm, which was somewhat shorter, was sealed to a small Pyrex flask with a side outlet. This flask served as an auxiliary condenser, and from its side-arm the gaseous products of the reaction were conducted through a small bubble counter to a tube containing moist calcium hypochlorite. The reaction flask was heated by a bath of Wood's metal whose temperature was determined by means of a thermocouple. Selenium was introduced through a short side-arm near the top of the reflux condenser.

Method.—Forty grams of friedelinol,[5] well mixed with 80 g. of powdered selenium, was heated in the reaction flask (metal bath temp. 315–325°), and 10-g. portions of selenium added every twenty-four hours until 40 g. had been added. The heating was continued until hydrogen selenide was no longer evolved (two hundred and forty hours). The reaction flask was then cut from the condenser and broken to recover the charge. The reaction products were finely ground in a mortar and exhaustively extracted with ether in a Soxhlet extractor. The reflux condenser and trap were rinsed with ether and the rinsings added to the ether extract. After extraction by ether was practically complete, the ether was replaced by benzene, and extraction continued until the residue was free from soluble material.

After evaporation of the ether from the first extract there remained 11.1 g. of dark red oil. A second dehydrogenation was conducted in the same apparatus using 50 g. of friedelinol mixed with 15 g. of powdered selenium as the initial charge. Selenium was added in 5-g. portions at intervals of an hour during the daytime until 150 g. in all had been added. Evolution of hydrogen selenide ceased at the end of seventy-five hours. The ether extract weighed 19.2 g., but 10 g. consisted of material boiling above 250° under 2 mm. pressure. The addition of selenium in small amounts appeared to speed up the dehydrogenation considerably, but had little effect on the type and amounts of products except that the first fraction described below was less than one-third as large in the second dehydrogenation as in the first.

Fractionation of the Ether Soluble Products.—The ether-soluble products were distilled under a pressure of 2 mm. in a Claisen flask with a short fractionating column. Fractions with the following boiling ranges, weights, $n^{25}D$ and $d^{20}{}_{20}$ were obtained: up to 70°, 2 g., 1.4585, 0.8232, sl. yellow liq.; 70–125°, 1.2 g., 1.5686, 0.9650, yellow liq.; 125–170°, 0.5 g., 1.6067, red-yellow liq.; 170–200°, 0.8 g., yellowish semi-solid; 200–250°, 1.0 g., yellowish solid; residue, 5.6 g., dark resinous solid.

The still residue was combined with the benzene extract, and the material left after removal of the benzene was sublimed under low pressure.

The Alkylcyclohexene.—The liquid hydrocarbon boiling up to 70° at 2 mm. pressure was redistilled at atmospheric pressure. Approximately 80% of the substance distilled from 180 to 185°. This substance would not form a solid bromide when treated with bromine in cold carbon tetrachloride, nor would it yield a picrate or a styphnate.

Anal. Calcd. for $C_{11}H_{20}$: C, 86.74; H, 13.26; mol. wt., 152. Found: C, 86.60, 86.32; H, 13.62, 13.61; mol. wt. (f. p. of benzene), 149, 152; $n^{25}D$ 1.4535; $d^{20}{}_{20}$ 0.8232.

The liquid was distilled several times over platinized asbestos at 300 and at 420°, but no dehydrogenation occurred. About 0.3 g. of the liquid was heated to 320° with 1.0 g. of selenium in a small sealed Pyrex tube for twenty-four hours. When the tube was opened hydrogen selenide escaped, proving dehydrogenation. The product was extracted with ether and later distilled; it boiled 187–192°, and had a considerably higher refractive index than before heating ($n^{25}D$ 1.4553). The liquid was cooled to 0° and a small amount of aluminum chloride and a few drops of bromine added. Hydrogen bromide was evolved and the mass partially solidified. After removal of excess bromine and recrystallization from alcohol the solid melted 169–175°. The melting point does not correspond to that of any of the recorded bromo derivatives of the polyalkylbenzenes.

1,2,7-Trimethylnaphthalene.—The liquid fractions which boiled from 70–125° and from 125–170° were converted into picrate, and recrystallized from ethyl alcohol. After eight recrystallizations a constant melting point of 125–127° was attained.

Anal. Calcd. for $C_{19}H_{17}N_3O_7$: C, 57.13; H, 4.29. Found: C, 57.27, 56.87; H, 4.04, 4.14.

The corresponding fractions from the second dehydrogenation were converted into styphnate and the latter

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(9) Mayer and Schiffner, *Ber.*, **67**, 67 (1934).

(10) Unpublished work.

recrystallized from ethyl alcohol to a constant melting point of 153–154°.[11]

1,2,8-Trimethylphenanthrene.—The fraction which boiled 170–200° was converted to picrate, but this derivative dissociated readily after a few recrystallizations from methyl alcohol had removed excess picric acid. The fluffy white hydrocarbon so obtained melted at 141–142°. Similar treatment of the corresponding fraction from the second dehydrogenation yielded more of the same substance.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.73; H, 7.27; mol. wt., 220. Found: C, 92.90, 92.45; H, 7.49, 7.23; mol. wt. (Rast), 204, 202.

The picrate of this hydrocarbon was crystallized from ethyl alcohol saturated at 0° with picric acid. The picrate melted 162–163°.

The solid fractions which boiled at 200–250° under 2 mm. pressure were recrystallized from ethyl alcohol five times. The resulting hydrocarbon was the same as the one described directly above; 0.03 g. of this substance was dissolved in boiling glacial acetic acid and 0.05 g. of chromic anhydride was added. The mixture was heated under reflux for thirty minutes, then cooled, and diluted with water. A small amount of an orange colored quinone which melted 189–190° was obtained. This quinone was dissolved in ethyl alcohol, an excess of *o*-phenylenediamine was added, and the solution was evaporated to dryness. The residue was taken up in ether, and extracted with 1% hydrochloric acid to remove unreacted diamine. Evaporation of the ether solution left a pale yellow quinoxaline which melted 129–131°. The melting points of hydrocarbon and the derivatives mentioned above (in the order discussed) are reported by Haworth[12] as 144–145, 163, 196–197, 131–132°, and by Ruzicka[13] as 142–143, 161–163, 194, 131–132°.

The Polymethylpicene.—The combined still residues from the ether extracts and the benzene extracts were sublimed at 300° under low pressure. The sublimed material was crystallized several times from benzene. After treatment with decolorizing carbon and further recrystallization, a product which melted 305–306° and crystallized in shiny flat platelets with a bluish luster was obtained.

Anal. Calcd. for $C_{25}H_{20}$: mol. wt., 320; C, 93.70; H, 6.30; for $C_{24}H_{18}$: mol. wt., 306; C, 94.09; H, 5.91. Found: mol. wt. (Rast), 306, 309; C, 93.80, 93.97; H, 6.17, 6.11.

The hydrocarbon dissolves in concentrated sulfuric acid with the production of a deep emerald green color, a reaction also given by picene,[14] and it is oxidized by chromic anhydride in glacial acetic acid to a reddish orange quinone which possesses no definite melting point (like picene quinone). Analysis of a sample of this quinone which had been recrystallized from dioxane indicated that it contained a considerable quantity of a substance richer in oxygen. Lack of material prevented further purification.

Summary

1. 1,2,7-Trimethylnaphthalene, 1,2,8-trimethylphenanthrene, a polymethylpicene and a polyalkylcyclohexene have been shown to be present among the products formed by dehydrogenating friedelinol by selenium.

2. Cerin and friedelin should be classed with the triterpenoids. They contain a hydrogenated pentacyclic nucleus.

3. A tentative structure has been assigned to friedelinol, the reduction product of the ketone, friedelin.

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(11) Ruzicka [*Helv. Chim. Acta*, **15**, 431 (1932)] gives the following melting points: picrate, 129°; styphnate, 157°.

(12) Haworth and Mavin, *J. Chem. Soc.*, **141**, 2720 (1932).

(13) Ruzicka and Hosking, *Helv. Chim. Acta*, **14**, 203 (1931).

(14) Burg, *Ber.*, **13**, 1834 (1880).

COLLEGE PARK, MD. RECEIVED JUNE 25, 1936

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

The Dehydrogenation of Ursolic Acid by Selenium[1]

BY NATHAN L. DRAKE AND HARRY M. DUVALL

During his study of polyterpenoid substances, Ruzicka dehydrogenated a small quantity (5 g.) of ursolic acid by means of selenium[2] and identified 1,2,7-trimethylnaphthalene (sapotalene) as one of the dehydrogenation products. In connection with certain other work in progress in this Laboratory, it seemed desirable to repeat this work using larger quantities of material, and we were very fortunate in obtaining for this purpose, through the courtesy of Drs. C. E. Sando and K. S. Markley of the U. S. Department of Agriculture, a considerable quantity of crude ursolic acid.

In addition to sapotalene we have obtained two other substances by the action of selenium at 320–340° on ursolic acid, *viz.*, 2,7-dimethylnaphthalene, and a polymethylpicene, apparently identical with a substituted picene obtained by Ruzicka[2] from related triterpenoid substances. This polymethylpicene is identical with the compound obtained by Drake and Haskins by the dehydrogenation of friedelinol.[3]

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(1) From the Ph.D. dissertation of H. M. Duvall.

(2) Ruzicka, Brüngger, Egli, Ehmann, Furter and Hoösli, *Helv. Chim. Acta*, **15**, 431 (1932).

(3) Drake and Haskins, THIS JOURNAL, **58**, 1684 (1936).

Experimental

Purification of Ursolic Acid.—Two hundred grams of crude ursolic acid was dissolved in a hot solution of 50 g. of potassium hydroxide in approximately 600 ml. of methanol and 300 ml. of water. A small quantity of insoluble brown material was skimmed off and the solution filtered with suction while hot through a large Büchner funnel. The hot filtered solution was then treated with 40 g. of decolorizing charcoal, filtered, and the charcoal treatment repeated twice. The resulting solution was next heated on the steam-bath to remove some of the methyl alcohol (not enough to cause separation of potassium ursolate); 1500 ml. of hot water was then added and the ursolate salted out by the addition of 50% potassium hydroxide solution (about 50 g. of potassium hydroxide in 50 ml. of water was necessary).

The precipitated potassium ursolate was collected on a large Büchner funnel, sucked dry, and then dissolved in 500–600 ml. of hot methanol. This solution, after filtration while hot, was acidified to Congo red by 6 *N* hydrochloric acid. The resulting precipitate was filtered and washed carefully twice by stirring it in a beaker with about a liter of boiling water acidified with hydrochloric acid. One recrystallization from ethyl alcohol yielded a product which melted 278–280°.[4] Further recrystallization raised the melting point to 283–284°.

Anal. Calcd. for $C_{30}H_{48}O_3$: C, 78.88; H, 10.60. Found: C, 79.05, 78.86; H, 10.69, 10.53.

The Dehydrogenations.—Two 50-g. portions and one 200-g. portion of ursolic acid were dehydrogenated. The apparatus and procedure were essentially as in our earlier work.[5] The products of the second and third dehydrogenations were worked up together; 59.5 g. of ether-soluble products and 13.7 g. of benzene-soluble products were so obtained.

Fractionation of the Ether-Soluble Products.—The ether-soluble material was distilled from a 200-ml. flask with a sausage side-arm. Fractions with the following boiling ranges, weights and physical states, were obtained (l. = liquid; s. = solid): 115–150° at 12 mm., 2.5 g., l.; 150–175° at 11 mm., 3.6 g., l.; 175–200° at 12 mm., 21.1 g., l.; 200–250° at 12 mm., 8.9 g., l.; 265–285° at 6–8 mm., 8.0 g., l. and s.; 285–310° at 2 mm., 7.9 g., s.; 350–365° at 3 mm., 6.1 g., s.

By redistillation at 11–12 mm. in a small Claisen flask, fractions 1, 2, 3 and 4 were separated into a principal fraction boiling from 130–140°, and a number of lower and higher boiling fractions. This principal fraction was then subjected to careful fractionation at 1–2 mm. in a column about 92 cm. in height packed with Wilson rings. After a small fore-run, the bulk of the material had a refractive index of n^{25}_{D} 1.5997–1.6001. This material was combined with other fractions of nearly the same index and used for preparation of derivatives of sapotalene.

The lower boiling fractions from the second distillation were likewise carefully fractionated in the ring-packed column. From the intermediate fractions of this distillation a solid was obtained, which after further purification proved to be 2,7-dimethylnaphthalene.

2,7-Dimethylnaphthalene.—This substance, isolated as described directly above, had a melting point of 96.5°; its picrate melted at 135–136°, and its styphnate at 159–160°. The corresponding values given in the literature[3] are 97, 136 and 159°, respectively.

Anal. Calcd. for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 91.93; H, 7.70. Calcd. for $C_{18}H_{15}O_7N_3$: C, 56.09; H, 3.93. Found: C, 56.25; H, 3.95. Calcd. for $C_{18}H_{15}O_8N_3$: C, 53.85; H, 3.77. Found: C, 53.84; H, 3.89.

1,2,7-Trimethylnaphthalene.—It did not prove feasible to purify sapotalene as such, so the substance was converted into picrate and purified by crystallization. The picrate was then decomposed by dilute aqueous ammonia and the styphnate prepared. The picrate melted at 128–129°, the styphnate at 157–157.5°; the melting points of these substances given in the literature[2] are 129 and 157°, respectively.

Anal. Calcd. for $C_{19}H_{17}O_7N_3$: C, 57.13; H, 4.27. Found: C, 57.42, 57.24; H, 4.53, 4.35. Calcd. for $C_{19}H_{17}O_8N_3$: C, 54.92; H, 4.11. Found: C, 55.19, 55.13; H, 4.19, 4.22.

The Polymethylpicene.—The fourth, fifth and sixth fractions from the initial distillation contained solid material. This solid was purified by recrystallization from benzene, and its melting point found to be 304°.

Anal. Calcd. for $C_{25}H_{20}$: mol. wt., 320; C, 93.70; H, 6.30; for $C_{24}H_{18}$: mol. wt., 306; C, 94.09; H, 5.91. Found: C, 94.07, 93.80; H, 5.92, 6.03; mol. wt. (Rast), 300, 296.

This hydrocarbon gave the same characteristic green color when treated with sulfuric acid as does picene,[6] and was oxidized by chromic anhydride in glacial acetic acid to a quinone which reacted with *o*-phenylenediamine to give a quinoxaline. To date we have not been able to obtain either quinone or quinoxaline in a state of analytical purity.

Summary

1. Sapotalene, 2,7-dimethylnaphthalene and a polymethyl picene have been obtained from ursolic acid by selenium dehydrogenation.

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(4) All melting points are corrected.

(5) Drake and Haskins, THIS JOURNAL, **58**, 1684 (1936).

(6) Beilstein, 4th ed., Julius Springer, Berlin, Vol. V, 1918, p. 735.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Studies of the Reducing Action of Mercury. II. Stability of Quinquivalent Molybdenum Solutions. A Method for the Determination of Molybdenum by Reduction with Mercury and Titration with Ceric Sulfate

BY N. HOWELL FURMAN AND W. M. MURRAY, JR.

Introduction

The volumetric determination of molybdenum has been studied frequently and many methods have been developed involving the reduction of molybdenum and subsequent titration with standard oxidizing agent. In practically all of these studies the reduced molybdenum solution has been protected from the air either by an atmosphere of some inert gas or by running the reduced solution into an excess of oxidizing agent. A few workers have reduced molybdenum to the quinquivalent stage and titrated this lower state without any precaution against air oxidation, but there seems to have been no systematic study of the stability of quinquivalent molybdenum solutions.

This investigation is concerned with the stability of quinquivalent molybdenum solutions and a new method for the determination of molybdenum based on reduction in acid solution with mercury, followed by titration with ceric sulfate solution using as indicator the ferrous complex of *o*-phenanthroline.

Chilesotti[1] observed that mercury would reduce a molybdic acid solution to the trivalent state if the hydrochloric acid concentration were about 9 *N*. This fact was carried no further than the preliminary observation. McCay and Anderson[2] observed qualitatively that molybdenum solutions were reduced by mercury.

Someya[3] reduced molybdenum to the quinquivalent state with bismuth amalgam. The extent of the reduction depended on the presence or absence of air and on the concentration of hydrochloric acid.

Stehlik[4] reduced molybdenum to the quinquivalent state with stannous chloride and titrated the reduced solution potentiometrically with standard ceric sulfate. Lang and Gottlieb[5] have proposed a new volumetric method for the determination of molybdenum. Their primary reducing agent is stannous chloride, and a thorough study of the effect of acidity on this reaction has been made.

Walden, Hammett and Edmonds[6] studied the reduction of molybdenum solutions in the silver reductor and also the titration of quinquivalent molybdenum with ceric sulfate using the *o*-phenanthroline ferrous complex indicator. The titration apparently was satisfactory, but the silver reduction technique did not give reproducible results.

Apparatus and Materials

All potentiometric titrations were performed in the classical manner using a saturated calomel reference electrode and bright platinum wire indicator electrode. Calibrated glassware was used.

The solutions used in the stability studies were prepared from purified molybdic oxide. The standard ammonium molybdate solutions were standardized by the silver molybdate method of McCay.[7] Typical data for the standardization of one such solution were: 0.1038, 0.1038, 0.1039. The standard ceric sulfate solutions which contain traces of iron were standardized against Bureau of Standards sodium oxalate according to the method of Willard and Young.[8]

In the experiments involving the shaking of molybdenum solutions and mercury, all the agitation was done by machine. This machine was run by an electric motor so that the rate of shaking was fairly constant. The motion was a short vertical stroke which kept the mercury splashing through the solution. The containers used were 250-ml. glass-stoppered soft glass bottles or, in case the solution was to be heated, glass-stoppered Pyrex Erlenmeyer flasks.

o-Phenanthroline Ferrous Complex as Indicator for the Titration of Quinquivalent Molybdenum with Ceric Sulfate

Several titrations of samples of quinquivalent molybdenum solutions with standard ceric sulfate were followed both potentiometrically and colorimetrically. It was soon found that the potentiometric end-point was vague, extending over a range of several drops of reagent. Graphs of the data showed a small secondary break within the larger one. Such behavior was encountered by Furman and Schoonover,[9] and they found the small secondary break was caused by iron in the ceric sulfate reagents. Iron was found to be present in the reagents used in our work, and the irregularity of the potentiometric curves is attributed to this cause. However, the end-point as indicated by the *o*-phenanthroline in the colorimetric titra-

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[1] Chilesotti, *Z. Elektrochem.*, **12**, 146 (1906).

[2] McCay and Anderson, THIS JOURNAL, **43**, 2372 (1921).

[3] Someya, *Z. anorg. allgem. Chem.*, **152**, 368 (1926).

[4] Stehlik, *Collection Czechoslov. Chem. Communications*, **4**, 418 (1932).

[5] Lang and Gottlieb, *Z. anal. Chem.*, **104**, 1 (1936).

[6] Walden, Hammett and Edmonds, THIS JOURNAL, **56**, 350 (1934).

[7] McCay, *ibid.*, **56**, 2548 (1934).

[8] Willard and Young, *ibid.*, **50**, 1322 (1928).

[9] Furman and Schoonover, *ibid.*, **53**, 2561 (1931).

tions was very sharp and satisfactory. The ferrous iron formed during the addition of the reagent to the reduced molybdenum solution must be oxidized by more ceric sulfate before the *o*-phenanthroline end-point occurs, so that the error caused by the iron in the potentiometric titrations is eliminated in the colorimetric method.

For the colorimetric titration, the acid concentration must be at least 2 *N* and the molybdenum concentration at the end-point must not exceed 0.25 g. per 300 ml. of solution. Otherwise, a red precipitate which is not destroyed by an excess of ceric sulfate tends to form and obscures the end-point. The formation of this precipitate is dependent on the simultaneous presence of cerous, molybdate, and *o*-phenanthroline ferrous ions in acid solution.

The procedure adopted in this work was to add 5–10 ml. of concentrated sulfuric acid to the quinquivalent molybdenum solutions which were already 2 *N* in hydrochloric acid. If necessary, the mixture was diluted with 2 *N* hydrochloric acid in order to keep the molybdenum concentration below the limit mentioned. Then two drops of 0.025 *M* *o*-phenanthroline ferrous complex indicator solution was added and the titration with ceric sulfate carried out at room temperature. Such a procedure was entirely satisfactory, the reaction being very rapid at room temperature and the color change at the end-point exceedingly sharp.

Stability of Quinquivalent Molybdenum Solutions

A concentrated solution of quinquivalent molybdenum was prepared by electrolytic reduction according to the method of Foerster and Fricke.[10] Portions of this reduced solution were diluted with water and hydrochloric acid to give (1) a solution 0.1 *M* in molybdenum and 2 *N* in hydrochloric acid and (2) a solution 0.1 *M* in molybdenum and 4 *N* in hydrochloric acid.

During the course of this work, samples of these two stock solutions of quinquivalent molybdenum were titrated at intervals in order to determine their respective normalities and follow the slow air oxidation of the reduced molybdenum. The relative instability of the solutions is evident from the following data.

QUINQUIVALENT MOLYBDENUM IN 2 *N* HCl

Days	0	2	8	14	44	202
Normality	0.08092	0.07978	0.07854	0.07565	0.06981	0.00505

QUINQUIVALENT MOLYBDENUM IN 4 *N* HCl

Days	0	1	3	4	5	6
Normality	0.1356	0.1353	0.1344	0.1325	0.1315	0.1298

The foregoing data show that quinquivalent molybdenum solutions are relatively unstable over extended periods of time, but the solutions are not appreciably oxidized in six or eight hours. It is thus possible to work with quinquivalent molybdenum solutions without precaution to exclude air if the solutions are to be oxidized within a short time. The acid concentration of such solutions must be above 1 *N*, however, for quinquivalent molybdenum is very unstable in neutral solution and tends to deposit molybdenum blue.

Reduction of Molybdic Acid by Mercury

Procedure.—The method of reduction is very similar to that described by McCay and Anderson.[2] The bottles or flasks used as reductors contained about 25 ml. of pure mercury. The sample of molybdate solution was pipetted directly into the reductor and the calculated volume of concentrated hydrochloric acid added to bring the acid concentration up to 3 *N*. The reductors were then agitated by machine, but vigorous shaking by hand is quite satisfactory. The sample is completely reduced with only five minutes of shaking. After the reduction, the solution is decanted from the mercury onto a filter, the filtrate being received in a 600-ml. beaker. The mercury and calomel in the bottle are washed five times with 20-ml. portions of dilute (1–5) hydrochloric acid, the mercury mass being well shaken with the wash solution each time, the solution then decanted through the filter. (No detectable amount of hydrogen peroxide is formed during the few seconds the dilute hydrochloric acid wash liquid is shaken with the mercury.)[11] In this manner, all of the mercury and some of the calomel is kept in the bottle. Such bottles are ready for use as mercury reductors again, for it is not necessary to start with fresh mercury each time. Four reductors were used in this way for at least seventy-five times each with no more care than that described above.

The reduced solution from the mercury reductor was titrated colorimetrically with ceric sulfate as described in the preceding section.

The reduction by mercury of molybdic acid solutions containing hydrochloric acid is very rapid, the solution changing almost immediately to light reddish-brown in color, which is typical of quinquivalent molybdenum in dilute acid. Five minutes of vigorous shaking is sufficient to cause quantitative reduction, further shaking having no effect.

TABLE I

DETERMINATION OF MOLYBDENUM BY REDUCTION WITH MERCURY AND TITRATION WITH STANDARD CERIC SULFATE SOLUTION

Molybdenum taken, g.	Error in molybdenum found, g.
0.2494	−0.0002
.2494	− .0001
.2494	.0000
.1968	− .0004
.1968	− .0005
.0806	− .0001
.0806	− .0001
.0806	− .0002

Effect of Acid Concentration.—The hydrochloric acid content of the molybdate solutions at the time of reduction has a marked effect on the state to which it is reduced. When the acid concentration is below 1 *N*, molybdenum blue frequently precipitates and interferes with complete reduction. When the hydrochloric acid concentration is between 1.5 and 3.5 *N* the reduction proceeds quantitatively to the quinquivalent state. However, if the acid concentration is above 4 *N*, reduction to the trivalent state becomes evident and in 9 *N* hydrochloric acid it is easily possible to reduce molybdenum completely to the trivalent state by shaking with mercury. (In strong acid, the solution of molybdenum in the trivalent state is sal-

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[10] Foerster and Fricke, *Z. angew. Chem.*, **36**, 458 (1923).

[11] Furman and Murray, THIS JOURNAL, **58**, 429 (1936).

mon pink in color.) The trivalent molybdenum solution is not stable in air, however, and if filtered and titrated with ceric sulfate the results may be low by 1% or more, due to air oxidation. Data illustrating this effect of acid concentration were obtained by reducing equal samples of molybdate at various acidities. The samples contained 0.1593 g. of molybdenum. When the hydrochloric acid concentration was 2, 3 and 3.5 *N*, the molybdenum found was 0.1592, 0.1591 and 0.1593 g. When the acid concentration was 4 *N*, the value for molybdenum found was 2% high, and when the acidity was stepped up to 9 *N*, the molybdenum found was 1.5% low on the basis of reduction to the trivalent state.

The dependence on acid concentration of the oxidation–reduction potentials of the systems Mo^6/Mo^5, Mo^5/Mo^3, and $Hg/Hg_2Cl_2/HCl$ has been studied. Curves showing these relations are plotted in Fig. 1. The data for the molybdenum systems were taken from the work of Foerster, Fricke and Hausswald[12] and the mercury system data were taken from the work of Ellis,[13] Linhart,[14] and Randall and Young.[15] Reduction to the trivalent state should begin when the Mo^5/Mo^3 system is less than 0.17 volt below the mercury system, and reduction to the trivalent state should be complete to 1 part per 1000 when the mercury system is more than 0.17 volt below the Mo^5/Mo^3 system. From the curves as plotted, reduction to the trivalent state should begin at about 1.5 *N* hydrochloric acid and be complete at about 6.5 *N* acid. Our experience was that reduction to the trivalent state did not interfere until the acid concentration became more than 3.5 *N*. Reduction to the trivalent state at lower acidities is probable, but any trivalent molybdenum formed is very likely oxidized by air during the filtration process.

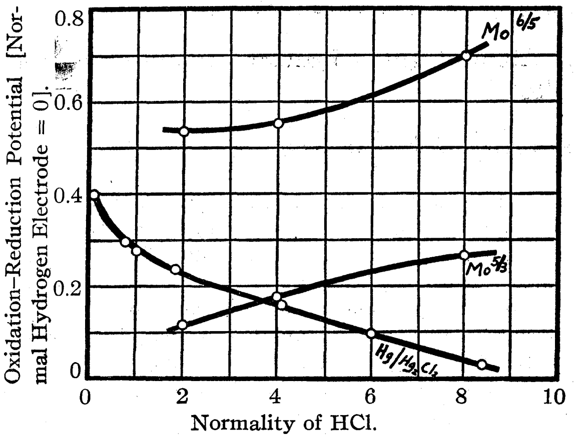

Fig. 1.—Graphs of oxidation–reduction potentials, E'_0 referred to the *N* hydrogen electrode as zero, against normality of hydrochloric acid. Equimolecular mixtures of Mo^{vi} and Mo^{v} or of Mo^{v} and Mo^{iii}, respectively, were present in the solutions.

Effect of the Wash Liquid.—It was evident at the start of this work that water is not a satisfactory wash liquid. It either does not get the molybdenum away from the mercury-calomel particles or some molybdenum is oxidized when pure water is used as a wash liquid. However, 2 *N* (1–5) hydrochloric acid was found to serve the purpose quite satisfactorily.

Determination of Molybdenum in the Presence of Certain Impurities.—Phosphate and arsenate frequently are associated with molybdenum and their effect on this procedure is of interest. It was found that the addition of either phosphate or arsenate ions in amounts up to 0.25 g. did not interfere with the determination of molybdenum samples of equal weight. There was a slight slowing of the rate of reduction with the occasional appearance of molybdenum blue in the early part of the reduction, but reduction to the quinquivalent state was complete in five minutes in every case.

In any analysis where the preliminary separation of other elements must be carried out before the molybdenum can be determined by this method, the solution will contain large amounts of ammonium salts. It was found that as much as five grams of ammonium salts as chlorides and sulfates did not interfere with the determination of 0.1 g. samples of molybdenum by this method.

Effect of Copper Salts.—Copper ions will cause a determination of molybdenum by this method to be seriously in error, even if the amount of copper present is only a fraction of a milligram. This subject of the interference of copper in the determination of molybdenum by the mercury reduction method will be considered more fully in a later paper. Suffice it to say at this time that the very slow air oxidation of quinquivalent molybdenum is apparently an autoxidation reaction and, like many reactions of this class, it is strongly catalyzed by minute amounts of copper.

Analysis of Unknowns by this Method.—Professor E. R. Caley prepared a solution of ammonium molybdate from pure molybdic oxide. The weight of molybdic oxide actually taken by Professor Caley was 6.0177 g. per 500 ml. of solution. Aliquot portions (25 ml.) of this solution were analyzed by one of us (M.) and the results calculated back to the original basis of 500 ml. of solution. The results found by the mercury reduction method were 6.0219, 6.0100, 6.0219, 6.0030 and 6.0129 g. of MoO_3 per 500 ml. of solution. The average of these values is 6.0139 g.

One of us (F.) prepared a mixture of iron and molybdenum by grinding known amounts of pure molybdic oxide, ferric oxide and potassium chloride in an agate mortar. The other (M.) then determined the percentage of molybdenum in the resulting powder by the mercury reduction method. Samples were dissolved in dilute hydrochloric acid, the iron removed by double ammonia precipitation according to the procedure of Hillebrand and Lundell,[16] and the molybdenum determined in the filtrate. The percentage of molybdenum found by the mercury reduction method was 33.20, 33.10, 33.09, 33.10—average 33.12. The percentage of molybdenum actually taken by weight in the preparation of the sample was 33.02.

Acknowledgments.—Gratitude is here expressed to Professors Leroy W. McCay and E. R.

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(12) Foerster, Fricke and Hausswald, *Z. physik. Chem.*, **146**, 81 (1929).

(13) Ellis, This Journal, **38**, 737 (1916).

(14) Linhart, *ibid.*, **39**, 2601 (1917).

(15) Randall and Young, *ibid.*, **50**, 989 (1928).

(16) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., N. Y., 1932, p. 251.

Caley for their interest and suggestions in this work.

Conclusions

1. Solutions of quinquivalent molybdenum are sufficiently stable in air at room temperature to be employed in any analytical procedure which is complete in a few hours time.

2. Molybdic acid solutions may be quantitatively reduced to the quinquivalent state by shaking with metallic mercury for five minutes if the hydrochloric acid concentration of the solution is between 2 and 3.5 *N*.

3. Quinquivalent molybdenum may be titrated with ceric sulfate at room temperature using the *o*-phenanthroline ferrous complex indicator if certain critical conditions are observed.

4. The mercury reduction method for determining molybdenum is rapid and accurate. The presence of considerable quantities of phosphate, arsenate or of ammonium salts is without effect upon the accuracy of the molybdenum determination.

PRINCETON, N. J. RECEIVED APRIL 27, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY]

The Systems Lithium Chloride–Water–Ethyl Alcohol and Lithium Bromide–Water–Ethyl Alcohol[1,2]

BY JOHN P. SIMMONS, HENRY FREIMUTH AND HARRY RUSSELL

The lithium halides show a marked tendency to dissolve in organic liquids, particularly the alcohols,[3] and to form addition products with them. The systems lithium chloride–water and lithium bromide–water have been carefully explored and the existence of four hydrates of each halide has been shown.[4] A study based on the phase rule of the ternary systems, lithium chloride–water–ethyl alcohol and lithium bromide–water–ethyl alcohol has not been attempted, the only related work being that of Santiago Pina de Rubies[5] which consisted of solubility measurements of lithium chloride in mixtures of water and ethyl alcohol and analyses of the solid phases.

The following data are the experimental results of a phase rule study of the two systems lithium chloride–water–ethyl alcohol and lithium bromide–water–ethyl alcohol.

Preparation of Materials

Anhydrous Lithium Chloride and Lithium Bromide.—Hydrated lithium chloride or bromide dried by heating under ordinary conditions suffers some hydrolysis, giving products which contain about 98.50% lithium salt and 1.50% lithium hydroxide. Drying these salts in an atmosphere of hydrogen chloride or hydrogen bromide was avoided because of the special apparatus required and because but small amounts of the salt could be made at a time. Drying by heating a mixture of lithium salt and corresponding ammonium salt did not give a product sufficiently free of lithium hydroxide. The method finally adopted consisted in drying triply recrystallized hydrated lithium chloride and bromide in an electric oven at 110°. The residue was treated with absolute alcohol whereupon the lithium salt dissolved, giving a turbid solution due to the presence of lithium hydroxide in suspension. This solution was filtered until clear and the filtrate evaporated to dryness. Analyses of the residue gave for lithium chloride 99.90% purity and for lithium bromide a purity of 99.88%. These products were considered of sufficient purity for the purpose desired and were stored in an oven at 110° until needed.

Ethyl Alcohol.—Absolute ethyl alcohol was prepared by refluxing laboratory absolute alcohol with freshly ignited lime for twelve hours. The alcohol was then distilled off, again refluxed with lime and again distilled. The product obtained gave a boiling point of 78.2°. The alcohol was stored in a bottle from which it could be siphoned and which was equipped with a phosphorus pentoxide guard tube.

Experimental Part

Ten solutions of alcohol and water were prepared, varying in composition from 7.53 to 94.43% alcohol by weight. These with pure water and absolute alcohol were used with anhydrous lithium chloride and bromide in this investigation. Complexes of known content of lithium chloride, water and alcohol and of lithium bromide, water and alcohol were placed in solubility tubes and allowed to come to equilibrium at 25.00 ± 0.02°.

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[1] The investigation of the system lithium bromide–water and ethyl alcohol was offered as partial fulfilment of the requirements for the degree of Master of Science by Mr. Henry Freimuth.

[2] The investigation of the system lithium chloride–water and ethyl alcohol was offered as partial fulfilment of the requirements for the degree of Master of Science by Mr. Harry Russell.

[3] Turner and Bissett, *J. Chem. Soc.*, **105**, 1783 (1914); J. Simon, *J. prakt. Chem.*, **20**, 371 (1879).

[4] Hüttig and Steudemann, *Z. physik. Chem.*, **126**, 105 (1927).

[5] S. Pina de Rubies, *Anal. soc. españ fís. quím.*, **11**, 422 (1912); **12**, 343 (1914).

A known weight of solution was then taken and the lithium salt determined by Mohr's volumetric method. The alcohol in the liquid phases was determined by taking a known quantity of the latter and distilling to dryness. The residue was twice moistened with water and the distillation repeated after each moistening in order to ensure as complete driving off of the alcohol as possible. The tube of the condenser was washed out several times with water, the total distillate and washings collected and made up to an exactly known volume. From density determinations the percentage of alcohol in the liquid phase was calculated. Preliminary investigation indicated that this distillation method for alcohol was accurate to about 1%. The percentage of water was obtained by difference. If the data obtained are plotted on triangular coördinate paper Figs. 1 and 2 result. A tie-line drawn through the known composition of the complex and the composition of the solution, when equilibrium is reached, will terminate at a point on the triangle which will indicate the composition of the solid phase present. As pointed out above, however, the method of analysis of the solution is liable to be in error to the extent of about 1% and thus may result in a composition of the solid phase slightly in error. The result obtained, however, will be sufficiently correct so that the exact composition of the solid phase may be determined by inspection. Knowing now the exact composition of the solid phase and of the complex, an exact method of plotting should enable us to arrive at a more accurate composition of the liquid phase than could be reached by the above method of direct analysis on the assumption that the analysis is correct with respect to lithium chloride and lithium bromide. As Hill and Ricci[6] have pointed out, this method of extrapolation is subject to error due to mechanical difficulties of exact plotting.

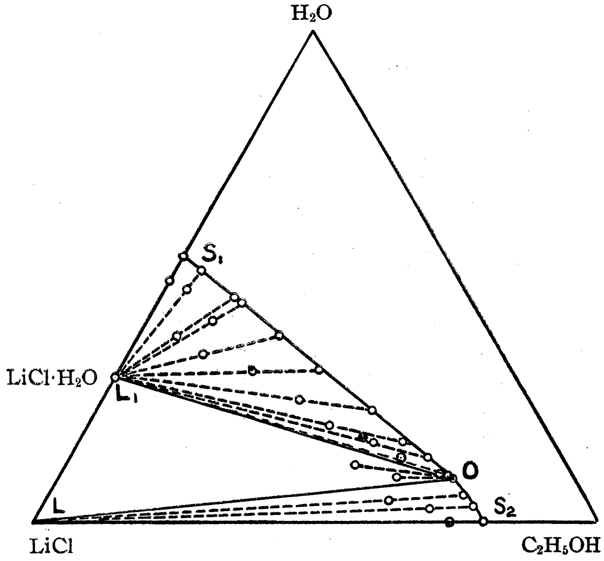

Fig. 1.

In this work the direct analysis of the liquid phase has been used to establish the composition of the solid phase and also as a check on results obtained by the Hill–Ricci method of extrapolation for the composition of the liquid phase. In the plotting of the results, Figs. 1 and 2, therefore, the composition of the solid phase has been determined by extrapolation using the known composition of the complex and the composition of the solution in equilibrium, determined by direct analysis, while the points representing the compositions of the solutions have been obtained by the Hill–Ricci method. The concentration of water and alcohol in the two transition complexes was determined from the intersection of the two curves checked by direct analyses using the distillation method for the alcohol. Tables I and II contain the data of these experiments.

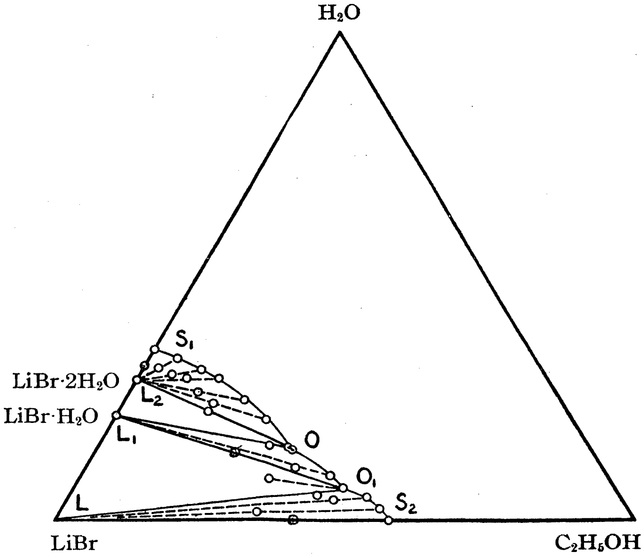

Fig. 2.

Discussion of Results

In Fig. 1, S_1OL_1 represents a divariant area which, with the fixing of the temperature at 25°, becomes univariant. Similarly the area LOS_2 is

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[6] A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4305 (1931).

TABLE I

TABULATION OF DATA FOR THE SYSTEM LITHIUM CHLORIDE–WATER–ALCOHOL AT 25°

Composition of complex		Solid phase	Composition of solution		
LiCl, %	C_2H_5OH, %		LiCl, %	Direct analysis Alcohol, %	Alcohol by Hill–Ricci method
50.01	0.00	$LiCl \cdot H_2O$	45.94	0.00	
47.94	3.92	$LiCl \cdot H_2O$	44.90	4.45	
54.87	6.99	$LiCl \cdot H_2O$	41.88	12.92	13.05
47.03	11.36	$LiCl \cdot H_2O$	40.65	14.49	
52.60	12.93	$LiCl \cdot H_2O$	37.02	24.39	23.91
45.17	23.78	$LiCl \cdot H_2O$	34.17	34.24	
41.06	34.39	$LiCl \cdot H_2O$	30.02	47.43	47.70
37.64	42.71	$LiCl \cdot H_2O$	27.19	56.42	
31.68	51.73	$LiCl \cdot H_2O$	25.43	60.24	
28.44	59.18	$LiCl \cdot H_2O$	23.09	66.77	65.93
37.41	50.23	$LiCl \cdot H_2O + LiCl$	22.41	69.04	
30.92	58.88	$LiCl \cdot H_2O + LiCl$	22.41	68.86	
35.28	60.10	LiCl	22.18	72.98	
28.27	68.56	LiCl	22.13	74.24	74.02
24.60	75.40	LiCl	20.18	79.82	

TABLE II

TABULATION OF THE DATA FOR THE SYSTEM LITHIUM BROMIDE–WATER–ETHYL ALCOHOL AT 25°

Composition of complex		Solid phase	Composition of solution		
LiBr, %	C_2H_5OH, %		LiBr, %	C_2H_5OH, % Direct analysis	Hill–Ricci method
68.21	0.00	$LiBr \cdot 2H_2O$	65.31	0.00	
66.22	2.53	$LiBr \cdot 2H_2O$	62.08	4.88	
64.43	5.50	$LiBr \cdot 2H_2O$	59.06	10.23	
62.10	8.85	$LiBr \cdot 2H_2O$	56.68	14.44	13.52
61.53	11.91	$LiBr \cdot 2H_2O$	55.24	20.09	
60.09	15.91	$LiBr \cdot 2H_2O$	52.98	26.59	25.63
62.05	15.33	$LiBr \cdot 2H_2O – LiBr \cdot H_2O$	52.07	33.05	
61.66	23.33	$LiBr \cdot H_2O$	50.79	35.43	
53.27	36.34	$LiBr \cdot H_2O$	47.63	43.28	
62.62	25.20	$LiBr \cdot H_2O$	46.70	47.57	46.59
57.89	33.85	$LiBr \cdot H_2O – LiBr$	46.63	46.53	
52.02	42.93	LiBr	46.51	47.86	
49.78	46.44	LiBr	44.13	51.66	50.72
62.59	35.91	LiBr	42.45	55.24	
56.23	43.77	LiBr	41.22	58.78	

isothermally univariant. The solid phases resulting from complexes represented by points in these areas are lithium chloride monohydrate and anhydrous lithium chloride, respectively. The compositions of the liquid phases in equilibrium with the monohydrate are the points on the line S_1O while those in equilibrium with anhydrous lithium chloride are the points on line OS_2. The area L_1OL, since it gives a system of *four phases*, exhibits one degree of freedom and with the temperature fixed becomes isothermally invariant. A complex taken in this area will give a system containing two solid phases, monohydrated lithium chloride and the anhydrous salt, and a liquid phase having the composition represented by O.

In the case of the system lithium bromide–water–ethyl alcohol three isothermally univariant areas exist, S_1OL_2, L_1OO_1 and LO_1S_2, the solid phases present at equilibrium being lithium bromide dihydrate, lithium bromide monohydrate and anhydrous lithium bromide, respectively. The area L_2OL and L_1O_1L are isothermally invariant and complexes having the compositions represented by points in these areas will give at equilibrium, in the former a mixture of lithium bromide dihydrate and monohydrate and a liquid phase having the composition represented by O, while in the latter a mixture of lithium bromide monohydrate and anhydrous lithium bromide will be in equilibrium with a liquid phase having the composition represented by O_1.

Summary

1. A convenient and satisfactory method for preparing anhydrous lithium chloride and lithium bromide has been devised.

2. A phase rule study of the systems lithium chloride–water–ethyl alcohol and lithium bromide–water–ethyl alcohol at 25° has been completed.

3. In the case of the lithium chloride system at 25°, two solid phases, the monohydrate and anhydrous salt, or a mixture of the two, exist in equilibrium with the liquid phase.

4. In the case of the lithium bromide system the dihydrate, the monohydrate, or the anhydrous salt, or a mixture of the dihydrate and monohydrate or monohydrate and anhydrous salt may be the solid phases present.

5. No alcoholates were found in either system.

NEW YORK, N. Y. RECEIVED JUNE 26, 1936

[CONTRIBUTION FROM THE DEVELOPMENT AND RESEARCH LABORATORY, PENNSYLVANIA SALT MANUFACTURING CO.]

Equilibrium in Fluoride Systems. I. Solubility of Cryolite in Aqueous Solutions of Iron and Aluminum Salts at 25°

BY FRANCIS J. FRERE

The solubility of cryolite in aqueous solutions of aluminum chloride has been long known, although it has never been generally recognized. More than thirty years ago the laboratories of the Oresunds Chemiske Fabriker, in Denmark, employed this reaction as the basis of a determination of quartz in cryolite. Although there is no record to be found in the literature of these results, it is presumed that the work was carried out either by or under the supervision of Julius Thomsen.

Recently the author had occasion to investigate the solvent action of a great many salt solutions on cryolite. It was found that cryolite was appreciably soluble in all aluminum salt solutions as well as those of iron. Qualitative tests also indicated a moderate degree of solubility in chromium and uranium salts. Except in limiting cases, this is not in general a characteristic property of sparingly soluble salts. Indeed, such abnormalities are quite generally accepted as being typical of a double salt formation.

In view of these facts, therefore, it seems quite appropriate and desirable that an investigation be made of the mechanism of the reaction involved. Obviously, the most suitable means of obtaining the necessary data is by an investigation of the ternary systems of the various salts of iron and aluminum and their respective fluorides. This phase of the problem is now in progress and some of the results will be reported in this Journal within a short time.

It is felt that these data on the solubility measurements as well as those which are to be presented on the ternary systems will be of special interest by reason of the fact that these systems have not been heretofore thoroughly investigated.

Experimental

Materials Used.—The salts used in the solubility measurements were obtained by recrystallization of analytical reagent grade chemicals. Analysis showed these materials to be of excellent quality and that the ions were present in the correct stoichiometric ratio to conform to the normal salts. Sodium, the most objectionable impurity, was in no case found to exceed 0.01%.

Natural cryolite obtained from Greenland was used in these experiments. It was very carefully selected by hand and was found to be free of impurities.

Procedure.—The bottles containing the solutions to be saturated were treated with an excess of finely-divided cryolite, stoppered with pure gum stoppers, sealed, and rotated from seventeen to twenty-one days in a thermostatically controlled bath. The bath temperature was maintained at 25 ± 0.02°. In order to establish the reliability of using stoppered bottles, several duplicate experiments were made in which the solutions were placed in sealed tubes and saturated. The results by the two methods checked within the error of the determination.

After saturation had been attained, the solutions were allowed to settle while standing in the bath and portions were drawn out of each bottle through a cotton filter, transferred to a tared weighing bottle and reweighed. The samples were washed into platinum dishes, treated with perchloric acid, and decomposed by evaporating to fumes of the latter. The solutions were then diluted to the desired volume and reserved for analysis.

Sodium was determined by precipitating with zinc uranyl acetate according to Barber and Kolthoff.[1]

Aluminum was determined by precipitating with 8-hydroxyquinoline and weighing as the oxime salt after drying at 130 to 140°.

Iron was determined by reducing in a Jones reductor and titrating with potassium permanganate.

Results and Discussion

The data on these solubility measurements are contained in Table I. Column 1 represents the salt concentration, columns 2 and 3 represent the

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[1] H. H. Barber and I. M. Kolthoff, THIS JOURNAL, **50**, 1625 (1928).

cryolite concentration on the basis of the aluminum and sodium, respectively, and column 4 represents the average cryolite concentration.

TABLE I

SOLUBILITY OF CRYOLITE IN AQUEOUS SOLUTIONS OF IRON AND ALUMINUM SALTS AT 25°

Concentrations Expressed in Moles of Salt Per 1000 Moles of Water

Salt concn., moles	Na_3AlF_6 on basis Al moles	Na_3AlF_6 on basis Na moles	Na_3AlF_6 average, moles
	2 [$Al(NO_3)_3$]		
...	0.34	0.34	0.34
0.49	.65	.65	.65
.96	1.10	1.11	1.11
3.05	2.92	2.89	2.91
5.09	4.39	4.35	4.37
7.06	5.67	5.71	5.69
10.03	7.75	7.69	7.72
12.12	9.00	9.02	9.01
14.37	10.66	10.57	10.62
19.76	14.30	14.41	14.36
	Al_2Cl_6		
0.50	0.67	0.65	0.66
1.02	1.14	1.14	1.14
3.23	2.95	2.93	2.94
5.12	4.10	4.14	4.12
7.22	5.40	5.37	5.39
9.25	6.57	6.57	6.57
12.03	7.93	7.90	7.92
15.27	9.56	9.50	9.53
20.28	11.42	11.40	11.41
	$Al_2(SO_4)_3$		
0.40	0.56	0.55	0.56
.74	.87	.87	.87
1.56	1.60	1.58	1.59
3.33	2.84	2.83	2.84
5.08	4.03	4.01	4.02
7.59	5.56	5.52	5.54
10.50	7.15	7.11	7.13
13.72	8.66	8.60	8.63
17.04	10.04	9.96	10.00
	2[$Fe(NO_3)_3$]		
0.99	0.81	0.81	0.81
3.09	1.88	1.85	1.87
4.90	2.50	2.49	2.50
6.98	3.16	3.19	3.17
9.80	3.93	3.93	3.93
14.90	5.06	4.99	5.03
19.82	6.05	5.98	6.02
24.88	6.88	6.84	6.86
	2($FeCl_3$)		
1.00	0.72	0.74	0.73
2.94	1.55	1.55	1.55
4.90	1.99	1.99	1.99
7.44	2.18	2.22	2.20
10.19	2.25	2.28	2.27
14.94	2.22	2.23	2.23
19.70	2.03	2.06	2.05
25.28	1.89	1.87	1.88
	$Fe_2(SO_4)_3$		
1.02	0.59	0.57	0.58
3.04	1.14	1.12	1.13
5.13	1.59	1.55	1.57
7.04	1.81	1.81	1.81
9.95	2.23	2.23	2.23
14.82	2.86	2.90	2.88
19.16	3.21	3.22	3.22
24.55	3.68	3.71	3.70

From the data presented, the most obvious assumption is that there is some chemical reaction taking place by which a considerable amount of some new substance is formed by combination of the ions present in the solution. In the case of the aluminum salts, the most probable explanation of the mechanism involved would seem to be one in which there is a complete exchange of ions resulting in the formation of aluminum fluoride and the sodium salt of the solvent anion, the aluminum fluoride in turn combining with the aluminum salt present to form a double salt.

This inference seems to be amply justified by the following facts. When solutions of three aluminum salts were saturated with cryolite at an elevated temperature, no reprecipitation of cryolite occurred upon cooling or even after the addition of the respective sodium salts to the point of saturation. If, on the other hand, the sodium salt was added to the solution at the start it exerted a depressing effect upon the solubility due to the action of the common ion. The rate of decrease in solubility increased quite rapidly with increasing concentration of the added salt. From the foregoing, it is clear that the reaction is not reversible and, hence, true equilibrium is not attained.

Upon plotting the solubility data, a slight irregularity in the curves will be noted which might indicate the presence of a second solid phase. An examination of the residues, however, showed them to consist only of unchanged cryolite. The most reasonable explanation for these irregularities seems to be that equilibrium is very slowly attained after the solutions have become nearly saturated.

Apparently, a similar mechanism is involved for the iron salts. The presence of a fourth ion, however, gives rise to a more complicated system and as a result may require a knowledge of the quaternary as well as the ternary system in order to establish definitely the identity of the final reaction product.

It will be noted from the data that the solubility of cryolite in the different salt solutions in all cases, excepting ferric chloride, follows in the order of the solubility of the corresponding sodium salts. Ferric chloride solutions act normally in concentrations up to 10.0 molar, at which point the solubility reaches a maximum then falls below that of the sulfate and continues to decrease with any further increase in concentration. This difference in behavior is in accord with the facts of the case and may be readily interpreted by a consideration of the ferric chloride–sodium chloride system.

It will be seen also that cryolite dissolves to a greater extent in aluminum salt solutions and that the amount dissolved is practically the same for the different iron and aluminum salts at the lower concentrations. Undoubtedly, in these dilute solutions a considerable portion of the cryolite is dissolved at the expense of the free acid resulting from the hydrolysis of the salts.

Summary

The solubility of cryolite has been determined at 25° over a wide range of concentrations in aqueous solutions of iron and aluminum chloride, nitrate and sulfate. It has been found that the solubility was greatest in the aluminum salt solutions, and that the amount dissolved by the different salts was in all cases, excepting ferric chloride, in the order of the solubility of the corresponding sodium salt.

An explanation of the mechanism of the reaction has been offered based on the formation of a double salt.

PHILADELPHIA, PENNA. RECEIVED MAY 26, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 143]

Condensations by Sodium. VII. A General Method for Stopping the Wurtz Reaction at the Intermediate Organo-Metallic Stages

BY AVERY A. MORTON AND INGENUIN HECHENBLEIKNER

Previous work[1] has revealed that alkyl sodium compounds, if formed as intermediates in the Wurtz synthesis, are stable only at low or moderate temperatures. Their great reactivity enables the final stage of reaction with more alkyl chloride to be completed easily. Such considerations suggested that a Wurtz synthesis might be stopped at this intermediate point if the reaction were carried out at low temperatures in the presence of excess sodium. Experiments have amply confirmed this conclusion. When *n*-amyl chloride was added gradually with stirring to a suspension of sodium sand in pentane or ligroin, the mixture stirred until after no more evolution of heat occurred, and the product carbonated, there was obtained both caproic and butylmalonic acids. The yield of combined acids, around 50% in many experiments, was sufficiently high to remove any suspicion that they were formed because of a concurrent reaction during carbonation. The general application of this method for obtaining organo-metallic compounds was demonstrated by runs with butyl halides (chloride, bromide and iodide), and a secondary, a tertiary and an aromatic chloride.

So far the best yield, 57% of total carboxylic acids, has been obtained with *n*-amyl chloride. Other chlorides in order of decreasing yield are *n*-hexyl chloride, chlorobenzene, *n*-butyl chloride, *t*-amyl chloride, 2-chloro-3-methylbutane and *n*-propyl chloride. Factors such as the temperature at which the reagents could be induced to react, the thermal stability of the resulting organometallic compound, and the readiness with which the product reacts with more organic chloride to complete a Wurtz synthesis, must be considered in each case. The first attempts were unsuccessful because the importance of these factors was not recognized. Subsequent experiments with amyl chloride demonstrated the possibilities under controlled conditions and the preliminary test with other halides confirmed the conclusion that the proper factors for preparation of organometallic compounds by direct action of sodium on the chloride had indeed been recognized.

An earlier discovery of an organo-metallic compound in a Wurtz synthesis has been recorded in some interesting work by Gilman and Wright,[2] who studied the action of sodium–potassium alloy on 3-iodofuran. A very small yield, 0.5%, of 3-

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[1] Morton and Hechenbleikner, THIS JOURNAL, **58**, 1024 (1936).

[2] Gilman and Wright, *ibid.*, **55**, 2893 (1933).

furoic acid was obtained. The obtention of the organo-metallic compound in that instance was ascribed to the extraordinary inertness of iodine in 3-iodofuran.

Continued evidence of the formation of a dicarboxylic acid from a monohalogen compound has been found in this work. The over-all equation for amylidene disodium used in calculating the yields of butylmalonic acid is

$$2C_5H_{11}Cl + 4Na \longrightarrow C_5H_{10}Na_2 + C_5H_{12} + 2NaCl \quad (1)$$

A possible mechanism by which amylidene disodium could be formed is by dismutation of amyl sodium as illustrated in equation (2). Opportunity was found to test this idea and adverse conclusions were drawn.

$$2C_5H_{11}Na \longrightarrow C_5H_{10}Na_2 + C_5H_{12} \quad (2)$$

In two series of experiments the intermediate sodium compounds were subjected to the action of heat, first at 60° and then at 80°. The products were carbonated and caproic and butylmalonic acids isolated. It was found that the yield of caproic acid progressively decreased with extended time at these temperatures, that a quantity of tarry acids appeared and continually increased with added severity of conditions, and that the amount of butylmalonic acid was unchanged. Amyl sodium was thus seen to be unstable thermally but amylidene disodium was not one of the primary decomposition products.

These facts permit a similar dismissal of any manner of thermal decomposition of the monosodium compound as a source of malonic acid. One such mechanism is shown in equation (3) which represents amyl sodium decomposing to sodium hydride and amylidene.

$$C_5H_{11}Na \longrightarrow NaH + C_4H_9CH< \quad (3)$$

The bivalent carbon atom would then add two atoms of sodium giving amylidene disodium. Carothers and Coffman[3] found good reasons for suggesting such a breakdown to explain their results with ethyl sodium. Our attempts to apply a parallel decomposition with amyl sodium have been without success as judged by the unchanged yield of the malonic acid. Negative tests for sodium hydride, reported in the previous paper on the action of sodium on diamyl mercury, while not conclusive by themselves, are nevertheless in full agreement with the view that equation (3) does not represent the decomposition of this compound.

The same authors have also pointed out that the hydrogen atoms in "sodium ethide" may be considered as being slightly acidic and capable of further replacement by sodium. An acidic nature of the hydrogen adjacent to sodium in amyl sodium was not revealed in our study of the feasibility of applying equation (2) to our results. It is possible, however, to derive a type of acidity from the presence of a carboxyl group and to consider that such a reactive hydrogen would be displaced by either sodium metal or the sodium in amyl sodium[4] after the manner set down in equation (4). Against this idea can be cited the fact that no increased yield of butyl-malonic acid was observed (a) when a large (over 100%) excess of sodium sand was used in the reaction; (b) when amyl sodium was formed in the presence of freshly prepared sodium caproate.

$$C_4H_9CH_2COONa \xrightarrow[NaC_5H_{11}]{Na\ or} C_4H_9CH(Na)COONa + H\ (or\ C_5H_{12}) \quad (4)$$

The observation of Bachmann and Clarke[5] that sodium acting on isoamyl bromide gave some pentadecane as well as the expected decane adds weight to the view that the disodium intermediate was formed prior to carbonation.

A reasonably safe conclusion can be drawn at this time that the malonic acids formed in the sodium condensations being reported in this series do not arise from any reaction of an intermediate alkyl sodium. Our data do not permit a differentiation between the plausible free radical-disproportionation path and the direct formation of an idene intermediate by splitting out of hydrogen chloride (Michael's mechanism).[6]

In addition to the discovery of a general method of interrupting the Wurtz synthesis, and the elimination of amyl sodium as a source of the malonic acid, a brief comment might be made on the surprising stability of amylidene disodium. A period of fourteen hours of heating at 80° left the amylidene disodium practically unaffected as contrasted with the 63% decomposition of amyl sodium under the same conditions.

Experiments

The reactions were carried out in a 3-necked 250-ml. flask provided with a mercury-sealed stirrer, dropping funnel, condenser, nitrogen inlet tube and thermometer.

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[3] Carothers and Coffman, This Journal, **51**, 588 (1929).

[4] We are grateful to a reviewer on a previous article for the suggestion of a reaction with amyl sodium.

[5] Bachmann and Clarke, This Journal, **49**, 2097 (1927).

[6] Michael, *Am. Chem. J.*, **25**, 419 (1901).

TABLE I

REACTIONS IN PENTANE

Constant factors: sodium sand, 12 g. in 50 ml. of *n*-pentane unless otherwise noted; *n*-amyl chloride, 25 ml. dissolved in 50 ml. of *n*-pentane unless otherwise noted.

No.	Addition of RX Time, min.	Addition of RX Temp., °C.	Stirred after addition Time, hrs.	Stirred after addition Temp., °C.	Caproic acid G.	Caproic acid %	Butylmalonic acid G.	Butylmalonic acid %	Total carboxylic acid, %
1	75	0–2	0.5	0–R[a]	4.9	22	2.2	13	35
2	75	0–4	13[b]	R	5.0	22.7	3.9	24	47
3	90	0	3	37–39	7.1	32	2.5	15.3	47
4	90	18–22	0.5	18–22	5.1	22.8	3.5	21.8	45
5	75[c]	36–38	.25	36–38	7.5	33.8	2.6	16.2	50
6	90[d]	36–38	.25	36–38	7.9	35.6	2.5	15.3	51

[a] Room temperature. [b] No stirring during this period. [c] Amyl chloride added undiluted with any pentane. [d] Amyl chloride added undiluted to 12 g. of sodium sand in 200 ml. of pentane.

TABLE II

EFFECT OF TEMPERATURE ON STABILITY OF INTERMEDIATE COMPOUNDS

Constant factors: sodium sand, 10 g. in 50 ml. of E. K. Co. ligroin, b. p. 90–120°; *n*-amyl chloride (E. K. Co. technical grade), 20 ml. in 50 ml. of ligroin; time required for addition of the alkyl chloride to sodium was 75 min. unless otherwise indicated; temperature 18–22°

No.	Stirred after addition Time, hrs.	Stirred after addition Temp., °C.	Caproic acid G.	Caproic acid %	Butylmalonic acid G.	Butylmalonic acid %	Total carboxylic acids, %
7	1	20	3.2	16	2.4	17	33
8	14	R	3.2	16	2.2	16	32
9	0.8	60	2.5	13	2.4	18	31
10	2	60–65	1.9	10	2.3	17	27
11	0.5	77	2.5	13	2.0	15	28
12	1	78	1.7	9	1.8	13	22
13	1	80	1.7	9	1.9	14	23
14	1	80	0.8	4	3.1	23	27
15	14	80	1.2	6	2.0	15	21
16[a]	0.3	60–62	1.3	7	9.5	7	14

[a] Ninety minutes required for addition of alkyl chloride, temperature 60–62°.

The sodium sand (from a stock quantity made by stirring 500 g. in hot kerosene) was placed in the flask with the desired solvent and the organic chloride added through the dropping funnel. Usually a little over an hour was required for addition. Stirring was continued for some period afterward, at least until no more heat was given off by the reaction. The temperature at any stage of the process was regulated by a bath or by the boiling point of the solvent. The color of the reaction mixtures usually changed from purplish-blue to green and red (on heating) during the reaction. Carbon dioxide was finally admitted (all colors disappeared) and the products separated in the same manner as described in the earlier paper.[7] Yields were calculated on the basis of the halide added. In Tables I and II (the numbering of the runs is for convenience in reference only) experiments in *n*-pentane (E. K. Co. practical grade) and in ligroin, respectively, are described. Attempts were made to isolate the products from pyrolysis of amyl sodium in experiments 9 to 15. Tarry acids insoluble in water and ligroin were found. The amount qualitatively increased with greater severity of the pyrolysis conditions. Only a poorly crystalline product

TABLE III

COMPARISON OF BUTYL IODIDE, BROMIDE AND CHLORIDE

Constant factors: alkyl chloride dissolved in 25 ml. of *n*-pentane; sodium sand in 75 ml. of same solvent; temperature 0–5° during addition of the alkyl halide; one hour required for addition of alkyl chloride except in number 18 in which the time was two hours; one hour of stirring at room temperature after addition of alkyl chloride was completed

No.	Halide	G.	Sodium, g.	Valeric acid G.	Valeric acid %	Propylmalonic acid G.	Propylmalonic acid %	Total carboxylic acids, %
17	Butyl iodide	13	50	Trace		Trace		
18	Butyl bromide	20	55	0.49	3.3	0.80	7.5	10.8
19	Butyl chloride	20	36	1.32	5.9	1.27	7.9	13.8

TABLE IV

EFFECT WITH OTHER ORGANIC CHLORIDES

Constant factors: *n*-pentane used as a solvent in all runs except in No. 21 where ligroin was employed; organic halide dissolved in 25 ml. of solvent; sodium sand (12 g. in all runs except in No. 24 where 10 g. was used) in 75 ml. of the solvent; one and one-half hours required for addition of the chloride

No.	Chloride,	ml.	Temp. during addition, °C.	Mono-acid G.	Mono-acid %	Di-acid G.	Di-acid %
20	2-Chloro-3-methylbutane	25	Room	Traces		Traces	
21	Chlorobenzene	25	[a]	5	16.8		
22	*t*-Amyl chloride	25	37–38[b]	0.15	0.7		
23	*n*-Hexyl chloride	30	37–38[c]	5.1	17.6	1.74	9.2
24	*n*-Propyl chloride	20	45–20[d]	Traces		Traces	

[a] Reaction started by addition of 1 ml. of *n*-hexyl chloride. Before carbonation the mixture was allowed to stand fourteen hours after addition was completed. [b] After addition and before carbonation the stirring was continued for one hour. [c] Stirring continued for one-half hour after addition and before carbonation. [d] Reaction started by addition of 5 ml. of *n*-hexyl chloride. The traces of acid products may be due to this starting agent. The mixture was stirred for one-half hour after addition and before carbonation.

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[7] Morton, LeFevre and Hechenbleikner, THIS JOURNAL, **58**, 754 (1936).

could be isolated from the crude mass. A titration of the acidity on the dried sample indicated that one carboxyl group per amyl residue was present. The amount was too small for further identification.

TABLE V

RESULTS WITH OTHER ALKALI METALS

Constant factors: *n*-amyl chloride (E. K. Co. tech. grade) 20 ml.; metal sand in 100 ml. of ligroin

No.	Metal	G.	Total time, hrs.	Caproic acid G.	Caproic acid %	Butylmalonic acid G.	Butylmalonic acid %
25	Potassium	19	2.5[a]	0.27	1.4	0.07	0.5
26	Lithium	4	0.7[b]	.36	1.9	.36	2.7

[a] Two hours required for addition of amyl chloride. Mixture stirred for one-half hour longer before carbonation. [b] Upon addition of the first 5 ml. of amyl chloride the temperature rose to 80°. The mixture was cooled to 35° and the remainder of the amyl chloride added at once. Stirring was continued one-half hour more before carbonation.

TABLE VI

MISCELLANEOUS EXPERIMENTS

Constant factors: sodium sand in 50 ml. of ligroin unless otherwise indicated; amyl chloride in 50 ml. of ligroin unless otherwise indicated

No.	Sodium, g.	Amyl chloride, ml.	Addition Time, min.	Addition Temp., °C.	Stirred after addition Time, min.	Stirred after addition Temp., °C.	Carbonation temp., °C.	Caproic G.	Caproic %	Butylmalonic G.	Butylmalonic %	Total carboxylic acids, %
27	20	20	75	22	60	30	25	8.5	44.2	1.6	12.5	57
28	10[a]	15	40	25	180	20	30	4.4	30	1.7	14.8	45
29[b]	10	20	45	28	..	..	..	8.1	42	1.5	11.1	53
30[c]	12	25		0	30		0[c]	7.5	31	1.3	8	39
31	20[d]	40[e]		−25	10	−25	0	10.7	27.7	0.78	2.9	31
32[f]	10[g]	20	30		60	80	30	1.5	7.5	1.2	8.8	17
33	10	20	180	22	60	22	30	6.7	34.6	1.5	10.7	45
34	10	20	23	20	30	25	30	4.6	24	1.3	9.9	34
35	10	20	[h]	20		20	20	5.1	26.6	1.8	13.8	41

[a] The sodium was first fused with 1.5 g. of mercury and then made into sand in the usual way. [b] Carbon dioxide was passed through the mixture during the addition. No oxalic acid was found among the products. [c] Pentane used as a solvent. Temperature rose to 20° during carbonation. [d] 10 ml. of solvent used. [e] 40 ml. of solvent used. Toward the end of the reaction the mass became so viscous that 50 ml. more ligroin was added. [f] *n*-Octane used as a solvent. [g] Only 30 ml. of solvent used with the sodium. [h] Half of the alkyl chloride added, and product carbonated after which the remainder was added, followed by a final carbonation.

Special attention is called to (a) the nearly complete agreement in respect to yields of reaction 7 and 8, although in the latter case the mixture stood thirteen hours before carbonation; (b) the constancy of the yields of butylmalonic acid which in 12 out of 16 runs varied between 13 and 17% in spite of wide fluctuations in time and temperature conditions to which the alkylidene disodium intermediate was subjected; (c) the surprising stability of the amylidene disodium compound which in fourteen hours' heating at 80° (run No. 15) was not appreciably decomposed; (d) the lack of thermal stability of the monosodium compound as exemplified by decreasing yield of caproic acid (to 10%) as the period of heating at 60° before carbonation was extended in reactions 9 and 10; (e) the greater thermal instability of the mono-sodium compound at the 80° level in reactions 11 to 15 where the yield of caproic acid fell to around 6%; (f) the general failure to observe any gain in butylmalonic acid in spite of a great loss of caproic acid (see reactions 9 to 15) thereby showing that the pyrolysis of sodium amyl did not lead to amylidene disodium; (g) the decidedly lower yield for both mono- and dicarboxylic acids when the temperature during addition of alkyl chloride to sodium was raised (reaction no. 16) to 62°.

In Tables III and IV the results with a number of other halides are given. The general method of separation of the mono- and the dicarboxylic acids was the same as described before.

Comparison of butyl iodide, bromide and chloride, Table III, showed that there was an increasing amount of interruption in the order named. This difference was not surprising in view of the common opinion of decreased activity of the halogen atoms in progressing from iodide to chloride. The butyl sodium formed in the initial phase can be assumed to react less readily with the least reactive halide and therefore can be isolated in larger amounts from the chloride reaction. The list in Table IV shows the results with a secondary, an aromatic and a tertiary chloride. In addition, experiments on two more primary chlorides are given. No attempt was made to discover the conditions which were best for each compound. A major difficulty was in getting the reaction started. The yield of benzoic acid was not in agreement with what might have been expected from the inactivity of the halogen atom in chlorobenzene (compare with *n*-hexyl chloride) which might suggest that an inactive halogen atom was not the only factor involved in isolation of intermediate products.

For the experiments with other alkali metals, Table V, potassium sand was prepared by shaking the metal in ligroin solution; lithium sand by stirring in hot kerosene. Potassium, the most active metal, reacted with such vigor that amyl chloride had to be added very slowly. Less than 2% of carboxylic acid was obtained. Since lithium is the least active of the alkali metals, a high yield could be expected. Lithium alkyl compounds have been shown already[8] to be isolable in benzene solution and capable of

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[8] Ziegler and Colonius, *Ann.*, **479**, 135 (1930).

being used in the same manner as the Grignard reagent. The unfortunately low yields of carboxylic acids which we obtained upon carbonation are not due therefore to any absence of the intermediate lithium alkyl but to the formation of secondary products as already shown by Gilman and Van Ess.[9] The position of the alkyl sodium appears to be unique in that it lacks the reactivity necessary to complete the Wurtz reaction under these conditions, yet does not participate in the formation of secondary products with sodium caproate.

Data for a number of miscellaneous experiments are set down in Table VI. Many of these runs were made in an effort to locate some factor which would lead to increased yields of butylmalonic acid. Special mention can be made of (a) the effect of using over 100% excess of sodium sand—reaction No. 27—which resulted in a maximum yield of 57% of combined carboxylic acids; (b) the failure to obtain an improved yield of butylmalonic acid in No. 28 from the simultaneous presence of mercury, a test inspired by the higher yields of this acid in some of the experiments reported in the previous paper on the action of sodium on diamyl mercury; (c) the failure of the simultaneous presence of carbon dioxide to increase materially the yield of combined organic acids over what was obtained when the amyl chloride was first allowed to react until long after all evidence of reaction—judged by a temperature rise—had ceased; (d) the failure to note any marked increase in the yield of malonic acid in reaction No. 35 when amyl chloride was added to sodium in the presence of freshly prepared sodium caproate in order to test the validity of equation 4; (e) the continued constancy in the yields of butylmalonic acid in runs 27, 28, 29 and 35.

Conclusions

The Wurtz reaction can be interrupted at the intermediate organo-metallic stage if the alkyl halide is added to excess sodium at low or moderate temperatures. The reaction has been studied in some detail with *n*-amyl chloride and has been tested in a preliminary way with a number of other organic halides.

In the case of *n*-amyl chloride, caproic and butylmalonic acids were obtained upon carbonation. The yield of combined acids in one instance was as high as 56%.

The formation of the malonic acid by way of the monosodium compound has been shown to be unlikely.

Amylidene disodium is thermally more stable than amyl sodium.

CAMBRIDGE, MASS. RECEIVED JUNE 12, 1936

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[9] Gilman and Van Ess, THIS JOURNAL, 55, 1258 (1933).

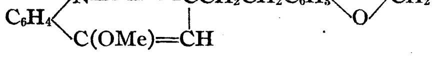
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

Researches on Quinazolines. XLIII. The Synthesis of a Quinazoline Derivative Structurally Analogous to Cusparine

BY DOMENICK PAPA[1] AND MARSTON TAYLOR BOGERT

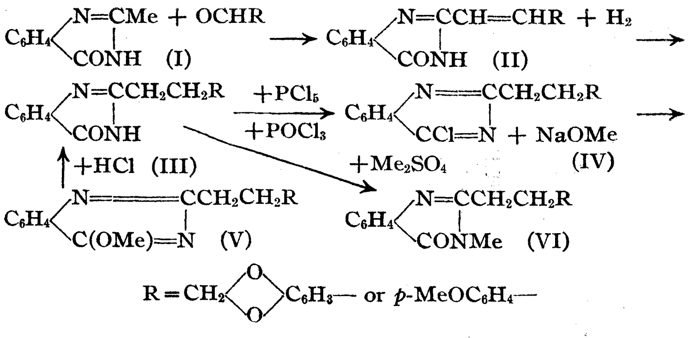
In a recent communication[2] from these Laboratories, there was described the synthesis of quinazoline derivatives akin structurally to the angostura alkaloids galipine and galipoline.[3]

The most important angostura alkaloid, however, is cusparine



The synthesis of its quinazoline analog is described in the following pages. The *p*-methoxyphenylethyl derivatives were also prepared, because they correspond, respectively to the galipoline and galipine analogs referred to above, but possess one less methoxyl group, and it seemed desirable therefore to include them in the series for pharmacological examination.

The steps involved in these syntheses were the following



Experimental

2-*p*-Methoxystyryl-4-quinazolone (II).—A mixture of 5 g. of 2-methyl-4-quinazolone (I) and 4.5 g. of *p*-anisaldehyde was heated for two hours at 170–175°. It liquefied after half an hour of heating and at the end of two hours

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[1] Fritzsche Fellow in Organic Chemistry, Columbia University, 1935–1936.

[2] Marr and Bogert, THIS JOURNAL, 57, 729 (1935).

[3] Through an unfortunate error in proofreading, this alkaloid appears in that article as "galiopine."—M. T. B.

was semi-solid. When cold, it was pulverized, boiled with 10 cc. of 96% ethyl alcohol, to remove unchanged initial materials, and crystallized twice from glacial acetic acid in the presence of Norite. The product was a pale yellow crystalline solid, m. p. 284–285° (corr.); yield 80%. For analysis, it was dried for two hours at 110°.

Anal. Calcd. for $C_{17}H_{14}O_2N_2$: C, 73.34; H, 5.05. Found: C, 73.47; H, 4.97.

2 - (3′,4′ - Methylenedioxystyryl) - 4 - quinazolone (II) was prepared from 2-methyl-4-quinazolone (I) and piperonal, as described by Bogert and Beal,[4] except that the crude product was purified as recorded above, and then appeared as a crystalline solid of very pale yellowish cast, m. p. 316–317° (corr.) with decomposition; yield 64%. Bogert and Beal reported a m. p. of 305°. Dried at 110°, it was analyzed with the following results.

Anal. Calcd. for $C_{17}H_{12}O_3N_2$: C, 69.94; H, 4.15. Found: C, 70.11; H, 4.35.

2-(beta-*p*-Anisylethyl)-4-quinazolone (III), prepared by the same process as the next compound, formed colorless lustrous crystals, m. p. 213–214° (corr.); yield 90%. For analysis, it was dried to constant weight at 110°.

Anal. Calcd. for $C_{17}H_{16}O_2N_2$: C, 72.85; H, 5.76. Found: C, 72.73; H, 5.47.

2-(beta-3′,4′-Methylenedioxyphenylethyl)-4-quinazolone (III).—The styryl compound (II) was reduced catalytically by the process used by Marr and Bogert[2] for the reduction of 2-styryl-4-quinazolone, except that the crude product was washed first with water and then with 50% ethanol. From 4 g. of the styryl derivative (II), 500 cc. of 96% ethanol, and 150 g. of 3% sodium amalgam, there was obtained 3.49 g. (85%) of a colorless crude product, m. p. 238.5° (corr.), which was recrystallized by careful dilution of its hot alcoholic solution, and then melted at 239–240° (corr.). For analysis, it was dried to constant weight at 110°.

Anal. Calcd. for $C_{17}H_{14}O_3N_2$: C, 69.38; H, 4.78. Found: C, 69.40; H, 4.77.

2-(beta-*p*-Anisylethyl)-4-chloroquinazoline (IV).—In the main, the procedure followed was similar to that used by Marr and Bogert[2] for the production of 2-phenylethyl-4-chloroquinazoline. A mixture of 2 g. of the 4-quinazolone derivative (III), 1.4 g. of phosphorus pentachloride, and 25 cc. of phosphorus oxychloride, was refluxed for ten hours. The cooled solution was poured upon cracked ice, immediately extracted with ether, the ether extract washed with dilute sodium carbonate solution, then with water, dried over calcium chloride and the ether evaporated. There was thus obtained 0.75 g. of yellow crystals, m. p. 125–128° (corr.), containing halogen.

No analysis was attempted, because the instability of the product rendered it unlikely that an analytically pure compound could be obtained.

For successful results in this preparation, the following precautions must be observed: (a) the initial quinazolone must be pure, dry, and finely pulverized; (b) the phosphorus oxychloride must be distilled just before use and collected under carefully maintained anhydrous conditions (the product used in our experiments was colorless, transparent, and boiled at 107.4–107.7° (corr.)); (c) the apparatus should be washed thoroughly with water, alcohol, and ether, and dried for twelve hours at 110°; (d) the heating period of ten hours must be continuous; (e) the temperature must not be permitted to rise above 115° for any length of time, or considerable decomposition will occur; (f) the rate of evaporation of the ether influences the physical state of the residue, for too rapid evaporation tends to leave an oil which solidifies only with difficulty.

2 - (beta - 3′,4′ - Methylenedioxyphenylethyl) - 4 - chloroquinazoline (IV), prepared like the above *p*-anisyl derivative, was obtained as an orange oil, which refused to congeal; yield 0.85 g., from 2 g. of initial quinazolone (III); qualitative test for halogen, positive.

2 - (beta - *p* - Anisylethyl) - 4 - methoxyquinazoline (V), prepared as described for the next compound, gave 0.3 g. of colorless crystals, m. p. 84.5–85.5° (corr.), from 0.75 g. of the chloro derivative (IV).

Anal. Calcd. for $C_{18}H_{18}O_2N_2$: C, 73.47; H, 6.17. Found: C, 73.41; H, 5.93.

Refluxed for thirty minutes with concentrated hydrochloric acid, a clear solution resulted, from which 2-(beta-*p*-anisylethyl)-4-quinazolone (III) was precipitated by dilution, m. p. 209–212° (corr.). Recrystallized from absolute alcohol, the m. p. was raised to 212–213°. Mixed with a sample of the anisylethyl-4-quinazolone (III) (m. p. 213–214°, corr.), synthesized as noted above, the m. p. was 212–213.5° (corr.).

2 - (beta - 3′,4′ - Methylenedioxyphenylethyl) - 4 - methoxyquinazoline (V).—To a solution of 0.85 g. of the chloro compound (IV) in 15 cc. of absolute methanol, there was added a sodium methylate solution prepared from 0.14 g. of sodium and 10 cc. of absolute methanol. After standing for twenty-four hours in a stoppered flask, the solution was filtered and the filtrate diluted. Yellow crystals (0.6 g.) separated after eighteen hours. These were digested with Norite in absolute ethanol solution, the mixture filtered hot and the filtrate diluted carefully. An emulsion formed which, after cooling overnight and heating again, separated crystals. Washed with dilute ethanol and dried in a vacuum desiccator, they melted at 67–68° (corr.).

Anal. Calcd. for $C_{18}H_{16}O_3N_2$: C, 70.10; H, 5.25. Found: C, 70.04; H, 4.86.

Hydrolyzed by concentrated hydrochloric acid, the corresponding quinazolone (III) was obtained, m. p. 239–240° (corr.). Mixed with a sample of the synthetic quinazolone (III) (m. p. 239–240°, corr.), the m. p. was 238.5–239.5° (corr.).

2-(beta-*p*-Anisylethyl)-3-methyl-4-quinazolone (VI).—The anisylethyl-4-quinazolone (III) was dissolved in sodium hydroxide solution and treated with dimethyl sulfate. The crude product was crystallized from diluted alcohol and then formed small colorless needles, m. p. 118–118.5° (corr.), which were not hydrolyzed by digestion with concentrated hydrochloric acid.

Anal. Calcd. for $C_{18}H_{18}O_2N_2$: C, 73.47; H, 6.17. Found: C, 73.81; H, 6.10.

2 - (beta - 3′,4′ - Methylenedioxyphenylethyl) - 3 - methyl-4-quinazolone (VI), prepared similarly, crystallized in long, thin needles which melted sharply at 94–94.5°

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[4] Bogert and Beal, THIS JOURNAL, **34**, 522 (1912).

(corr.), and were not hydrolyzed by digestion with concentrated hydrochloric acid.

Anal. Calcd. for $C_{18}H_{16}O_3N_2$: C, 70.10; H, 5.25. Found: C, 70.20; H, 5.17.

2,3-Dimethyl-4-quinazolone.—Incidentally this compound was also prepared from 2-methyl-4-quinazolone (I), by the same method as the two just reported above. It was obtained in thin colorless needles, m. p. 111–111.5° (corr.), which were not hydrolyzed when boiled with concentrated hydrochloric acid. Bogert and Seil[5] obtained it by the action of methylamine upon acetanthranil and gave its m. p. as 110°.

Summary

1. 2-Methyl-4-quinazolone has been condensed with *p*-anisaldehyde and with piperonal to the corresponding styryl derivatives, and the olefin bond of the latter has been saturated by catalytic hydrogenation.

2. These substituted 2-phenylethyl-4-quinazolones have been converted into the corresponding substituted 2-phenylethyl-4-chloro and 4-methoxy quinazolines, of which the 2-(beta-3′,4′-methylene dioxyphenylethyl)-4-methoxyquinazoline is the quinazoline analog of the angostura alkaloid cusparine.

3. The substituted 2-phenylethyl-3-methyl-4-quinazolones were also synthesized, to learn in what respects these N-methyl derivatives differed from their O-methyl isomers.

4. The pharmacological properties of these compounds have not yet been studied.

NEW YORK, N. Y. RECEIVED JULY 10, 1936

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[5] Bogert and Seil, THIS JOURNAL, **29**, 531 (1907).

[CONTRIBUTION FROM THE LABORATORIES OF CHEMISTRY AND PHYSICS, AMHERST COLLEGE]

A Sensitive Manostat for Low Pressures and its Application to the Adsorption of Hydrogen and Deuterium on Copper

BY THEODORE SOLLER, SEYMORE GOLDWASSER AND RALPH A. BEEBE

In the course of experiments conducted in the Amherst[1] Laboratory of Chemistry on the rates of hydrogen and deuterium adsorption on copper at gas pressures in the region of 2 mm., it became apparent that rate data were needed under conditions of constant pressure. The most sensitive manostat described in the literature is that of Huntress and Hershberg[2] who claim control of pressure to ±0.15 mm. Because this amount of variation was prohibitive for work at 1 to 2 mm. total pressure, a new automatic manostat has been developed which regulates the pressure to better than ±0.005 mm. and is applicable to all pressures. Provision has also been made for the continuous reading of the volume of gas entering the system during the course of adsorption. With the new manostatic technique it has been possible to investigate in detail the relative rates of adsorption of the two hydrogen isotopes on copper at low pressures. At 0° we have found a marked difference in the rates of adsorption of hydrogen and deuterium under identical conditions. Moreover, the temperature inversion in the ratio H_2/D_2 adsorbed has again been observed. This inversion has been found previously by Beebe *et al.*[1] and more recently has been predicted by Pease and Wheeler[3] from a statistical mechanical approach to the problem.

A. The Manostat

The general plan of the control mechanism is as follows. A slight decrease in the pressure of the system causes the mirror of the differential manometer to be tilted downward in such a way as to throw a light beam onto a photo-electric cell. Working through an amplifier, this cell actuates the solenoid which opens the mercury valve, thereby admitting a small amount of gas to the system. The admission of this gas causes a slight increase of the pressure and the valve is closed *via* the mirror, the photo-electric cell, and the solenoid, thus completing the cycle.

The Differential Manometer.—A modified form of the mercury manometer described by Johnson and Harrison[4] was used. To eliminate the rather troublesome task of fusing the platinum strip into a glass roller rod, a 1.6 mm. steel rod was substituted. The platinum strip was then easily attached by spot welding. Three leveling screws supporting the whole float and mirror mechanism made the device more readily adjustable. The whole manometer was placed in a small water thermostat, control of which was necessary to ±0.1° to prevent undue change in the volume of the mercury supporting the glass float. Because a quick response to pressure change was essential, the dead-beat feature of the manometer of Johnson and Harrison was sacrificed by using a 10-mm. tube to connect the mer-

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[1] Beebe, Low, Wildner and Goldwasser, THIS JOURNAL, **57**, 2527 (1935).

[2] Huntress and Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **5**, 145 (1933). The authors also include a complete review of the subject up to 1933.

[3] Pease and Wheeler, *ibid.*, THIS JOURNAL, **58**, 1665 (1936).

[4] Johnson and Harrison, *J. Sci. Instruments*, **6**, 305 (1929).

cury in the two arms of the instrument. This resulted in a slight surging back and forth after the admission of a gas increment but had no undesirable effect on the successful functioning of the control mechanism.

The Photo-electric Relay.—The photo-electric relay circuit is a modification of one suggested by F. H. Shepard.[5] Its advantages are the use of standard parts and operation directly from 110-volt, 60-cycle power circuit, no rectifier being necessary. The diagram of the circuit used is given in Fig. 1.

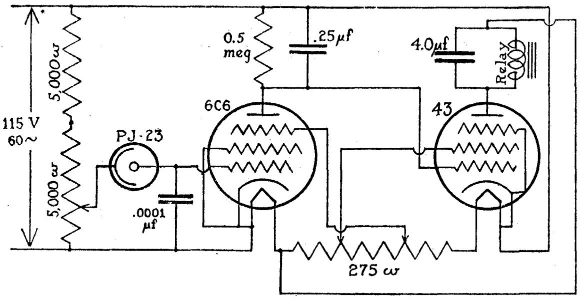

Fig. 1.—Diagram of photo-electric relay circuit.

Light from a straight-line filament lamp operating on 10 volts and 3.5 amperes falls on the mirror of the differential manometer, is reflected and brought to a focus at the PJ-23 photo-cell by a lens of one meter focal length. The sensitivity of the circuit is controlled by the position of the moving contact of the 5000 ohm potentiometer. The relay used in the output of the 43 tube is a Struthers Dunn ASBTS, operating on 15 m.a. half wave rectified current, having an A. C. core, No. 190 coil, and secondary contacts capable of carrying 10 amperes at 110 volts.

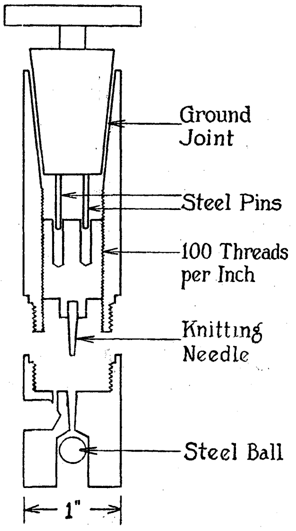

Fig. 2.—Adjustable leak.

The Adjustable Leak.—A rather large variation in rates of adsorption was anticipated during the different stages of the various processes to be studied. Moreover, it was found desirable for the effective functioning of the control mechanism that the rate of flow of the gas entering the system with the mercury valve open be of the same order of magnitude as the rate of removal of gas from the system by adsorption. The adjustable steel leak shown in Fig. 2 has met this requirement very satisfactorily. Because of the rigid construction of the glass apparatus, it was necessary that the leak be designed in such a way that neither the inlet nor the outlet glass tube should be moved during adjustment of the leak. For convenience in construction, the leak was made in two parts which fitted together at the joint J. This joint, which was in a fixed position while in use, was made vacuum tight with picene cement.

Gas Buret.—The gas buret, operated under reduced pressure for increased sensitivity, is maintained at constant pressure by an electrolysis device (see Fig. 3) built on the same principle as that of Taylor and Strother.[6] When the mercury touches the platinum tipped tungsten contact C, a 0.25 ampere current is allowed to flow between C and D; this current, acting through a simple relay, closes a switch which permits a 3 ampere current to flow through the solution of the electrolytic cell between the electrodes E and F. This relay system reduced difficulties from sparking at the contact C. A specially designed iron plate float with a platinum center helps to eliminate trouble from clinging of the mercury to the contact C, thus giving closer control of the pressure in the gas buret. The quantity of gas leaving the buret over any time interval is a linear function of the change in height of the mercury column. For the buret tube used, a change in height of 1 mm. represented 0.0132 cc. of gas at standard conditions when the buret pressure was 10 cm.

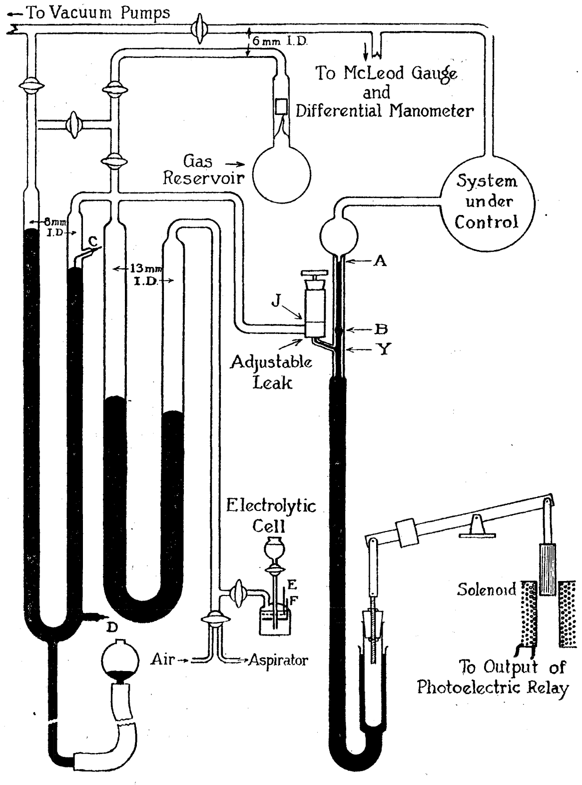

Fig. 3.

The Mercury Valve.—The mercury valve is so arranged that in its closed position the difference in height in mm. between the top of the mercury column A, Fig. 3, and the top of the ball valve in the metal adjustable leak slightly exceeds the gas pressure in mm. in the gas buret. This prevents any passage of gas when the mercury valve is closed. In the open position of the mercury valve, the mercury column stands, of course, slightly below the junc-

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(5) F. H. Shepard, *Electronics*, **8**, 304 (1935).

(6) Taylor and Strother, THIS JOURNAL, **56**, 586 (1934).

tion Y. The vertical glass section just above the Y junction is of 3 mm. inside diameter to eliminate appreciable expansion or compression of the gas in the system under control because of changes in volume of the system during the opening or closing of the mercury valve. A small enlargement, B, in the bore of the tube serves to prevent trapping of a short mercury column above the incoming gas increment. It was found that the amount of each increment could conveniently be made as small as 0.008 cc. (at standard conditions).

The successful operation of the apparatus is illustrated in Fig. 4. Volumes of gas delivered from the buret to the system under control are plotted against time. In obtaining the data for curve 2, the system to be controlled was initially at 1.003 mm. pressure. Gas was allowed to leak out of the system through a very narrow glass capillary tube (not shown in Fig. 3) directly to the mercury diffusion pump; gas then entered the system through the mercury valve at a rate sufficient to maintain the pressure constant to ±0.005 mm. as was shown on a McLeod gage. The straight line obtained in curve 2 under these conditions is evidence that all parts of the apparatus were functioning properly. For curve 1, the gas leaked out through a still finer capillary at first, but at point A the path of the leak was changed to the coarser capillary used for curve 2. For curve 3, the gas was allowed to leak out of the system, the pressure in which was 1.325 mm. at the start, into an evacuated bulb (not shown in Fig. 3). Because the rate of leak out of the system decreased with time as the pressure in the initially evacuated bulb was built up, a corresponding decrease was obtained in the rate of leak into the system as is shown in Fig. 4. For adsorption measurements, the tube containing the adsorbent would correspond to the bulb and capillary attachment used for curve 3.

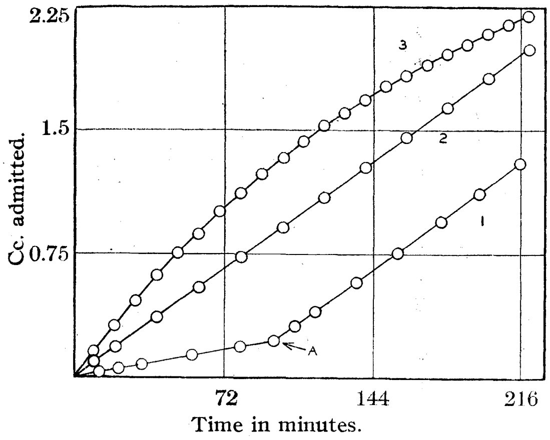

Fig. 4.

Owing to its differential principle, the manometer and consequently the manostat should operate satisfactorily at all pressures up to 760 mm. Obviously the percentage of variation in the pressure would be much less at higher pressures. Moreover, by drawing gas out of the system under control through the adjustable metal leak and mercury valve into an evacuated system, the manostat should be equally adaptable to control in a system in which gas is slowly being evolved or admitted from outside.

B. Adsorption Experiments

Apparatus.—The apparatus was that referred to and described above. All the measurements were made at 2.63 ± 0.005 mm. pressure.

Materials.—The copper powder supplied through the courtesy of the General Metals Powder Company was prepared in the same way as copper 3 described in the earlier work;[1] it came from a different batch, however. The copper was outgassed for fourteen to sixteen hours at 170° before each run.

The deuterium gas containing less than 0.5% of hydrogen was received from the Princeton Laboratory of Chemistry in October, 1935.

The sources of the hydrogen and helium have been described previously.[1]

Experimental Results

The relative rates of adsorption of hydrogen and deuterium at 0° are shown in Fig. 5. For example, the average rates from 0.20 cc. to 0.50 cc. absorbed bear the ratio: $H_2/D_2 = 5.5$. The rates which were investigated at the higher temperatures were too rapid to make the H_2/D_2 ratio significant.

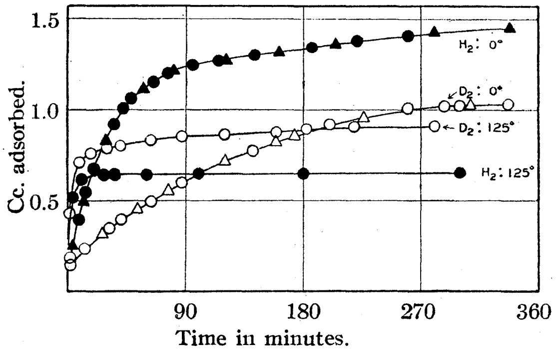

Fig. 5.—Adsorption of hydrogen and deuterium on 109 g. of copper powder.

The temperature inversion in the amounts of hydrogen and deuterium adsorbed is also apparent in Fig. 5, hydrogen being adsorbed in greater amount at 0° but in lesser quantity than deuterium at 125°. We estimate from these experiments at 0 and 125° together with experiments at 100° not shown, that the inversion temperature for this sample of copper was approximately 95°. This is to be compared with 60° previously observed on another copper sample.

The order of experiments was: H_2 at 0°, H_2 at 0°, H_2 at 100°, D_2 at 0°, D_2 at 100°, H_2 at 100°, D_2 at 125°, H_2 at 125°, D_2 at 0°, H_2 at 0°. In Fig. 5, points for 0° represented by circles are plotted from data taken at the beginning of the series, and those represented by triangles at the end of the series of rate measurements. The reproducibility of the data at 0° indicates the stability of the copper surface as well as the dependability of the manostatic technique throughout the whole series of measurements.

Discussion

The large difference in the rates of adsorption which we have observed appears to be in disagreement with the recent work of Melville and Rideal,[7] who have investigated the adsorption of hydrogen and of a 70% deuterium to 30% hydrogen mixture on copper at low pressures over the temperature range 71 to 171° and have found no difference in rates in the lower part of the temperature interval. The fact that we have found a threefold difference in rates for the two isotopes makes it seem probable that the results obtained by Melville and Rideal would have been different if they had used pure deuterium although the apparent discrepancy between their results and ours may conceivably be attributed to a difference in the nature of the copper surfaces studied.

Moreover, Melville and Rideal have not reported the temperature inversion of H_2/D_2 adsorbed which has been found in the Amherst laboratory by two different experimental methods. It seems probable that their failure to observe this phenomenon is due to the limited time interval over which the process was studied. For instance, referring to Fig. 3, p. 85, of their paper it would appear that the rate curve at 137° for the 70% deuterium mixture would actually cross the hydrogen curve, if extrapolated, instead of bending downward as shown. This would mean that although the rate for hydrogen was greater, more deuterium would be adsorbed at equilibrium at the higher temperatures.

Using the value 5.5 as the H_2/D_2 ratio of the average rates of adsorption on copper from the second to the forty-second minute at 0°, it is possible to show that the difference in activation energies is 0.75 kcal., making due allowance for the $\sqrt{2}$ collision factor. From this it may be inferred that the difference in zero point energies of hydrogen and deuterium in the activated state is 1.05 kcal. This result, which indicates that not all the zero point energy is contributed to the energy pool in the activating collision, is in accordance with the data of other investigators[7] (p. 77) for several homogeneous reactions.

The work of Pace and Taylor[8] as well as that of Kohlschütter[9] indicates that the rates of adsorption of hydrogen and deuterium on chromic oxide are identical at atmospheric pressure. Because our results make it clear that there is a marked difference in the rates for the two isotopes on copper at low pressures, it seems apparent that the adsorption of the two gases should be studied on both the adsorbents mentioned over a wide range of pressures. This series of measurements for copper adsorbent is now being undertaken making use of the constant pressure technique.

Our thanks are due to the Committee on Grants-in-Aid of the National Research Council for supplying funds for technical assistance in this work.

Summary

1. A device is described for the control of gas pressures to ±0.005 mm. and its applicability to the measurement of adsorption rates at low pressures is demonstrated.

2. At 0° and 2.63 mm. the relative rates of adsorption of hydrogen and deuterium on copper bear the ratio 3.35 to 1; and the difference in activation energies of adsorption for the two isotopes on copper at 0° is 0.48 kcal.

3. The temperature inversion in the ratio of adsorbabilities of hydrogen and deuterium on copper, which had been observed previously, has been confirmed using the new manostatic technique.

AMHERST, MASS. RECEIVED JUNE 30, 1936

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[7] Melville and Rideal, *Proc. Roy. Soc.* (London), **A153**, 89 (1935).

[8] Pace and Taylor, *J. Chem. Phys.*, **2**, 578 (1934).

[9] Kohlschütter, *Z. physik. Chem.*, **A170**, 300 (1934).

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Photochemical Studies. XXIV. The Photochemical Chlorination of the Dichlorobenzenes

BY CHARLES F. FISK AND W. ALBERT NOYES, JR.

The photochemical chlorination of benzene and of its chlorine substitution products has been the subject of several previous investigations.[1] In the gas phase, the initial reaction proceeds by short chains and results largely in the addition of chlorine to the aromatic nucleus. Products soon condense on the walls and most of the reaction after the initial stages must take place in the solid or liquid phase. With prolonged photochemical chlorination both benzene and chlorobenzene give eventually C_6Cl_{12}.

The present study was undertaken to compare the rates of addition of chlorine to *o*-, *m*- and *p*-dichlorobenzene and to investigate particularly the mechanism of the latter by measuring the rate of pressure decrease as a function of several different variables. The extent of the chlorination and a value for the quantum yield have also been obtained. An explanation of the data is given.

I. Experimental

The preparation of the chlorine was similar to that previously used.[1c] The dichlorobenzenes were all C. P. products from the Eastman Kodak Company. The *p*-dichlorobenzene was subjected to several fractional crystallizations from its own liquid. The fraction chosen melted sharply at 52.2–52.3° (corr.). Finally this 1-g. sample was fractionally distilled in vacuum and stored behind a mercury trap so that it was not exposed to the air once it had been freed from volatile substances by evacuation. Somewhat less care was taken with the *o*- and *m*-dichlorobenzenes since they were investigated much less completely than the para compound. They were both fractionally distilled, the middle fraction being treated by vacuum distillation before use.

All other chemicals were of standard C. P. quality.

The reaction vessel was a cylindrical fused quartz cell attached to the main vacuum line, pressure gages, etc., by a quartz to Pyrex graded seal. The vessel was held in a fixed clamp on an optical bench so that its position could be duplicated.

The technique of filling the reaction vessels has already been described.[1] All pressure measurements were made with an all glass gage of the Bourdon type. For determining the rate of pressure change with time it became necessary to measure pressure changes of about 0.04 mm. with an accuracy of about 5% at a total pressure of around 40 mm. For this purpose the Bourdon gage was modified by making the primary pointer operate a lever swung on a glass axle and bearing to give a magnification of fifteen to thirty times that obtained with the unmodified gage. With good luck a sensitivity of 0.001 mm. pressure per 0.01 mm. motion (as measured by a filar micrometer) could be obtained. This gage was calibrated and used as a direct deflection instrument for rate measurements. Although the experiments were carried out at room temperature, this was sufficiently constant during a run so that when the gage was balanced at 40 mm. pressure the needle position was constant in time, since small temperature variations operated nearly equally on both sides of the gage. This modified gage was used in the study of the dependence of rate on light intensity. For other experiments the ordinary gage was used.

For measuring the outside pressure used to balance the gages when they served as null point instruments a dibutyl phthalate manometer was employed.

The light source was a water cooled capillary mercury arc similar to that described by Forbes and Harrison.[2] It was operated at atmospheric pressure on 35 volts and 5 amperes. The light was filtered by 3 mm. of greenish window glass plus 3 mm. or more of number 986 red purple Corex. A number 586 violet ultra filter was used for low intensities.[3] From the intensity distribution in the arc, the transmissions of the various glasses and the absorption coefficients of chlorine it is possible to show that approximately 97% of the radiation absorbed by the chlorine in these experiments was in the group of lines around 3660 Å.

Although parallel light is to be desired in experiments involving chain reactions, it was necessary to use a focused beam in order to obtain the desired intensity. However, a simple calculation showed that the effect due to divergence in these experiments is negligible. The arc lamp was clamped in such a way that its position was reproducible. The lens was mounted on the optical bench so that an image of the arc was produced in the center of the reaction vessel without any part of the beam hitting the walls. The light intensity was varied by changing the number of filters. The shape of the light beam always remained the same. Light intensities were measured by means of a photoelectric cell which could be placed in reproducible positions either in front or in back of the reaction vessel.

The *p*-dichlorobenzene was first admitted to the desired pressure, controlled by the temperature of the supply bulb, and the reaction vessel sealed off. The chlorine was then admitted by breaking a capillary magnetically. The ingoing chlorine undoubtedly concentrated the *p*-dichlorobenzene slightly in the reaction vessel, but this effect was minimized as much as possible by the geometry of the system. An hour was always permitted to elapse after

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[1] (a) Lane and Noyes, THIS JOURNAL, **54**, 161 (1932); (b) Smith, Noyes and Hart, *ibid.*, **55**, 4444 (1933); (c) Hart and Noyes, *ibid.*, **56**, 1306 (1934). These articles contain references to earlier work.

[2] Forbes and Harrison, *ibid.*, **47**, 2449 (1925).

[3] The authors wish to express their appreciation to the Corning Glass Co. for furnishing these filters.

filling the cell for the attainment of equilibrium of mixing. The total pressure was measured and the chlorine pressure obtained by difference.

The arc lamp was started and a Wratten green filter interposed to prevent reaction. The ratio of intensity in front to that in back as determined by the photo-cell was used as a check on the optical system. The color filters to be used during the run were then placed in position and the zero deflection obtained by interposing a Wratten number 2 filter which cuts off quite sharply at 4000 Å.

The pressure was always found to remain constant for an hour before the actual run was started. After a definite time of irradiation, during which the variations in intensity were obtained by measurements behind the cell, a shutter was interposed and upon moving the photocell to the front of the reaction vessel the incident intensity was again noted. The pressure stayed constant, except for the Budde effect, after the light was cut off. This procedure will be called Technique I.

The magnitude of the quantum yield was obtained by comparing intensities as measured with the photo-cell with the decomposition produced in a uranyl sulfate–oxalic acid actinometer.[4] Corrections were applied for absorption and reflection by the windows, but a high accuracy for the absolute values of the quantum yields is not claimed.

Some early runs were made in all Pyrex reaction vessels made by sealing optically plane windows on the necks of Erlenmeyer flasks. Two identical cells, one containing the actinometer solution, were operated on opposite sides of the mercury arc in a thermostat. Color filters similar to those previously mentioned were used and pressure measurements were made in the manner already described. The over-all intensity was about one hundred times that used in the other technique. This less accurate method will be referred to as Technique II.

Since the vapor pressures of the *o*-, *m*- and *p*-dichlorobenzenes are low (approximately 1.05, 1.35 and 0.64 mm. at 20°, respectively), the rate measurements were much more difficult of execution than those for benzene and chlorobenzene. The total pressure change (assuming negligible vapor pressures for the addition products) is four times the initial pressure of the dichlorobenzene in a given run. The smoothness of the total pressure–time curves indicated definitely that this assumption is valid.

II. Results

(a) The Vapor Pressures of the Dichlorobenzenes.—In order to obtain the effect of pressure of dichlorobenzene on the reaction rate, it was necessary to measure the vapor pressures of the three substances at a series of temperatures. This was accomplished by the use of the pressure gages described in the previous section and while a high order of accuracy was not obtained the results were accurate enough for the purpose at hand. Since these vapor pressures do not seem to be given in the literature they are presented (interpolated to even temperatures) in Table I.

TABLE I

VAPOR PRESSURES OF THE DICHLOROBENZENES

Temp., °C.	Dichlorobenzene vapor pressure, mm. *p*-(solid)	*m*-(liquid)	*o*-(liquid)
0	0.07	0.30	0.25
5	.15	.47	.38
10	.25	.68	.55
15	.40	.96	.76
20	.64	1.35	1.05
24	.90	1.75	1.35

(b) The Dark Reaction.—The dark reaction had been found to be appreciable in the case of benzene and small, although negligible compared to the photochemical rate, in the case of chlorobenzene. Several bulbs were prepared containing chlorine at a pressure of 40 mm. and *p*-dichlorobenzene at a pressure of 0.7 mm. At various intervals over a period of months the chlorine was determined by standard procedure.[1] The results showed no disappearance of chlorine. Similarly no pressure decrease was observed due to dark reaction over periods of several days in the apparatus used for photolysis.

(c) The Budde Effect.—A Budde effect was always observed when the reaction mixture was irradiated. That this was due to the transformation of radiant energy into thermal energy was demonstrated by the fact that it was proportional to the light intensity but independent of the pressure of *p*-dichlorobenzene. The effects were of the order of hundredths of a millimeter.

(d) Effect of Impurities, etc.—The following seemed to have no influence on the results: (1) air or oxygen at pressures below 0.5 mm.; (2) mercury or mercury chlorides in small amounts (due to the presence of mercury vapor before the admission of the chlorine); (3) quite large variations in the treatment of the reaction vessel by flaming, baking out, etc. There may possibly be some effect due to the condition of the walls, but no definite statement in this connection is possible.

Some chlorine compounds of silicon may have been formed at the moment the reaction vessel was sealed off from the chlorine supply bulb. However, attempts to exaggerate this effect by longer heating, etc., produced no noticeable change in the results. There still remains the possibility that chlorine atoms may react with the walls to produce silicon compounds which would act as inhibitors.[5] However, this effect must have been reproducible from run to run if it exists at all.

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[4] Leighton and Forbes, THIS JOURNAL, **52**, 3138 (1930).

[5] *Cf.* Bodenstein and Unger, *Z. physik. Chem.*, **11B**, 253 (1931); Schumacher and Steiger, *ibid.*, **7B**, 369 (1930).

(e) The Magnitude of the Absolute Quantum Yield.—By comparison of the uranyl sulfate–oxalic acid actinometer with the photoelectric cell it was found that 1 cm. deflection was equivalent to 5.9 × 10^{14} quanta per second. If the initial reaction leading to pressure change is the addition of one molecule of chlorine to one molecule of *p*-dichlorobenzene (see later discussion), then one-half of the initial rate of pressure change is equal to the rate of disappearance of chlorine by the addition reaction. In one run (number 13a) the following data were obtained: chlorine pressure, 31.2 mm.; *p*-dichlorobenzene pressure, 0.64 mm.; intensity, 7.45 cm. deflection; window transmission, 0.85; fraction of radiation absorbed by the chlorine, 0.441; volume of system, 45 cc.; quanta absorbed per sec., 1.65 × 10^{15}; molecules of Cl_2 disappearing per second, 6.44 × 10^{14}; quantum yield, 0.39.

TABLE II

ADDITION OF CHLORINE TO *p*-DICHLOROBENZENE

(Run 11)

(Press. *p*-$C_6H_4Cl_2$: 0.64 mm.; press. Cl_2, 32.6 mm.)

Time, min., t	Pressure decrease, mm. ΔP_t	Fraction final pressure change, $\Delta P_t/\Delta P_\infty$	Intensity behind cell (arbitrary units), D_{b_t}	$(D_{b_t}/D_{b_0})/(D_{f_0}/D_{f_t})$	$(dP/dt)/(dP/dt)_0$ (corr. to const. D)
0	0				
0.5	0.047	0.020	4.10	1.00	(1.00)
1	.093	.041	3.70	0.95	
2	.174	.076	3.60	.94	0.98
3	.254	.111	3.45	.92	
5	.428	.188	3.46	.92	.95
6	.506	.222	3.60	.94	
7	.580	.255	3.70	.95	.88
8	.658	.289	3.35	.91	
9	.729	.320	3.35	.90	.85
10	.800	.351	3.70	.95	.81
12	.937	.412	3.50	.92	.80
13	1.005	.441	3.40	.91	
14	1.068	.469	3.40	.91	.77
15	1.122	.493	3.35	.91	
16	1.191	.523	3.40	.91	
17	1.251	.551	3.25	.89	.75
19	1.368	.601	3.20	.88	.70
21	1.478	.649	3.15	.88	.67
23	1.577	.692	3.15	.88	.61
25	1.667	.732	3.20	.88	.55
32	1.925	.847	3.00	.86	.47
36	2.027	.893	2.70	.81	.35
41	2.113	.930	2.62	.80	.22
46	2.178	.957	2.61	.80	.17
52	2.200	.972	2.60	.80	.07
∞	2.265	(1.000)	2.30	.75	(0.00)

(D_f is the intensity in front of the cell in arbitrary units.) The final pressure change is not exactly four times the pressure of the *p*-dichlorobenzene because some of the tubing was not included in the reaction zone and diffusion was slow enough to prevent all of the substance initially present from reacting. The difference is quite closely accounted for on this basis.

This value of the quantum yield may not be compared directly with values for benzene and chlorobenzene which were obtained at higher pressures. Rough estimates indicate that the value for *p*-dichlorobenzene is lower if anything than for the other two substances under comparable conditions.

(f) The Form of the Total Pressure–Time Curve.—In all some seventy different runs were made and it would be useless to present the data in detail. Table II shows the data obtained for one typical run with Technique I.

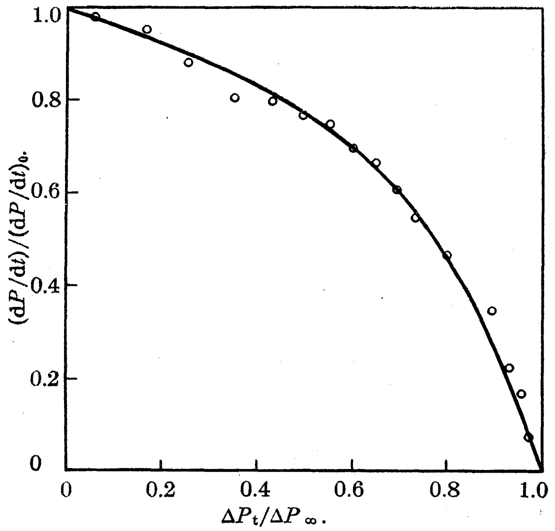

Fig. 1.—Behavior of rate at low light intensity.

Figure 1 shows a plot of $(dP/dt/(dP/dt)_0)$ against $\Delta P/\Delta P_\infty$ for the data in Table II (run 11). Figure 2 shows a similar plot for a run at very high light intensity using Technique II. The fact that the plot is curved at low light intensities would seem to signify that a steady state is not reached as regards all of the chemically stable intermediate addition products. At high intensities such a steady state seems to be reached. Little can be said concerning the mechanism of the reaction after the early stages because a mist is produced which settles out on the walls and a large fraction of the reaction must occur at the interface between the liquid or solid and the gas phase.

In benzene and chlorobenzene the amount of substitution occurring during the early stages of the reaction was small.[1] It was impossible to obtain an adequate proof of this point for *p*-dichlorobenzene due to the small amount of it which could be obtained in the vapor phase. However, the results indicated that this substance did behave in much the same way as the other two. It is assumed, therefore, in treating the rate data that the main initial reaction is one of addition. The next problem is to study the rate of the initial reaction as a function of the different variables using total pressure change as a measure of reaction rate.

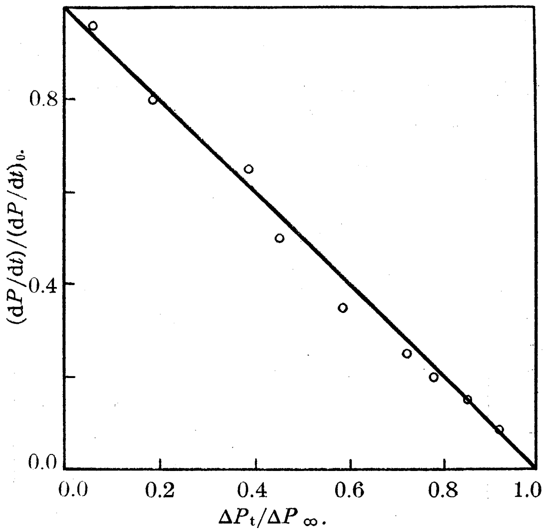

Fig. 2.—Behavior of rate at high light intensity.

(g) The Effect of Light Intensity on the Rate.—Table III presents data showing the effect of light intensity on the rate for the runs made at fairly low light intensities. It will be noted, however, that the intensity has been varied by a factor of nearly fifty. In the sixth column the intensity (expressed in cm. deflection) is multiplied by the fraction absorbed by the chlorine and in the seventh column the rate of pressure change in mm./min. is divided by the corresponding figure in column six. The values in the seventh column are reasonably constant, indicating that within experimental error the rate of pressure change is proportional to the light intensity when the intensity is fairly low.

In ascertaining whether the rate is proportional to a particular power of the light intensity for chain reactions, the number of quanta absorbed per cc. per second is the really important quantity. Thus variations in intensity from one part of the beam to another, the geometry of the beam and the volume of the reaction vessel must all be taken into account in making comparisons. As pointed out above the runs at very high light intensity were made with a different technique from those at low intensity and hence a direct comparison between the two sets of data is difficult. In Table IV the data obtained at high intensities are presented. The figure of 0.33 cc. of 0.1 *N* potassium permanganate per minute for the average intensity of the first group of runs corresponds to about ten times the highest number of quanta absorbed per cc. per second in Table III. It is seen that over the data in both tables the number of quanta absorbed per cc. per second has been varied by a factor of nearly 500.

TABLE III

EFFECT OF VARIATION IN INTENSITY AT LOW LIGHT INTENSITIES ON THE RATE OF ADDITION OF CHLORINE TO *p*-DICHLOROBENZENE

(Pressure *p*-dichlorobenzene, 0.64 mm. Volume, 45 cc.)

Run	$(dP/dt)_0$ mm./min. × 10^2	Intensity in front (cm. deflection) D_f	Chlorine pressure	Fraction absorbed, F_a	I_a ($= F_a \times D_f$)	$\frac{(dP/dt)_0}{I_a} \times 10^2$
11	8.66	10.20	32.6	0.455	4.65	1.86
13a	5.27	6.34	31.2	.441	2.80	1.88
13b	0.84	1.04			0.46	1.83
13c	2.64	2.79			1.23	2.14
13d	4.93	5.89			2.60	1.89
14	3.13	3.56	32.5	.454	1.62	1.93
17	12.22	12.50	44.2	.562	7.03	1.74
18a	11.18	11.50	43.8	.558	6.42	1.74
18b	3.75	3.92			2.19	1.71
19a	9.06	8.97	45.4	.573	5.14	1.76
19b	4.65	4.58			2.63	1.77
19c	1.09	1.06			0.61	1.78
19d	0.32	0.33			.19	1.68

(D_f is already corrected for window transmission.)

TABLE IV

EFFECT OF VARIATION IN INTENSITY AT HIGH INTENSITIES ON THE RATE OF ADDITION OF CHLORINE TO *p*-DICHLOROBENZENE

(Calculated to pressure of *p*-dichlorobenzene = 1 mm.)

Run no.	$(dP/dt)_0$ mm./min.	I_a (cc. 0.1 *N* $KMnO_4$ per min.)	$\frac{(dP/dt)_0}{I_a}$	$\frac{(dP/dt)_0}{I_a^{1/2}}$	$\frac{(dP/dt)_0}{I_a^{.65}}$
o-4	1.10	0.37	3.0	1.8	2.1
o-5	0.89	.28	3.2	1.7	2.0
o-28	1.20	.39	3.1	1.9	2.2
o-31	1.18	.28	4.2	2.2	2.7
Av.	1.09	.33	3.3	1.9	2.24
o-29	0.57	.09	6.3	1.9	2.7
o-30	.43	.11	3.9	1.3	1.8
o-32	.39	.06	6.5	1.6	2.4
o-33	.47	.08	5.9	1.7	2.4
Av.	.465	.085	5.5	1.6	2.26

It is seen that the proportionality to light intensity which is found within experimental error at low light intensities cannot be extrapolated to very high intensities. This will be taken up in the Discussion of Results. The quantum yield for the first four runs in Table IV averages about 0.08, while for the second group of runs it is 0.14.

(h) The Effect of Pressure of *p*-Dichlorobenzene on the Rate.—The effect of *p*-dichlorobenzene pressure on the rate was determined with runs made at intensities similar to those in Table III. The technique was Technique I previously described. Table V presents the results.

TABLE V

EFFECT OF *p*-DICHLOROBENZENE PRESSURE ON RATE

Run	$(dP/dt)_0$ mm./min. $\times 10^2$	Chlorine pressure, mm., P_1	p-$C_6H_4Cl_2$ pressure, mm., P_2	I_a	$\frac{(dP/dt)_0}{I_a}$	$\frac{(dPtd/)_0}{I_a \times P_2)}$
22	2.27	37.1	0.64	1.56	1.46	2.3
23	5.06	37.3	.30	5.98	0.85	2.8
24	6.89	36.4	.47	5.68	1.21	2.6
26	2.62	34.1	.22	4.39	0.60	2.7
27	4.84	28.1	.64	3.18	1.52	2.4
29	7.03	29.9	.91	3.14	2.24	2.5

The results in Table V indicate quite clearly that the rate is proportional to the pressure of *p*-dichlorobenzene within experimental error.

(i) Dependence of Rate on Chlorine Pressure.—Here again the same technique was used as for the runs in Table III. Table VI presents the results.

TABLE VI

EFFECT OF CHLORINE PRESSURE ON RATE

Pressure p-$C_6H_4Cl_2$, 0.64 mm.

Run	$(dP/dt)_0$ mm./min. $\times 10^2$	D_f deflection, cm.	%, absorbed	I_a	Chlorine pressure, mm.	$\frac{(dP/dt)_0}{I_a}$
27	4.84	13.9	22.9	3.18	28.1	1.52
30	3.06	12.9	13.9	1.80	16.1	1.70
31	1.16	11.5	6.5	0.75	7.1	1.55
32	3.51	10.0	23.9	2.39	29.2	1.47
11[a]	8.66	10.2	45.5	4.65	32.6	1.86
19[a]	9.06	8.97	57.3	5.14	45.4	1.76

[a] Runs 11 and 19 were made in a different quartz cell from the others, the length being twice as great as for the other runs.

(j) The Extents of Addition and Substitution.—Benzene and chlorobenzene could be chlorinated eventually to the cyclic compound C_6Cl_{12}. Chlorination of the dichlorobenzenes to the same final product should lead to the disappearance of 7 molecules of chlorine per molecule of dichlorobenzene present at the beginning of a run. That this seems to be the case is indicated by the data in Table VII. If the final product has a negligible vapor pressure, the total pressure should change by an amount equal to four times the initial pressure of *p*-dichlorobenzene. Final chlorine pressures were determined by titration.

TABLE VII

EXTENTS OF SUBSTITUTION AND ADDITION (*p*-DICHLOROBENZENE)

Run	p-$C_6H_4Cl_2$ pressure, mm., P_1	Change in total pressure, ΔP	$\Delta P/P_1$	Change in chlorine pressure, ΔP_2	$\Delta P_2/P_1$
o-26	0.98	2.89	2.95	4.87	5.0
o-25	.79	1.82	2.3	2.97	3.8
o-24	.99	3.69	3.7	6.87	6.9
o-23	.98	3.86	3.9	5.86	6.7
o-28	.91	3.28	3.6	5.10	5.6

(k) Comparison of the Ortho, Meta and Para Compounds under Similar Conditions.—The three dichlorobenzenes were compared as to reaction rate using technique similar to that for the data in Table III. Table VIII gives the data.

TABLE VIII

COMPARISON OF RATES OF CHLORINATION OF ORTHO, META AND PARA DICHLOROBENZENES

Run	Compound	$(dP/dt)_0$ mm./min. $\times 10^2$	Intensity in front (cm. deflection) D_f	Chlorine pressure, mm.	I_a	$\frac{(dP/dt)_0}{I_a} \times 10^2$
32	para	3.51	10.0	29.2	2.39	1.47
33	meta	4.85	11.2	32.1	2.91	1.66
34	meta	3.76	10.2	34.4	2.81	1.34
35	ortho	4.40	11.0	34.8	3.06	1.44
36	ortho	4.40	10.2	36.5	2.95	1.49

The three compounds do not exhibit differences in behavior greater than experimental error.

III. Discussion of Results

The following facts seem to stand out from the results of the experimental work: (1) the rate of pressure change in a system of chlorine and *p*-dichlorobenzene is proportional to the pressure of the latter and independent of the pressure of the former except in so far as the amount of radiation absorbed is dependent on this quantity; (2) at moderate light intensities the rate is proportional to the intensity within experimental error, but at very high intensities (and also in a larger vessel) the rate depends on some power of the light intensity between 0.5 and 1.0; (3) the rates for the ortho, meta and para compounds do not differ appreciably.

As happens so frequently in studies of kinetics of reactions, one mechanism cannot be selected as fitting the data better than any other on the basis of reaction rate studies alone. One which is adequate is represented by the following equations

$$\begin{array}{rcllr} Cl_2 + h\nu &=& 2Cl & & (1) \\ Cl + A &=& ACl & k_2 & (2) \\ ACl + Cl_2 &=& ACl_2 + Cl & k_3 & (3) \\ Cl + \text{walls} &=& \text{removed} & k_4 & (4) \\ Cl + Cl &=& Cl_2 & k_5 & (5) \end{array}$$

where A represents a molecule of dichlorobenzene. The rate of disappearance of chlorine is

$$-\mathrm{d}P_2/\mathrm{d}t = (k_2k_4/2k_5)P_1((1 + 8k_5I_a/k_4^2)^{1/2} - 1) \quad (6)$$

Equation (6) gives a dependence on a power of I_a between 1.0 and 0.5 at high intensities and reduces to

$$-\mathrm{d}P_2/\mathrm{d}t = 2k_2I_aP_1/k_4 \quad (7)$$

at low light intensities. (P_1 = pressure of $C_6H_4Cl_2$; P_2 = pressure of Cl_2; I_a = intensity absorbed in the proper units.)

The mechanism represented by equations (1) to (5) resembles in one respect those postulated for benzene and chlorobenzene in that the addition of a chlorine atom to the substance being chlorinated is postulated as the first step following absorption of radiation.

To account for the effect of intensity, the recombination of chlorine atoms (or some other unsaturated groups) must be allowed to proceed both on the walls and homogeneously in the gas phase. Since the rate of diffusion of atoms to the walls will depend on the pressure, decreasing as the pressure increases, whereas the homogeneous recombination will take place as the result of three-body collisions which increase in number with the pressure, the effect of total pressure on the rate of reaction may not be very marked over quite large changes in that quantity.[6] Nevertheless, one will expect wall recombination to be most important at low pressures and in vessels of small diameter, while three-body collision recombination will be most important at high pressures and in vessels of large diameter. The transition from preponderance of one to preponderance of the other may take place over a relatively short pressure interval.[7] An exact treatment would necessarily include both the rate of diffusion of atoms to the walls and the effect of total pressure (or more specifically of the partial pressures of all of the constituents of the gas phase) on the rate of recombination of chlorine atoms.

The results in Table VI show no pronounced effect of the total pressure (which will depend almost entirely on the chlorine pressure since the pressure of p-$C_6H_4Cl_2$ is always small). It seems necessary to conclude, therefore, that in a small vessel over the pressure range investigated the rate of diffusion to the walls is rapid. If one assumes that the concentration of chlorine atoms is not far from uniform throughout the reaction vessel, one finds the number of chlorine atoms hitting the walls per second to be

$$N_1 = 1.69 \times 10^{22}\, P_3 \quad (8)$$

where P_3 is the pressure of chlorine atoms in mm. and the area of the walls is 49 sq. cm. Turning to run 13a in Table III, one finds the rate of production of chlorine atoms to be

$$2 \times 6.34 \times 0.441 \times 5.9 \times 10^{14} = 3.30 \times 10^{15} \text{ per sec.} \quad (9)$$

If α is the fraction of the collisions with the walls which lead to removal of chlorine atoms, the postulation of a steady state leads to

$$P_3 = 1.95 \times 10^{-7}/\alpha \text{ mm.} \quad (10)$$

In a steady state the rates of reactions (2) and (3) are equal, the rate of removal of chlorine molecules by the formation of the addition product will be equal to the number of collisions between p-$C_6H_4Cl_2$ molecules and chlorine atoms multiplied by a steric factor, β, multiplied by the fraction of the collisions involving sufficient energy to produce reaction which may be written as exp $(-E/RT)$. If σ, the distance between centers at closest approach for these collisions, is taken as 6×10^{-8} cm., the total number of collisions per second in a volume of 25 cc. will be

$$z = 1.43 \times 10^{25}\, P_1P_3 \quad (11)$$

if P_1 and P_3 are expressed in millimeters.

The rate of change of chlorine pressure is one-half the rate of change of total pressure and multiplying by 3.26×10^{16} (the number of molecules per cc. at 1 mm. pressure at 25°) and by the volume gives the number of molecules of chlorine disappearing per second. Equating this to the effective number of collisions per second gives

$$\alpha/\beta = 4.33 \times 10^{3} \exp(-E/RT) \quad (12)$$

where β is the steric factor. In round numbers, therefore

$$E = 5000 - 1365 \log_{10} \alpha/\beta \quad (13)$$

If the proper collision radius has been chosen both α and β must be fractions and will probably not differ greatly from unity. The heat of activation of reaction (2) is thus of the order of magnitude of 5000 calories per mole. This may be compared to 6100 calories for the reaction $Cl + H_2 = HCl + H$.[8] If the reaction between chlorine and p-

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[6] Jost and Jung, *Z. physik. Chem.*, **3B**, 92 (1929), find little change in the value of the reaction rate constant for the hydrogen-bromine reaction at pressures greater than thirty or forty mm.

[7] Rabinowitch and Wood, *Trans. Faraday Soc.*, **32**, 907 (1936).

[8] Rodebush and Klingelhoefer, THIS JOURNAL, **55**, 130 (1933).

dichlorobenzene could be studied at higher pressures comparable to those used in the hydrogen chlorine reaction, the lengths of the chains would probably become quite large.

A word might be said with regard to other possible mechanisms for the reaction. Equations (2) and (3) may not be combined into one equation involving Cl, A and Cl_2 without introducing a factor of the chlorine pressure in the final rate equation. This is contrary to the experimental evidence. The evidence for or against the molecule Cl_3 is not conclusive. At low light intensities the proper form of rate equation may be based on the following series of reactions

$$Cl_2 + h\nu = 2Cl \qquad (14)$$
$$Cl + Cl_2 = Cl_3 \qquad (15)$$
$$Cl_3 + A = ACl_2 + Cl \qquad (16)$$
$$Cl_3 + \text{walls} = 3/2Cl_2 \qquad (17)$$

With this mechanism the numerical factors will be changed somewhat due to differences in the masses of the molecules involved and in the collision radius, but the heat of activation of reaction (16) will be of the order of that given by equation (13).

Most of the other mechanisms tried gave equations disagreeing very definitely with the experimental data.

It should be reëmphasized that at high light intensities it is necessary to introduce a homogeneous recombination of atoms or radicals which is partly responsible for the stopping of chains.

Since the treatment of the rate data applies only to the addition reaction, under conditions such that the substitution reaction is small, it should be noted that the possible mechanisms bear some resemblance to those postulated by other authors to explain reactions of a similar type.[9]

Some mention of the relationship of the work described in the present article to the work on benzene and chlorobenzene may be made. Two runs were made in the present apparatus with benzene (Technique II). The rate for *p*-dichlorobenzene, corrected to the same pressure and intensity, was two-thirds to one-half that for benzene, indicating that the heat of activation for the reaction corresponding to (2) or (16) is lower for the latter substance.

At low light intensities the rate of chlorination of benzene was found to be proportional to the pressure of chlorine, or in other words to the intensity absorbed. At higher intensities and in vessels of fairly large volume so that the distance the chlorine atoms had to traverse to reach the walls was much larger than in the present experiments, the rate was found to be proportional approximately to the square root of the light intensity, the pressure of the chlorine and the pressure of the benzene. With chlorobenzene the incident intensity could not be varied conveniently with the apparatus used, but the volume of the apparatus was again large and the rate was again best represented by an expression involving the square root of the light intensity. As regards the effect of light intensity the agreement between the expressions for the three substances may be said to be complete. The differences center largely upon the effects of the chlorine pressure and of the pressure of the substance being chlorinated. The pressure of benzene was varied from about 1.6 mm. to about 12.5 mm., while that of chlorobenzene was varied from about 1.5 mm. to about 8.3 mm. In both cases the initial rate was found to be proportional to the pressure of the substance being chlorinated, thus agreeing with the work on the dichlorobenzenes.[10] The square root of the chlorobenzene pressure (or of some quantity proportional to the amount of uncompleted addition reaction) seemed to be involved in calculating constants for the course of runs beyond the initial stages.

For both benzene and chlorobenzene the chlorine pressure appeared in the final rate expression, thus disagreeing with the work on the dichlorobenzenes. This may possibly be due to the fact that when the pressure of the substance to be chlorinated is higher than in the present experiments reactions (2) and (3) follow each other so rapidly that their sum may be written as one step. It is probable also that in the case of chlorobenzene where the volume of the vessel was large and the intensity high, the total gas pressure (primarily dependent on the pressure of the chlorine) affected the rate of diffusion of atoms to the walls, thus making it necessary to introduce this quantity into the rate expression.

Thus while there are some superficial differences in the rate expressions obtained for these various substances, many aspects of the reactions

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[9] Dickinson and Carrico, THIS JOURNAL, **56**, 1473 (1934); Stewart and Weidenbaum, *ibid.*, **57**, 2036 (1935). See articles under Ref. 1 for other references. Booher and Rollefson, *ibid.*, **56**, 2293 (1934), feel that the use of triatomic halogen molecules offers satisfactory explanations of many different halogenation reactions. See also Rollefson, "Symposia on Quantitative Biology," The Biological Laboratory, Cold Spring Harbor, L. I., N. Y., Vol. III, 1935, p. 42.

[10] Ref. 1b, p. 4457, Ref. 1c, Table IV, p. 1307.

are similar and the mechanisms probably are not widely different.

Summary

1. The rates of photochemical chlorination of the three dichlorobenzenes have been investigated. Most of the measurements were made on the para compound, although little difference in behavior between the three was noted.
2. The rate of chlorination is proportional to the intensity at low intensities, but depends on some power of the intensity between 0.5 and 1.0 at higher intensities.
3. The rate is independent of the chlorine pressure, except in so far as this determines the light absorption, but is proportional to the pressure of the dichlorobenzene.
4. Various possible mechanisms of the reaction have been discussed and a brief comparison with the results for benzene and chlorobenzene has been made.

Providence, R. I. Received June 25, 1936

[Contribution from the Chemical Laboratory of the University of Texas]

The Determination of the Heat Capacities and the Heat Capacity Ratios of Gaseous Hydrogen Cyanide and of Hydrogen Sulfide[1]

By W. A. Felsing and G. W. Drake

Object of the Investigation.—The purpose of this investigation was the experimental determination of the heat capacities and of the heat capacity ratios at different temperatures of gaseous hydrogen cyanide and hydrogen sulfide. Heat capacity data for gaseous hydrogen cyanide were necessary for the thermodynamic treatment of the thermal decomposition data for monomethylamine obtained in this Laboratory.[2] Hydrogen cyanide is one of the products of this decomposition, and since published data for the heat capacities of this substance are meager and discordant it was decided to measure these needed quantities. It constitutes an integral part of the study of the methylamines as refrigerating fluids in the absorption type refrigerating units as carried out in this Laboratory.[3]

Since the apparatus was available and the heat capacity data for gaseous hydrogen sulfide are rather meager, this substance was included in this investigation.

Previous Investigations.—Bryant proposed,[4] on the basis of spectroscopic measurements, the following relation for gaseous hydrogen cyanide

$$C_p(\text{cal./mole})\ \text{HCN (g)} = 7.01 + 0.006600T - 0.000001641T^2$$

This relation is claimed to apply over the region 300–2000°K. with an accuracy of about 3%. Usherwood,[5] Partington and Carroll[6] and Bredig and Teichmann[7] have determined heat capacity ratios for gaseous hydrogen cyanide at different temperatures. The latter investigators also calculated values of C_p and C_v from their heat capacity ratios.

Eastman proposed a relation for gaseous hydrogen sulfide,[8] which he based upon a review of all existing data; for the region 300–600°K. he proposed

$$C_p\ (\text{cal./mole})\ H_2S\ (g) = 7.2 + 0.0036T$$

for which he claimed only a 5–10% accuracy. Bryant[4] proposed a relation based upon spectroscopic measurements

$$C_p(\text{cal./mole})\ H_2S\ (g) = 6.48 + 0.00558T + 0.000001204T^2$$

This relation is to apply over the range 300–2000°K. with an accuracy of about 2%. Partington and Shilling[9] give a résumé of all heat capacity ratios for gaseous hydrogen sulfide as determined through 1923. Recently Giauque and Blue[10] determined the heat capacities of solid and liquid hydrogen sulfide.

The Method of this Investigation.—The method selected for the experimental determination of the heat capacities was the closed system continuous flow method of

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[1] From a thesis presented by George Wilson Drake to the Graduate Faculty of the University of Texas in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

[2] F. W. Jessen, Ph.D. Dissertation, University of Texas, 1933.

[3] (a) Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929); (b) Felsing and Wohlford, This Journal, **54**, 1442 (1932); (c) Felsing and Jessen, *ibid.*, **55**, 4418 (1933); (d) Felsing and Ashby, *ibid.*, **56**, 2226 (1934).

[4] Bryant, *Ind. Eng. Chem.*, **25**, 820 (1933).

[5] Usherwood, *J. Chem. Soc.*, **121**, 1604 (1922).

[6] Partington and Carroll, *Phil. Mag.*, **49**, 1665 (1925).

[7] Bredig and Teichmann, *Z. Elektrochem.*, **31**, 449 (1925).

[8] Eastman, *Bur. Mines Tech. Paper* 445 (1929).

[9] Partington and Shilling, "The Specific Heats of Gases," Ernest Benn Limited, London, 1924, pp. 139, 199.

[10] Giauque and Blue, This Journal, **58**, 831 (1936).

Scheel and Heuse,[11] with certain modifications suggested by Thayer and Stegeman[12] and by Haas and Stegeman.[13] Modifications dealing with calorimeter design, the heating unit, and the gas circulating pump as developed during this investigation are described in the appropriate sections following.

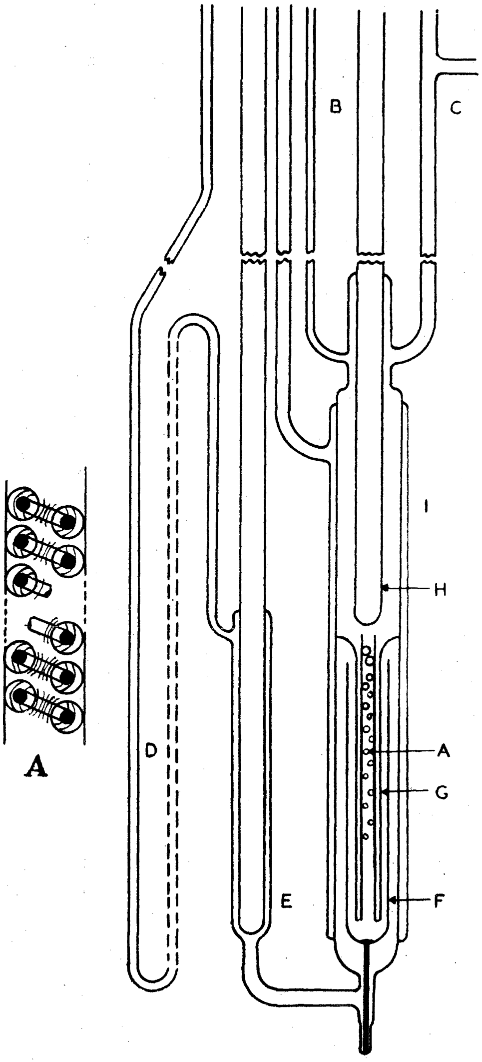

Fig. 1.

The Calorimeter.—The calorimeter is shown in Fig. 1. An enlarged section shows the heating unit design. This unit consisted of approximately 3.66 meters of No. 34 B. & S. bare manganin wire; it was wound smoothly in a lathe on 1.58 mm. diameter rod. A Pyrex rod spiral, which fitted loosely into the heater tube, was constructed; upon this the coiled heating wire was threaded. The glass spiral and its covering of coiled wire was then inserted into the heater tube; the coils fitted tightly against the walls and there was no open channel for the gas to travel through without coming in contact with the heating unit many times. The return wire from the lower end of the coil was brought through a small glass tube extending through the center of the glass spiral. Thus 3.66 meters of bare wire were placed into a tube 4.75 mm. in diameter and 7.6 cm. long.

The Thermoelement.—A 10-junction copper–constantan thermoelement, constructed with the usual precautions, was used to measure the temperature difference between the incoming and outgoing gas. In calibration, nine observations were made at each calibration point, the hot and cold junctions differing by about 3.5° as measured by calibrated Beckmann thermometers. The values of $\Delta E/\Delta t$ thus determined at a given point differed by only 2 parts in 2500 from the average.

The Circulating Pump.—The pump first used was of the type described by Scheel and Heuse,[11] by Thayer and Stegeman,[12] and by Haas and Stegeman.[13] But, since it was found impossible to prevent oscillation of the conventional mercury valves at higher rates of flow with the consequent irregularity of flow, a new design of pump was introduced. The details of this pump are shown in Fig. 2. Mercury valves were abandoned and replaced by ground glass ones, as shown at A and B of Fig. 2. The operating mechanism is shown at K; a crank was mounted on the face-plate of an ordinary speed reducer and the pin of the crank was carried on a threaded bar. This bar was supported at each end by brass blocks and the stroke was varied by turning the threaded bar; this changed, of course, the rate of flow of the gas.

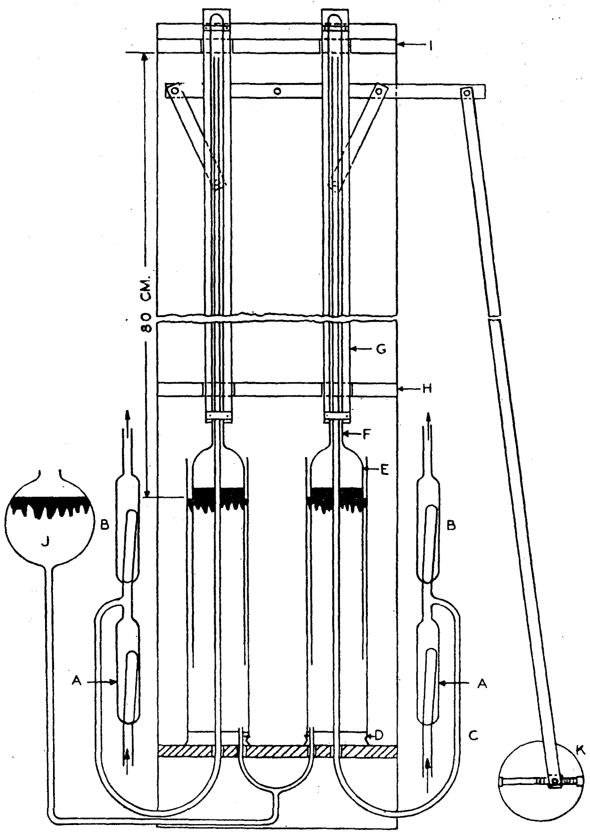

Fig. 2.

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[11] Scheel and Heuse, *Ann. Physik*, **37**, 79 (1912); **40**, 473 (1913).

[12] Thayer and Stegeman, *J. Phys. Chem.*, **35**, 1505 (1931).

[13] Haas and Stegeman, *ibid.*, **36**, 2127 (1932).

The rate of flow was determined as usual by the calibrated bulb method provided, however, with automatic timing. In addition, a flow-meter, calibrated against the bulb, was inserted in the system and the pressure drop measured with a differential manometer filled with olive oil.

The Thermostat.—The thermostat containing the calorimeter consisted of a large Dewar flask (15 × 50 cm.). It was filled with liquid paraffin and was maintained constant at each temperature to within ±0.005°.

The Kundt Tube.—This apparatus does not differ in essentials from that described by Felsing and Jessen,[3c] except in the method of sound production. A General Radio (Type 213, 1000 cycle) audio oscillator produced the current which was sent through a General Radio filter section (Type 330E, 1000 cycle, 600 ohm impedance) and a General Radio band-pass filter (Type 534-B, 1000 cycle, 2000 ohms impedance). This current, impressed upon a telephone receiver in its special housing, produced a sound wave in the tube of such a nature that the minima could be detected easily. The listening tube was closed, the sound being transmitted to a thin aluminum disk fitted into an old-style telephone receiver. The tube was approximately 4 cm. in diameter and it was accurately thermostated.

The Preparation of the Gases.—Hydrogen cyanide was prepared from potassium cyanide and sulfuric acid as recommended by Gilman.[14] The gas was freed from spray, dried by passage over calcium chloride, and condensed by an ice–salt mixture. Repeated fractional distillation under reduced pressure yielded a pure product, which was stored in a reservoir under its own vapor pressure.

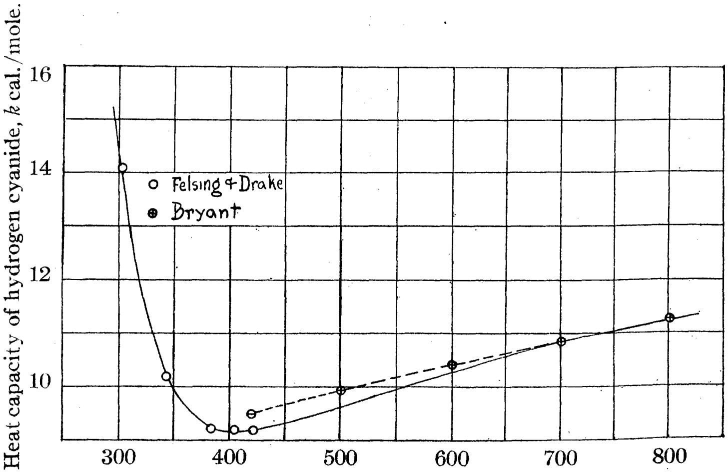

Fig. 3.—Temperature, deg. Kelvin.

Hydrogen sulfide was prepared from aluminum sulfide and water by the method of Keyes and Felsing.[15] The gas was dried by passage over aluminum sulfide.

The Heat Capacities.—The heat capacities for gaseous hydrogen cyanide were measured at 30, 70, 110, 130 and 148°; for hydrogen sulfide they were 30, 70 and 110°. The apparatus was calibrated carefully with pure air (moisture and carbon dioxide free) and the heat loss constant for the apparatus, at different rates of flow, was determined with the aid of the heat capacities listed for air in "I. C. T."[16] The loss determined for air at each temperature and given rate of flow was then assumed to be the loss for the two gases investigated under like conditions. This assumption seems justified for gases of about the same density. The following table presents the data obtained; each value listed is the average of six separate, closely agreeing determinations.

Table I

The Specific and Molecular Heat Capacities of Gaseous Hydrogen Cyanide and Hydrogen Sulfide

Temp., °C.	Heat input J./g./deg.	Heat loss J./g./deg.	Heat capacity Specific J./g.	Heat capacity Molecular cal./mole
		Hydrogen Cyanide		
30	2.697	0.513	2.185	14.107
70	2.147	.567	1.580	10.201
110	2.065	.637	1.428	9.219
130	2.085	.661	1.424	9.194
148	2.095	.667	1.422	9.181
		Hydrogen Sulfide		
30	1.475	0.513	0.962	7.838
70	1.540	.567	.973	7.928
110	1.640	.637	1.003	8.172

The values for the heat capacity for hydrogen cyanide were plotted against the temperature as shown in Fig. 3; on the same plot is included the equation by Bryant.[4] The very rapid change in heat capacity at and near room temperature is due most likely to the fact that the gas is associated, as is shown in the table of densities determined during this investigation. As the temperature rises, the gas density approaches normal; Ingold[17] stated that the density of this gas becomes normal above 170°, a fact substantiated by the density measurements listed below. These were made with great care, observing every precaution for high accuracy.

Accordingly, the continuous line, representing the most probable values, does not join the Bryant line until about 700°K. It is assumed that

Table II

The Densities of Gaseous Hydrogen Cyanide

Temp., °C.	Density (1 atm.) (g./cc.)	Obsd. density/ Calcd. density
30	0.0011615	1.07050
70	.0009880	1.03013
110	.0008735	1.01699

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[14] Gilman, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, p. 307.

[15] Keyes and Felsing, This Journal, **42**, 246 (1920)

[16] "I. C. T.," Vol. V, p. 81.

[17] Ingold, *J. Chem. Soc.*, **129**, 26 (1926).

above that temperature the Bryant relation may yield values of the heat capacity. Since, however, the heat capacity changes so rapidly at or near 400°K. two relations were obtained: one for the region 280–400°K. and the other for the region 400–1000°K. These are given as follows

$$(280\text{–}400^\circ\text{K.}):\ C_p(\text{cal./mole})\ \text{HCN(g)} = 121.03 - 0.58130T + 0.00754T^2$$

$$(400\text{–}1000^\circ\text{K.}):\ C_p(\text{cal./mole})\ \text{HCN(g)} = 6.650 + 0.00675T - 0.000001125T^2$$

The relation best expressing the heat capacities of hydrogen sulfide over the temperature range investigated is

$$(273\text{–}450^\circ\text{K.}):\ C_p(\text{cal./mole})\ H_2S\text{(g)} = 12.157 - 0.02883T + 0.0000048125T^2$$

Since this relation contains rather large temperature coefficients it is not advisable to extrapolate it far past the temperature limits specified.

The Heat Capacity Ratios.—The γ values are presented in Table III; the values in the column marked "uncorrected" resulted from the relation

$$\gamma\ (\text{uncorr.}) = 1.403\ \frac{M}{28.96}\ \frac{l_2^2}{l_1^2}$$

while the values in the "corrected" column resulted from the application of the correction relation

$$\gamma\ \text{corr.} = \gamma\ (\text{uncorr.})\cdot\Phi$$

where $\Phi = 1 - {}^9/_{64}\ \pi\ \tau\ (1 - 6\tau^2)$, as suggested by Partington and Shilling[9] (p. 50). Here $\pi = p/p_c$ = actual pressure/critical pressure and $\tau = T_c/T$ = critical temperature/actual temperature. The critical data for hydrogen cyanide are those of Bredig and Teichmann,[7] while those for hydrogen sulfide are due to Pickering.[18]

TABLE III

VALUES OF C_p/C_v FOR HYDROGEN CYANIDE AND HYDROGEN SULFIDE

Gas	Temp., °C.	γ, uncorr.	γ, corr.
HCN	30	1.144	1.087
	50	1.252	1.201
	75	1.276	1.235
H_2S	10	1.349	1.322
	25	1.343	1.321
	50	1.330	1.313
	75	1.314	1.301

The increasing values of γ for hydrogen cyanide may be explained by the apparently greater complexity, as indicated by the density; if values had been extended to higher temperatures, the γ values would most likely have gone through a maximum as is shown by the results of Bredig and Teichmann (maximum at 140°).[7]

The Accuracy of the Determinations.—From a consideration of all sources of error, it is believed that the heat capacity data are accurate to within *one* per cent.; the accuracy of the heat capacity ratios is within 0.2%; and the density data for gaseous hydrogen cyanide are believed to be accurate to within 0.5%.

Summary

1. The heat capacities of gaseous hydrogen cyanide and of hydrogen sulfide have been determined over a limited temperature interval with an accuracy of approximately 1%. These have been expressed as functions of the temperature.

2. Improvements in measurement of the rate of flow in the construction of the heating unit, and in the gas circulating pump have been described.

3. The densities of gaseous hydrogen cyanide have been measured with an accuracy of approximately 0.5%.

4. The heat capacity ratios for hydrogen cyanide and sulfide have been measured over a temperature range with an accuracy of about 0.2%.

AUSTIN, TEXAS

RECEIVED JUNE 19, 1936

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[18] Pickering, *J. Phys. Chem.*, **28**, 97 (1924).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Non-Rotation of Molecules in a Number of Solids

BY S. A. MCNEIGHT AND C. P. SMYTH

This paper presents the negative results of investigation through dielectric constant measurements on a number of solids in which the size and shape of the molecule or the properties of the substance indicated the possibility of molecular rotation. The apparatus and method employed was essentially the same as that described in earlier papers.[1] The work on benzophenone was carried out by Dr. W. S. Walls.

Purification

Methylamine.—This was prepared by the action of a concentrated potassium hydroxide solution on Merck C. P. methylamine hydrochloride, dried by passing over fused potassium hydroxide, condensed by a carbon dioxide–acetone slush and fractionally distilled, the middle third being collected directly in the dielectric constant cell. Evaporation of the last third of the material at about 183°K. left no residue, m. p. 179.7°K.

Ethyl Ether.—The material used was part of a sample carefully purified for freezing point measurements.[2]

Acetone.—C. P. acetone was dried by standing over fused calcium chloride for some weeks with a subsequent fractional distillation from a fresh supply of calcium chloride; m. p. 178.2°K.; b. p. 329.3°K.

Benzophenone.—Material from the Florasinth Laboratories, Inc., was dissolved in a small amount of benzene and filtered. The benzene was distilled off and the residue fractionally crystallized ten times; m. p. 321.2°K. A portion of the original material was fractionally distilled under reduced pressure and a sample boiling from 457.6 to 458.1°K. was collected and measured. This material showed such dispersion of the dielectric constant that the sample purified by fractional crystallization was used for the measurements reported in Table I.

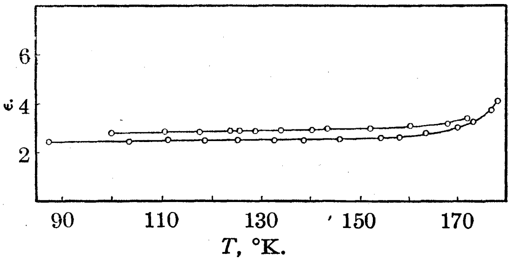

Fig. 1.—Temperature dependence of the dielectric constants (at 50 kc.) of acetone and methylamine; upper curve, acetone; lower curve, methylamine.

Succinic Acid.—C. P. succinic acid was recrystallized from water three times; m. p. 455.9°K. The material on which measurements were made probably contained appreciable amounts of succinic anhydride since melting was necessary in order to fill the condenser and a melting point determination made at the conclusion of the measurements gave 453.6°K.

Experimental Results

The dielectric constants ϵ and the specific conductances $k(\text{ohm}^{-1}\,\text{cm}^{-1})$ are given in Table I, the absolute temperatures being given in the first column and the frequencies in kilocycles across the top of each group of data. Unless otherwise indicated, the values were obtained with rising temperature. As the material in each case is frozen between the fixed plates of the measuring condenser, the value found for the dielectric constant does not change because of change in the number of molecules per cc. with temperature. For an approximate calculation of the polarization of the solid at any temperature, the density at the melting point is the one to be used. Many values of the dielectric constant at intermediate frequencies and temperatures have been omitted for the sake of brevity. As no appreciable dependence upon frequency was observed for ether, its dielectric constant values are given only at 5 kc. and its specific conductances, 0.02×10^{-9} for the solid and 0.04×10^{-9} for the liquid at 5 kc., are omitted.

Discussion of Results

As methyl alcohol has been found to show rotation with some difficulty above a transition point, methylamine, which has a melting point 4° higher, a dipole moment 1.23 instead of 1.68×10^{-18} and a molecule rather similar in shape and size, might also be expected to show molecular rotation. Figure 1 shows that the dielectric constant rises rapidly above 160°K., the rapidity increasing with increasing temperature and decreasing frequency. The first part of the rise appears like the curves for ice, in which the molecules evidently turn with difficulty, but the very steep rise as the melting point is approached and the great increase in conductance as compared to a maximum in the conductance curve shown by ice and by methyl alcohol show that this rise in dielectric constant is not due to the setting in of molecular rotation in the solid but is caused by impurities, which give rise

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[1] Smyth and Hitchcock, THIS JOURNAL, **54**, 4631 (1932); **55**, 1830 (1933).

[2] Huettig and Smyth, *ibid.*, **57**, 1523 (1935).

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC CONDUCTANCES

Methylamine (m. p. 179.7°K.)

Kc	50	5	0.5	50	5	0.5
T, °K.		ε			$k \times 10^9$	
87.6	2.47	2.46	2.42	0.58	0.01	0.01
91.8	2.48	2.46	2.40	.58	.01	.01
103.7	2.48	2.46	2.41	.67	.01	.01
111.3	2.50	2.48	2.42	.67	.01	.01
118.6	2.52	2.48	2.44	.67	.01	.01
125.3	2.52	2.49	2.46	.67	.03	.01
132.9	2.55	2.52	2.48	.76	.03	.01
138.6	2.56	2.53	2.53	.76	.03	.03
145.8	2.57	2.59	2.84	.93	.21	.09
150.0	2.58	2.64	3.16	1.30	.35	.15
154.4	2.60	2.78	3.68	1.91	.61	.21
158.1	2.66	3.01	4.56	3.17	1.06	.35
163.4	2.83	3.60	5.91	6.41	2.18	.91
170.1	3.05	4.14	7.37	9.46	3.22	1.50
173.4	3.22	4.47	7.68	11.0	3.76	1.93
177.2	3.78	5.21	9.22	15.9	4.84	2.14
178.4	4.12	6.62	12.6	20.3	9.25	8.04
179.0		9.17			23.0	

Ethyl Ether (m. p. 156.8°; f. p. 149.8°K.)

Kc........	5	Kc........	5	Kc........	5
T, °K.		T, °K.		T, °K.	
	Cooling		Warming		
173.0	9.04	145.0	2.28	167.8	9.49
169.9	9.55	147.8	2.28	172.2	9.05
164.1	9.91	148.7	2.29	198.3	7.25
161.4	10.17	149.3	2.30	205.9	6.87
160.1	10.32	149.5	2.30	213.0	6.55
156.4	10.72	149.7	2.30	223.1	6.13
154.3	11.02	150.0	2.30	232.3	5.80
153.2	11.21	150.2	2.30	243.9	5.45
151.5	11.36	151.6	2.31	250.7	5.26
150.8	11.47	152.5	2.33	263.4	4.96
150.1	11.55	153.6	2.35	272.6	4.75
149.3	11.64	155.6	2.43	287.2	4.42
148.7	11.73	155.9	2.46	294.2	4.27
147.6	11.88	156.0	2.52	295.9	4.17
147.0	11.98	156.2	2.58	Refrozen, warming	
146.3	12.07	156.4	2.73	89.9	2.20
145.2	12.22	156.5	2.82	91.6	2.20
149.8	8.02	156.6	3.38	99.5	2.20
149.8	7.71	156.7	4.08	106.2	2.20
149.8	3.20	156.8	6.46	117.0	2.21
Solid		156.9	8.28	128.7	2.30
149.8	2.26	157.0	10.02	136.9	2.30
148.6	2.24	Liquid			
146.7	2.22	157.0	10.42		
136.0	2.18	157.2	10.37		

Acetone (m. p. 178.2°K.)

Kc	50	5	0.5	50	5	0.5
T, °K.		ε			$k \times 10^9$	
100.2	2.80	2.82	2.84	0.20	0.02	0.01
103.9	2.80	2.83	2.85	.20	.02	.01
110.7	2.82	2.85	2.86	.20	.02	.01
117.5	2.85	2.88	2.89	.20	.02	.01
123.7	2.87	2.90	2.92	.20	.02	.01
124.9	2.87	2.90	2.93	.24	.02	.01
125.7	2.88	2.90	2.93	.27	.03	.01
126.7	2.88	2.92	2.94	.28	.03	.01
128.8	2.89	2.93	2.97	.29	.04	.01
134.0	2.92	2.99	3.00	.47	.05	.01
140.3	2.99	3.04	3.04	.59	.03	.01
143.3	3.00	3.04	3.06	.48	.03	.01
152.0	3.04	3.08	3.17	.33	.07	.04
160.2	3.10	3.22	3.57	.55	.22	.10
168.0	3.20	3.49	4.59	1.51	.70	.29
172.4	3.39	4.01	5.96	4.11	1.97	1.33

Benzophenone (m. p. 321.2°K.)

Kc T, °K.	70	12	3	0.7	0.3
200.4	3.16	3.15	3.15	3.16	3.15
214.1	3.16	3.15	3.15	3.16	3.15
222.6	3.16	3.15	3.15	3.16	3.15
235.1	3.16	3.15	3.15	3.16	3.15
244.6	3.16	3.15	3.15	3.16	3.16
255.1	3.16	3.15	3.15	3.16	3.16
266.3	3.16	3.15	3.15	3.16	3.15
279.6	3.16	3.15	3.15	3.16	3.16
288.9	3.16	3.15	3.16	3.17	3.17
297.6	3.16	3.16	3.16	3.18	3.19
306.1	3.17	3.16	3.17	3.20	3.23
313.3	3.18	3.17	3.20	3.25	3.31
319.6	3.26	3.27	3.30	3.37	3.42
			Liquid		
320.6	11.50	11.51	11.55	11.73	12.01
321.6	11.45	11.47	11.52	11.70	11.98
325.6	11.26	11.28	11.35	11.58	11.85

Succinic Acid (m. p. 455.9°K.)

Kc	5	5	Kc	5	5
T, °K.	ε	$k \times 10^9$	T, °K.	ε	$k \times 10^9$
	Cooling				
387.4	5.35	1.27	270.5	2.56	0.03
370.0	2.90	0.24	258.3	2.56	.03
334.1	2.74	.06	247.2	2.54	.03
305.4	2.66	.03	238.1	2.53	.03
298.2	2.64	.03	217.0	2.53	.03
289.6	2.58	.03			
285.2	2.56	.03			
276.9	2.56	.03			
	Warming				
223.1	2.52	0.03	260.2	2.36	0.05
228.5	2.51	.03	271.0	2.42	.11
237.3	2.51	.03	271.7	2.43	.12
252.0	2.53	.03	272.3	2.44	.14
Melted and refrozen			272.6	2.46	.17
(m. p. 453.6°K.)			273.1	2.47	.17
100	2.29	0.01	273.2	2.48	.18
112	2.29	.01	273.4	2.49	.19
122.2	2.29	.01			
175.3	2.30	.01			
188.8	2.31	.02			
205.5	2.31	.02			
214.7	2.32	.02			
222.5	2.34	.04			
234.7	2.35	.03			
247.1	2.36	.04			

to traces of liquid and probably ionic displacements. The presence of these impurities is indicated by the fact that the melting point of the sample used was 0.9° lower than that found by Timmermans and Mattaar[3] and lacking in sharpness. The size, shape and dipole moment of the methylamine molecule are such that its rotation in the solid might occur at least as easily as that of the methyl alcohol molecule. As this begins to show limited rotation only 15.5° below its melting point, the rotation of the methylamine molecule might be expected to begin a few degrees below its melting point. However, the uncertainty in the effects of the various factors is more than enough to make possible the postponement of rotation in the solid until a temperature above the melting point is reached. Methylamine resembles ammonia, which shows no molecular rotation in the solid, much as methyl alcohol does water, which turns with difficulty in the solid. The absence of any rotation of the —NH_2 group in the molecule is like that in aniline, which shows no molecular or group rotation.[1]

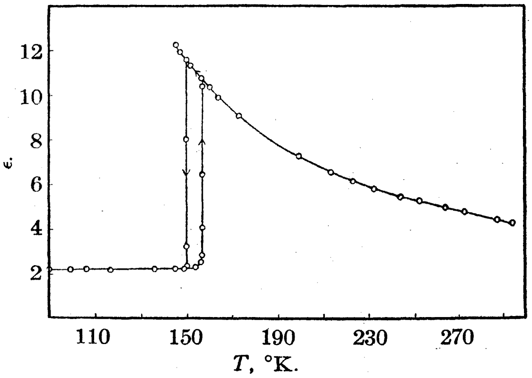

Fig. 2.—Temperature dependence of the dielectric constant (at 5 kc.) of ethyl ether.

It may be concluded from the low dielectric constant values found[4] for solid methyl chloride, bromide and iodide that there is no molecular rotation around any axis perpendicular to the carbon–halogen line, the dielectric constant giving no information as to rotation around the carbon–halogen line, in which the molecular dipole lies. Low dielectric constants found[4] for solid methylene chloride and chloroform show that these molecules do not rotate around any axes perpendicular to their one axis of symmetry. It is probable that all of these molecules are so located in their lattices as to block one another's rotations around axes perpendicular to those in which their dipoles lie, such rotation being presumably much more difficult than rotation of the methylamine molecule around the C–N line or of the methyl alcohol molecule around the C–O line.

The dielectric polarization of ethyl ether in solution and in the pure liquid state shows very little orienting force between the molecules.[5] As the freezing point is 7° lower than the melting point, a change from an unstable to a stable form apparently occurring in the solid, one would anticipate a considerable amount of molecular freedom in the solid. The dielectric constant–temperature curve in Fig. 2 shows clearly the different freezing and melting temperatures and shows equally clearly by its low and almost horizontal position below the freezing point the absence of molecular rotation in the solid. The curves for falling and rising temperature are coincident below the freezing point and show no sign of any transition, therein agreeing with the absence of discontinuity in the temperature–time curves run in this Laboratory.[2] The curve gives no sign of the behavior reported for liquid ether by Mazur,[6] whose measurements showed a rise in dielectric constant from 4.18 at 303.7°K. to a maximum of 12.39 at 167.7°K. followed by a decreasingly rapid decrease with further lowering of temperature, then a slight increase with only a small break downward on freezing. Mazur ascribed this phenomenon to the formation of two liquid phases by the ether, which was supposed to undergo a transition at 167.7°K., but Smits[7] has concluded that Mazur's results are due to the presence of impurities. The material measured in the present work appeared to be very pure, since the melting point was shown by temperature–time curves to be very sharp and in excellent agreement with the carefully determined value of Timmermans and Martin[8] as well as that of Skau.[9] The failure to find the abnormal behavior reported by Mazur for liquid ether parallels a similar failure in the case of nitrobenzene.[1] The specific volume 1.156[10] at 150°K. and the dielectric constant 2.20 from 89.9 to 106.2°K. give a polarization value 24.5, from which subtraction of the electronic

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[3] Timmermans and Mattaar, *Bull. soc. chim. Belg.*, **30**, 213 (1921).

[4] Morgan and Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

[5] Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, 1931, p. 180.

[6] Mazur, *Nature*, **126**, 649 (1930).

[7] Smits, *Z. physik. Chem.*, **A160**, 225 (1932).

[8] Timmermans and Martin, *J. chim. phys.*, **25**, 411 (1928).

[9] Skau, *J. Phys. Chem.*, **37**, 609 (1933).

[10] Isnardi, *Z. Physik*, **9**, 160 (1922).

polarization 22.0[11] gives 2.5 for the atomic polarization in fair agreement with the value 3.3 obtained by Fuchs.

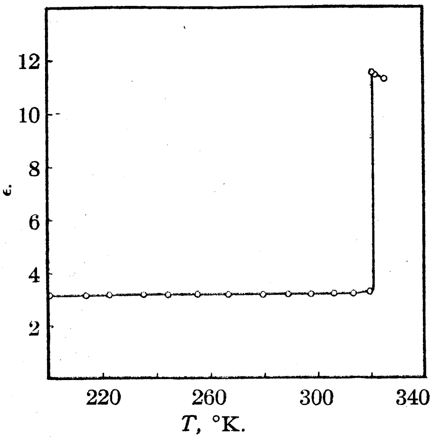

Fig. 3.—Temperature dependence of the dielectric constant (at 70 kc.) of benzophenone.

The considerable departure of the acetone molecule from a spherical or cylindrical shape would lead one to expect no rotation in the solid. This expectation is borne out by the dielectric constant values in Table I and Fig. 1, the rapid increase of both dielectric constant and conductance and their variation with frequency as the region of the melting point is approached being caused by impurities as in the case of methylamine. Special care was taken with the measurements in the neighborhood of 126°K., where a small hump had been found[12] in the specific heat–temperature curve but no irregularity was observed in the dielectric constant–temperature curve at any of the frequencies used. Pauling has suggested[13] that the small hump sometimes observed in specific heat–temperature curves is due to the setting in of rotation of a group within the molecules. Although the dielectric constant values show that the entire molecule does not rotate in the solid, they would not be affected appreciably by rotation of the methyl groups in the molecule, which may be the cause of the hump in the specific heat curve. Use is made of the density 0.9686 of solid acetone at its melting point given by "International Critical Tables" to calculate the polarization of the solid at 100°K. The value 22.7 thus obtained gives an atomic polarization value 7, which is almost certainly too high. The small but not negligible variation of dielectric constant with frequency and temperature even down to 100°K. shows that it has not quite settled down to the value which arises wholly from induced shifts of charge in the molecule.

Although benzophenone exists in an unstable monoclinic form as well as in a stable rhombic, the large size of its molecule and its great departure from spherical shape render molecular rotation even more improbable than in acetone. The absence of molecular rotation is established very clearly by the data in Table I and Fig. 3, which show a dielectric constant value independent of frequency and temperature for temperatures more than 20° below the melting point. The considerable rise on melting is due to the large dipole moment of the molecule.

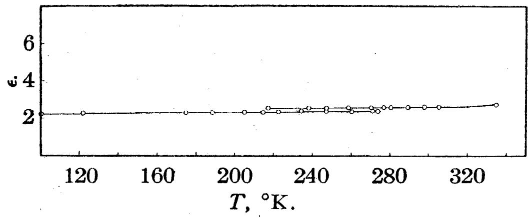

Fig. 4.—Temperature dependence of the dielectric constant (at 5 kc.) of succinic acid; lower curve after remelting and refreezing.

As the variation of the dielectric constant of succinic acid (Fig. 4) apparently was caused by impurities, the values at frequencies other than 5 kc. are omitted from Table I. It was necessary to melt the substance in order to fill the space between the condenser plates which undoubtedly produced appreciable quantities of succinic anhydride as shown by the somewhat lower melting point obtained on a second melting. To investigate the effect of increasing quantities of the anhydride, the dielectric constant–temperature curve for the refrozen sample was obtained but, aside from a decrease in the temperature at which variation with frequency became pronounced, little change was observed. The specific heat–temperature curve of succinic acid[14] shows a hump, with a heat effect of 41 cal. per mole at 272°K. The dielectric constant values give no indication of any effect as they vary slightly but steadily both on heating and cooling through this temperature. It would appear therefore that this effect cannot be due to rotation of the molecule or of any groups within the molecule since such rota-

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(11) Fuchs, *Z. Physik*, **63**, 824 (1930).

(12) Kelley, THIS JOURNAL, **51**, 1145 (1929).

(13) Pauling, *Phys. Rev.*, **36**, 430 (1930).

(14) Parks and Huffman, THIS JOURNAL, **52**, 4381 (1930).

tion would cause an increase of the dielectric constant at the temperature of its appearance. Unfortunately it proved impossible, due to the high conductance, to investigate the transition at 310°K. where a transition from a triclinic to a monoclinic form has been observed.[15]

Such variation of dielectric constant and conductance with frequency and temperature as has been found for these substances has been dismissed as not being significant of rotation. The ordinary direct current conductance rises with rising temperature as does that of a liquid and the alternating current conductance increases with increasing frequency.[16] The apparent capacity of a condenser and, hence, the value of the dielectric constant calculated from it, increases with decreasing frequency and resistance.[17] At very high frequencies and resistances the effect upon the apparent capacity is slight or negligible, but at the lower frequencies employed in these measurements and with the lower resistances in the region of the melting point, the effect is considerable. It is well illustrated by the dielectric constant values for liquid benzophenone (Table I), where there can be no question of a true anomalous dispersion. The value for the slightly supercooled liquid increases only 0.01 on lowering the frequency from 70 to 12 kc., but increases 0.50 on further lowering the frequency from 12 to 0.3 kc., more than half of the increase occurring between 0.7 and 0.3 kc. A temperature rise of 5° lowers the resistance and thus increases the effect slightly. As the conductivity of a material of low conductivity is tremendously affected by the presence of minute traces of ionic impurities, the effects under discussion have been attributed mainly to impurities rather than to the properties of the pure substances under examination. Although the effects are undoubtedly due primarily to the conductances of the materials examined, there remains a possibility, particularly in the case of methylamine, that an occasional molecule may have sufficient freedom of rotation to orient in the electric field or that a larger number of molecules executing small rotational oscillations in their lattices may each contribute very slightly to the dielectric constant through a distortion of the oscillation by the field.

Summary

The dielectric constants of solid methylamine, ethyl ether, acetone, benzophenone and succinic acid have been measured over a wide range of temperature and frequency to investigate the possibility of rotation of their molecules. Although the molecular shape of methylamine is such that rotation might well occur and although ether shows different freezing and melting points, benzophenone shows polymorphism, and acetone and succinic acid show humps in their specific heat–temperature curves, no molecular rotation has been found in these solids.

The low dielectric constants of solid methyl chloride, bromide and iodide, methylene chloride and chloroform are used to show that, in the solid state, their molecules cannot rotate around any axes perpendicular to the axis of molecular symmetry.

Princeton, New Jersey Received June 25, 1936

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[15] La Tour, *Compt. rend.*, **193**, 180 (1931); *Ann. phys.*, **18**, 199 (1932).

[16] *Cf.* Murphy, *Trans. Am. Electrochem. Soc.*, **65**, 133 (1934).

[17] Joffé, "The Physics of Crystals," McGraw-Hill Book Company, Inc., New York, 1928, p. 148.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Molecular Rotation in Solid Arsine and Other Hydrides

BY C. P. SMYTH AND S. A. MCNEIGHT

This paper presents measurements of dielectric constant made in continuation of previous work[1,2] on the rotation or non-rotation of molecules in solid hydrides and discusses the results in relation to the properties of the other hydrides and the factors affecting rotation. The apparatus and technique employed were essentially the same as that described in earlier papers[1,3] from this Laboratory, the same bridge being used. However, because liquid hydrogen cyanide attacked the gold cylinders of the measuring cell normally used, a new condenser was made for this substance from tin tubes turned to such a size as to give a geometrical capacity of 10 micromicrofarads. When liquid hydrogen became available for the first time for the measurements on arsine, the brass block surrounding the glass cell containing the condenser was replaced by a similar block of lead in order to obtain greater heat capacity and slow down the rate of temperature change at very low temperature. For the measurement of these low temperatures the calibration of the platinum resistance thermometer used in the other measurements was extended by using the boiling point of hydrogen as an additional fixed point.

Preparation of Materials

Hydrogen Cyanide.—This material was prepared from potassium cyanide and sulfuric acid according to the directions given in "Organic Syntheses."[4] It was condensed at 0° and the middle portion distilled into the condenser cell; m. p. 259.2°K.

Hydrogen Selenide.—Hydrogen selenide was prepared in an oxygen-free apparatus by dropping freshly boiled, dilute hydrochloric acid upon aluminum selenide, which had been prepared by the ignition of an intimate mixture of powdered aluminum and selenium containing a 50% excess of selenium over that required by the formula Al_2Se_3. The gas was dried by passage over calcium chloride and phosphorus pentoxide and condensed by means of a slush of acetone and solid carbon dioxide, which froze it immediately to the solid, preventing possible decomposition in the liquid phase.

Arsine.—Arsine was generated in a system previously flushed out with oxygen-free hydrogen by dropping 30% sulfuric acid upon an alloy of 53% zinc and 47% arsenic according to the method used by Cohen.[5] It was dried by passage over calcium chloride and phosphorus pentoxide and condensed by a slush of acetone and solid carbon dioxide.

Experimental Results

The dielectric constants ϵ and the specific conductances k (ohm^{-1} cm.$^{-1}$) are given in Table I, the absolute temperatures being given in the first column and the frequencies in kilocycles across the top of each group of data. Many determinations at intermediate temperatures and frequencies are omitted for the sake of brevity, but more values than usual are included for arsine because of its peculiar behavior. All the values listed were obtained with rising temperature, but arsine was taken up and down several times between liquid air temperature and the melting point. The upper transition temperature and the melting point obtained were identical with those in Table I and the shape of the dielectric constant–temperature curve obtained for this region was the same as that in Fig. 3. As the liquid was refrozen each time, small differences naturally occurred in the absolute values of the dielectric constant. Consequently, none of these check values are given in Table I and most of the specific conductances, which did not change significantly above the lowest transition, are omitted. As the hydrogen selenide measurements, through an unfortunate chain of circumstances, are incomplete, only the dielectric constant values are given.

Discussion of Results

The first attempt to measure solid hydrogen cyanide by Dr. W. S. Walls in this Laboratory was unsuccessful because the interaction of the liquid cyanide with the gold condenser was sufficient to give high conductance on solidification. The first results obtained in the present investigation were uncertain for the same reason, but the results in Table I obtained with a tin condenser appear satisfactory. The melting point 259.2°K. obtained for this sample of hydrogen cyanide is in excellent agreement with the value 259.1°K. given by "International Critical Tables" and 259°K. found by Lewis and Schutz,[6] but its lack

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[1] Smyth and Hitchcock, THIS JOURNAL, **55**, 1830 (1933).

[2] Smyth and Hitchcock, *ibid.*, **56**, 1084 (1934).

[3] Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932); Smyth and Kamerling, *ibid.*, **55**, 462 (1933).

[4] "Organic Syntheses," John Wiley and Sons, Inc., New York, Coll. Vol. I, 1932, p. 307.

[5] Cohen, *Z. physik. Chem.*, **25**, 483 (1898).

[6] Lewis and Schutz, THIS JOURNAL, **56**, 1002 (1934).

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC CONDUCTANCES

Hydrogen Cyanide (m. p. 259.2°K.)

Kc.	50	5	0.5	50	5	0.5
T, °K.		ϵ			$k \times 10^9$	
86.7	2.35	2.39	2.33	0.40	0.07	<0.05
102.2	2.38	2.41	2.36	.40	.07	< .05
111.9	2.40	2.42	2.38	.66	.07	< .05
122.0	2.42	2.42	2.41	.73	.07	< .05
130.1	2.43	2.45	2.41	.73	.07	< .05
137.2	2.44	2.46	2.43	.86	.07	< .05
159.8	2.56	2.57	2.53	1.06	.07	< .05
167.6	2.58	2.60	2.56	1.06	.07	< .05
182.2	2.65	2.68	2.63	1.06	.07	< .05
193.5	2.70	2.73	2.72	1.06	.13	< .05
197.4	2.73	2.75	2.76	1.06	.13	< .05
211.2	2.81	2.86	2.97	1.25	.26	.07
223.7	2.91	3.01	3.22	2.11	.33	.07
226.5	2.95	3.03	3.33	2.24	.46	.13
246.8	3.61	4.70	8.17	17.4	6.89	4.92
250.9	5.2	7.9	19.4	109	95	119
252.1	5.6	9.1	26.0	125	151	163

Hydrogen Selenide

Kc.	50	5	0.5
T, °K.			
86.8	7.21	7.21	7.11
88.6	7.19	7.17	7.08
97.3	7.03	7.01	6.94
101.4	6.96	6.93	6.84
105.0	6.88	6.86	6.77
109.3	6.76	6.74	6.66
116.1	6.58	6.55	6.48
125.3	6.35	6.32	6.23
130.6	6.22		
186.0	5.45	5.41	5.40
196.3	5.34	5.29	5.35
200.2	5.36	5.37	5.54
203.8	5.36	5.37	5.59
208.5	5.15	5.20	

Arsine (m. p. 156.4°K.)

Kc.	50	20	5	1	0.5
T, °K.		$k \times 10^9$			
20.5	0.73	0.65	0.23	0.07	0.07
20.7	.73	1.05	.40	.13	.09
20.8	1.27	0.81	.27	.07	.05
21.9	1.27	.81	.27	.07	.05
25.8	1.27	.60	.14	.05	.05
30.9	0.36	.18	.11	.05	.05
33.7	.36	.09	.09	.05	.05
156.1	.36	.16	.09	.04	.04
			Liquid		
194.5	.36	.16	.09	.04	.04

			ϵ		
20.5	2.80	2.82	2.85	2.91	2.93
20.7	2.82	2.84	2.89	2.97	3.00
20.8	2.82	2.83	2.88	2.94	2.97
21.9	2.84	2.88	2.94	3.00	3.01
25.8	3.02	3.06	3.09	3.11	3.11
27.7	3.12				
28.4	3.14				
30.9	3.17	3.17	3.15	3.16	3.18
31.5	3.19				
31.8	3.21				
32.1	3.39				
32.1	3.46				
32.2	3.46				
32.4	3.45				
32.8	3.44				
33.7	3.42	3.41	3.38	3.38	3.38
34.6	3.39				
40.2	3.27				
44.1	3.22				
45.8	3.19	3.17	3.14	3.14	3.13
47.8	3.17	3.15	3.14	3.14	3.14
54.9	3.10	3.09	3.08	3.09	3.12
58.0	3.08	3.06	3.06	3.08	3.07
71.9	2.96	2.95	2.94	2.97	2.98
76.2	2.92	2.90	2.90	2.92	2.93
79.5	2.85	2.84	2.84	2.86	2.85
82.5	2.78				2.82
86.5	2.72				2.77
88.5	2.70	2.72	2.71	2.74	2.75
93.4	2.69	2.69	2.68	2.71	2.72
98.0	2.68	2.67	2.66	2.70	2.71
103.9	2.67	2.66	2.66	2.68	2.70
106.4	2.66				
106.6	2.66				
106.6	2.71				
107.0	2.71	2.70	2.70	2.72	2.75
113.6	2.70	2.68	2.67	2.68	2.70
116.7	2.69	2.68	2.66	2.67	2.69
121.8	2.68	2.67	2.65	2.67	2.68
127.3	2.68	2.67	2.65	2.66	2.68
134.0	2.68	2.66	2.64	2.66	2.67
140.1	2.67	2.66	2.64	2.66	2.67
143.5	2.67	2.66	2.64	2.66	2.69
151.2	2.67	2.66	2.64	2.66	2.69
156.1	2.64	2.62	2.62	2.63	2.64
156.3	2.51				
156.4	2.52				
156.4	2.58				
			Liquid		
157.1	2.57	2.56	2.54	2.58	2.60
165.5	2.54	2.54	2.52	2.53	2.54
171.4	2.52	2.51	2.50	2.54	2.53
181.1	2.48	2.46	2.45	2.45	2.48
187.6	2.46	2.44	2.44	2.45	2.48
194.5	2.41	2.40	2.40	2.40	2.41
200.9	2.38	2.38	2.38	2.39	2.41

of sharpness is indicative of the presence of impurities, which are presumably responsible for the rapid increase in the dielectric constant and conductance of the solid as the melting point is approached. The conductance becomes so high near the melting point that the dielectric constant can no longer be measured with any accuracy but a temperature–time curve shows the absence of any transition in this region. The dielectric constant–temperature curve in Fig. 1 shows no transition and gives no positive evidence of molecular rotation. The gradual rise with temperature below the region of the melting point is probably due to the effect of increasing conductance and the rapid rise in the region of the melting point together with increasing dependence upon frequency is due both to the rapid increase in conductance resulting from the formation of liquid and the presence of ions and to the direct effect of liquid of high dielectric constant and ions in raising the dielectric constant. The value[7] for liquid hydrogen cyanide 194.4 at 259.7°K., the highest found for any pure liquid, shows that the presence of appreciable quantities of liquid in the solid would raise the dielectric constant markedly and also shows that freedom of rotation in the solid would give a dielectric constant over 200 instead of between 2 and 3. Use of a density value 0.925 at 233°K.[8] and of the Grüneisen rule together with a dielectric constant value from Table I gives a molar polarization 9.2 for the solid at 100°K. Subtraction of the electronic polarization 6.3[9] gives 2.9 for the atomic polarization as compared to the zero value found in the more accurate measurements on the gas.[9] The rough value 2.9, as far as it is significant at all, probably indicates that the dielectric constant values even at 100°K. are a little high because of conductance. However, the results certainly do not preclude the possibility of the rotation of an occasional molecule in the lattice of the solid, particularly as the region of the melting point is approached, but make it apparent that it is at most only a very occasional molecule that might have the freedom necessary for rotation.

In view of the freedom of molecular rotation in solid hydrogen chloride, bromide and iodide,[1] one might anticipate rotation in solid hydrogen cyanide. However, the factors which tend to prevent rotation are obviously stronger in the latter substance. The linear triatomic molecule of hydrogen cyanide must depart farther from a spherical shape than do the molecules of hydrogen chloride, bromide and iodide, as the minimum value for the distance of the hydrogen from the nitrogen nucleus would seem to be about 1.34 Å.[10] as compared to an internuclear distance 1.28 Å. in hydrogen chloride and the maximum molecular diameter perpendicular to this axis in which the nuclei lie must be considerably smaller in the hydrogen cyanide molecule. The hydrogen cyanide lattice, which has not yet been subjected to x-ray analysis, would seem, therefore, to offer the possibility of a molecular arrangement such that any considerable turning of the molecules would cause them to overlap and prevent further turning and, consequently, give no chance for free rotation. This appears to be the case in the cubic lattice of the linear carbon dioxide molecule.[11] If molecular rotation is not prevented by overlapping, the potential energy barrier which the molecule has to pass in order to rotate through an angle of 360° should be high because of the large dipole moment[9] 2.93×10^{-18}, which is nearly three times as large as that of the hydrogen chloride molecule,[12] 1.03×10^{-18}. This potential energy barrier may well be so large that the thermal rotational energy of the molecules is too small below the melting point to make it possible for the molecules to pass, that is, to rotate. A possible third factor is the formation of a hydrogen bond between molecules, which gives abnormal properties to ammonia, water and hydrogen fluoride and hinders or prevents molecular rotation in the lattices of their solid forms. The first two factors, however, are quite sufficient to account for the non-rotation of the hydrogen cyanide molecule in the lattice of its solid form and Lewis and Schutz[6] conclude that the great abnormality of the liquid form is due not to hydrogen bond formation but to the high dipole moment of the molecule.

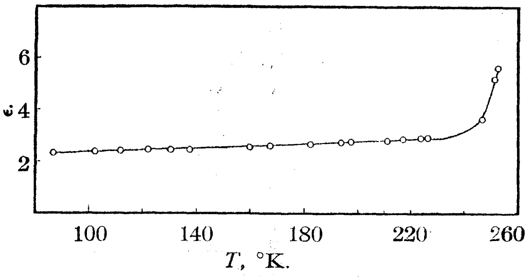

Fig. 1.—Temperature dependence of the dielectric constant (at 50 kc.) of hydrogen cyanide.

The x-ray photographs of potassium cyanide, which crystallizes in a cubic lattice, give no evidence of separate carbon and nitrogen positions, which is probably indicative of rotation of the cyanide ion in the lattice[11] (p. 364). The potential barrier to rotation of this ion should be much

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(7) Fredenhagen, *Trans. Am. Electrochem. Soc.*, **60**, 153 (1931).

(8) Werner, *Z. physik. Chem.*, **B4**, 371 (1929).

(9) Smyth and McAlpine, THIS JOURNAL, **56**, 1697 (1934).

(10) *Cf.* Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

(11) Wyckoff, "The Structure of Crystals," The Chemical Catalog Company, Inc., New York, 1931, p. 235.

(12) Zahn, *Phys. Rev.*, **24**, 400 (1924).

smaller than that for the hydrogen cyanide molecule for the departure of the ion from sphericity must be less than that of the molecule, its dipole moment should be much smaller, and the factor of the possible hydrogen bond is absent. There is, therefore, no conflict between the interpretation of the x-ray photographs as showing rotation of the cyanide ion in the potassium cyanide lattice and the non-rotation here found for the hydrogen cyanide molecule in its lattice.

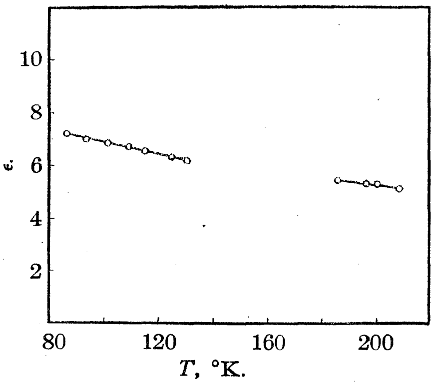

Fig. 2.—Temperature dependence of the dielectric constant (at 50 kc.) of hydrogen selenide.

The incomplete measurements on solid hydrogen selenide in Table I and Fig. 2 show by the high values of the dielectric constant and their increase with decreasing temperature as required by the Debye equation for polar molecules in the liquid and gaseous states that the molecules are able to rotate, probably with much the same freedom as in the liquid. The dielectric constant–temperature curve below 130.6°K. is sufficiently different from that above 186.0°K. to suggest a probable discontinuity somewhere between these two temperatures resulting from a transition like the upper transition found in hydrogen sulfide[2] and in hydrogen iodide.[1] Use of Natta's density value 2.456 for the cubic lattice at 103°K.[13] and the Grüneisen rule gives a density value of 2.33 at the melting point, which, combined with the dielectric constant value at 86.8°K., gives a molar polarization value 23.4. As the molar refraction for the H_α line is 11.95[14] and the atomic polarization must be small, this gives a value of about 12 for P_M, the polarization due to the dipole moment of the molecule. From this the apparent moment of the molecule is calculated to be 0.4×10^{-18}, little lower than the rough value $0.5\text{–}0.6 \times 10^{-18}$ which one would estimate from consideration of the moments of other hydrides. Naturally, this is not to be taken as a determination of the dipole moment of hydrogen selenide, but is to be regarded as evidence that the molecule has much the same freedom of rotation in its lattice down to liquid air temperature that it has in the liquid.

Although the melting point of the arsine used was 3.2° below that given in "International Critical Tables," melting occurred sharply, but because of some tendency toward decomposition, the sample was probably not of a high degree of purity. In considering the data for arsine in Table I and Fig. 3, it should be borne in mind that, because of its small dipole moment[15] 0.16×10^{-18}, the dielectric constant is small and increases but slowly with falling temperature. On this account, the scale used in Fig. 3 for the dielectric constant is much larger than that usually employed so that secondary effects having nothing to do with the fundamental factors involved may affect the shape of the curve. The drop of the dielectric constant during melting below the value for either the solid or the liquid has not been previously observed as far as the authors know, although a sharp rise above the value for either the solid or the liquid has been observed in some cases where two phases presumably existed below the melting point because of considerable quantities of impurity.[16] This drop and rise which occurs within a temperature range of only 0.3° is clearly shown by numerous values determined during the rising temperature run represented in Table I, but does not appear in either the cooling or the heating curve previously run through the melting point with the

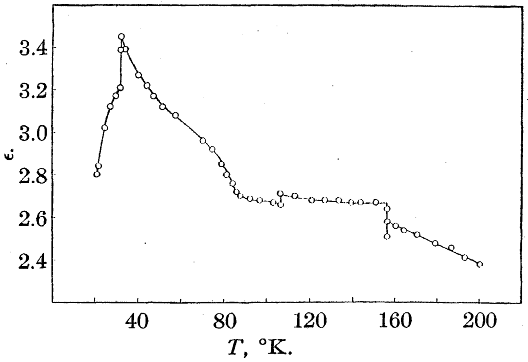

Fig. 3.—Temperature dependence of the dielectric constant (at 50 kc.) of arsine.

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(13) Natta, *Nature*, **127**, 129 (1931); *Atti accad. Lincei*, **11**, 749 (1930).

(14) Frivold, Hassel and Skjulstad, *Physik. Z.*, **37**, 134 (1936).

(15) Watson, *Proc. Roy. Soc.* (London), **117A**, 43 (1927).

(16) *Cf.* Yager and Morgan, This Journal, **57**, 2071 (1935).

same sample. The upper transition point evident at 106.6°K. was checked accurately by a temperature–time curve. This transition appears similar to the slight upper transitions occurring in hydrogen bromide,[1] iodide,[1] sulfide[2] and, probably, in the selenide. As in these substances, the rate of change of the dielectric constant with temperature is much more rapid below it than above it. The two points of inflection between the two transitions probably arise from secondary effects of which we are unaware. A single unexplained point of inflection was found in the curves for hydrogen chloride, bromide and iodide, and in an unpublished curve for a sample of hydrogen sulfide slightly less pure than that for which a curve without inflection was published.

As incomplete cancellation of the effects of the inductance of the circuit causes small errors in the dielectric constant values, differences of 0.01 or 0.02 between values at different frequencies are meaningless. However, a pronounced anomalous dispersion is evident during the lower part of the transition which is incomplete at the lowest temperature reached. Although the material was maintained within 0.3° of this temperature for three hours, the rising temperature values in Table I agree well with those obtained during the relatively rapid initial cooling, showing that stable equilibrium existed throughout. The variation of the dielectric constant with frequency is greatest at 20.7°K., where the apparent conductance actually shows a maximum at 20 kc. Evidently at least some of the arsine molecules can rotate at 20.5°K. with a difficulty which decreases rapidly with rising temperature, the variation of the dielectric constant with frequency having disappeared at 30.9°K., where the transition is still incomplete. Above 31.8°K. the acquisition of rotational freedom occurs almost as sharply as does the entire process in hydrogen chloride at its one transition. Although the thermodynamic behavior of solid hydrogen[17] requires molecular rotation and the specific heat–heat temperature curve for methane[18] shows the setting in of rotation at 20.4°K., no molecule other than these has been found to rotate at so low a temperature as that here found for arsine.

Application of the Grüneisen rule to the density value[19] 1.96 found for arsine at 103°K. gives the density at the melting point, which is used with the values in Table I to calculate a molar polarization 16.0 at 20.5°K., 19.1 at 33.7° and 15.3 at 151.2°. The apparent dipole moment calculated for the molecule from the variation of polarization with temperature in the region between 33.7 and 80°K. is 0.15×10^{-18}, indistinguishable from the value 0.16×10^{-18} obtained for the gas,[15] which would seem to indicate freedom of molecular rotation in this region comparable to that in the liquid state.

In the three groups of hydrides of which ammonia, water and hydrogen fluoride are the first members, the smallest molecule does not rotate in the cases of solid ammonia[2] and hydrogen fluoride[20] and rotates only with great difficulty in ice, probably because of hydrogen bonds between the molecules or, possibly, merely because the smallest molecules with their large dipole moments are surrounded by the strongest fields of force. The larger molecules of these three groups of hydrides show rotation which extends to lower temperature the smaller the dipole moment, arsine being the molecule of smallest moment. In the next group of hydrides, methane, the first member, having zero dipole moment and no possibility of hydrogen bond formation, rotates down to very low temperature.[18] It is evident that the moment of inertia of the molecule does not have the dominant effect in determining rotation or non-rotation that has been attributed to it at times. Monosilane[21] requires a temperature 43° higher to bring about molecular rotation than does methane, but this may be due to stronger intermolecular forces rather than to the larger moment of inertia of the molecule.

Of these hydrides which have been considered, all have cubic lattices in the regions of free molecular rotation except hydrogen iodide, which is tetragonal, its *a*- and *c*- axes differing by only 8%, and possibly monosilane which has not been determined. Since free rotation gives spherical symmetry to a molecule, it is natural that molecules possessing it form lattices corresponding to an arrangement of close-packed spheres, which is roughly approximated by the molecular arrangement in a liquid. It is not surprising, therefore, that the dielectric behavior of solid arsine above its lower transition could be roughly approximated by extrapolation of the curve for the liquid. Indeed, from a molecular point of view these solid

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[17] Pauling, *Phys. Rev.*, **36**, 430 (1930).

[18] Clusius and Perlick, *Z. physik. Chem.*, **B24**, 313 (1934).

[19] Natta, *Gazz. chim. ital.*, **60**, 851 (1930).

[20] Clusius, Hiller and Vaughen, *Z. physik. Chem.*, **B8**, 427 (1930); Clusius, *Z. Elektrochem.*, **39**, 598 (1933).

[21] Clusius, *Z. physik. Chem.*, **23**, 213 (1933).

hydrides with rotating molecules differ little from liquids.

Summary

The dielectric constants and specific conductances of solid hydrogen cyanide and hydrogen selenide have been measured from liquid air temperature to the regions of the melting point and those of arsine have been measured from liquid hydrogen temperature to the region of the boiling point over a frequency range from 0.5 to 50 kilocycles. No molecular rotation is found in solid hydrogen cyanide while the molecule rotates freely in the selenide even at liquid air temperature. The arsine molecule rotates freely down to 32.1°K. where a transition sets in, which is not complete at 20.5°K. and is accompanied by some anomalous dispersion. The molecules of the hydrides tend to rotate more readily the smaller their dipole moments.

PRINCETON, NEW JERSEY RECEIVED JUNE 29, 1936

[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Thermal Data. VI. The Heats of Combustion and Free Energies of Seven Organic Compounds Containing Nitrogen

BY HUGH M. HUFFMAN, EMORY L. ELLIS AND SIDNEY W. FOX

In the first paper[1] of this series we presented heat capacity data for the following seven compounds, *d*-alanine, *l*-asparagine (anhydrous), *l*-asparagine monohydrate, *l*-aspartic acid, *d*-glutamic acid, creatine and creatinine. These data were used to calculate the entropies of the compounds, which were further utilized in conjunction with the heats of combustion and certain other auxiliary data to calculate the standard free energies of formation of these compounds.

Due to the general unreliability of the older combustion data appearing in the literature, we have redetermined this quantity for each of the seven compounds mentioned above. In so doing we have kept constantly before us the necessity of establishing the purity and the physical state of the compounds as well as the need for calorimetry of high precision and accuracy.

These new combustion data have been used in conjunction with the entropies obtained by Huffman and Borsook[1] and certain other auxiliary data to calculate new and more reliable free energy data for these compounds.

Calorimetric Method

The method and apparatus used have been described in previous communications.[2] No essential changes in method or apparatus have been made. All of the combustions were made in a Parr bomb having a volume of 0.380 liter with an initial oxygen pressure of 30 atm. and with 1 ml. of water in the bomb. The platinum wire technique[2a] was used exclusively. During the course of this investigation our resistance thermometer developed a short circuit. After repair the thermometer characteristics were found to have changed but upon recalibration identical results for the energy equivalent of the calorimeter were found. Numerous calibrations of the calorimeter have been made, at irregular intervals throughout the course of this investigation, with Bureau of Standards benzoic acid, samples 39d and 39e, having for its isothermal heat of combustion at 25.0° the value 26,419 international joules per gram true mass. We have used oxygen from several cylinders supplied by the "Linde Air Products Company" and at cylinder pressures varying from 1950 to 450 pounds. The precision of our calibration data has remained the same as that previously reported, namely, an extreme deviation from the mean of slightly more than 0.01%. The precision error calculated from the formula recommended by Rossini[3] was 0.005%.

In several cases we have found it necessary to use oil as an auxiliary substance. The combustion value of this oil has been controlled by occasional combustions and the value found was 10,830 ± 3 cal. per gram weighed in air. When the mass of the oil is determined by difference after adding it directly to the sample in the crucible an additional uncertainty is introduced when the material is hygroscopic. To avoid this uncertainty as well as to permit the addition of small quantities, the following method was adopted. The oil was kept in a small hypodermic syringe and the amount added was determined from the mass difference in this syringe.

Units and Corrections

The unit of energy used throughout this paper is the defined conventional calorie which is derived from the international joule by multiplying by the factor 1.0004/4.185. The method of calculation, the corrections and the symbols used are the same as those given by Stiehler and Huffman.[2b] The molecular weights are based on the 1935 table of atomic weights. In applying the correction for true mass

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[1] Huffman and Borsook, THIS JOURNAL, **54**, 4297 (1932).

[2] (a) Huffman and Ellis, *ibid.*, **57**, 41 (1935); (b) Stiehler and Huffman, *ibid.*, **57**, 1734 (1935).

[3] Rossini, *Chem. Rev.*, **18**, 233 (1936).

we have used approximate densities obtained from the mass and volume of the pelleted material when other data were not available in the literature. All of the thermal data are given for the isothermal process at 25°.

In some cases the combustion was incomplete, leaving a small residue of carbon in the crucible. The mass of this carbon was determined from the mass of the crucible before and after ignition and corrected for. In no case did this correction exceed 0.003%. Some of the preparations left a residue of ash in the crucible. When this was appreciable it was corrected for by arbitrarily subtracting the weight of the ash from the weight of the sample. In the extreme case this correction was about 0.03%.

Purity and Dryness of the Materials Used

We have followed the general methods of Stiehler and Huffman[2b] to assure ourselves of the purity and dryness of the combustion samples. As mentioned above we have made routine ash determinations on each sample burned. We have also made suitable analyses such as nitrogen determinations, titrations and measurement of the optical rotation. We have attempted, furthermore, to define accurately the physical state of the compounds by photomicrographs of their crystalline condition (Fig. 1) as well as by a precise description of the method of preparation.

Preparation, Purification and Heats of Combustion of the Compounds

***d*-Alanine.**—Combustions were made on two commercial samples of this material which were purified in the following manner.

(a) A material from an unknown source was twice crystallized from water[4] by dissolving in hot water and allowing the solution to cool and deposit crystals.

(d) A Hoffmann–LaRoche product was twice crystallized from water in the above manner.

Nitrogen determinations[5] on sample (a) gave the theoretical results. The ash content of (a) was less than 0.01% and that of (d) undetectable. The specific rotation of (d) has been reported by Huffman and Borsook.[1]

This compound was very troublesome to burn as it had a decided tendency to jump out of the crucible when partially burned. We have tried all of the tricks at our command to overcome this unfortunate tendency, such as varying the crucible weight, using large amounts of oil, increasing the oxygen pressure, etc., but with little success. In all five preparations of *d*-alanine were used and the three values given in the table are the usable results from fifteen attempted combustions. *d*-Alanine appears to exist in at least two crystal modifications (see Fig. 1). Since our combustions are on a single type we cannot be sure that these are polymorphous forms.

l-Asparagine Hydrate

Material from four different commercial sources was utilized to prepare eleven combustion samples.

(a) Merck *l*-asparagine, which had been recrystallized several times for heat capacity measurements, was subjected to three additional crystallizations by dissolving in boiling water and allowing crystals to form as the solution cooled.

(b) A preparation from Hoffmann–LaRoche was used without further purification.

(c) A portion of (b) was once crystallized from water by cooling the hot solution.

(d) A portion of (b) was twice crystallized from water as in (c).

(e) Material from Pfanstiehl was twice crystallized from water.

(f) Material from Eastman was twice crystallized from water.

(g) A sample from Merck recently purchased (1936) for this research was twice crystallized from water.

(h) A portion of (a) was converted to the copper salt, which was purified by one crystallization from a large volume of water. The copper was precipitated with hydrogen sulfide and the regenerated asparagine was further purified by several crystallizations from water.

(i) A portion of (e) was recrystallized by dissolving in hot water and seeding heavily with *l*-asparagine which had been dehydrated at 100°.

(j) A portion of (e) which had been dehydrated at 100° was rehydrated by allowing to stand several days covered with water at room temperature.

(k) A part of (a) was twice more crystallized from water.

The nitrogen content of (a) was the theoretical. Measurements of the rotation of samples (a) and (b) in HCl solutions with the ratio (HCl/asparagine hydrate) equal to 12.3 gave values for $(\alpha)^{20}\mathrm{D}$ of 30.3 and 27.9, respectively. The ash content of all of the samples with the exception of (a), (h) and (k) was undetectable. In sample (h), the worst case, it was less than 0.01%.

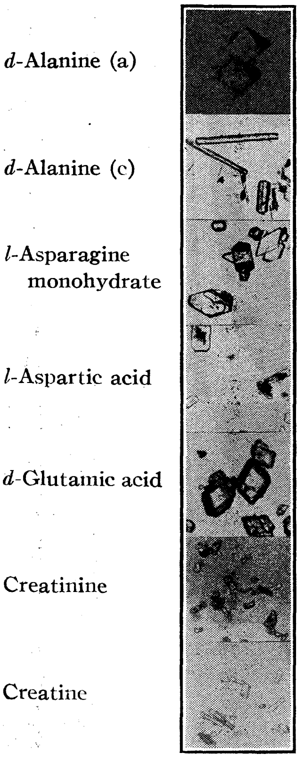

Fig. 1.

Numerous combustions on sample (a) dehydrated at 100° consistently gave results about five calories higher than the accepted value. For this reason preparations (h) and (k) were made. The result of one combustion on (k) agreed with those on (a) while the result of one combustion on (h) was about midway between those on (a) and the accepted value. Further attempts at purification were impossible because of lack of this material. When a new sample (g) was purchased from Merck it was found to yield values which agreed with the accepted result.

The combustions on anhydrous *l*-asparagine are further complicated by the fact that it appears to exist in two modi-

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[4] Redistilled water for all of the purifications.

[5] All of the nitrogen determinations with the exception of that on creatine were by micro Kjeldahl.

fications.[5a] Several combustions on specimens of (a) and (b) which had been dehydrated in the vacuum oven at 65–70° gave results from 23 to 28 calories higher than those dehydrated at 100°. Furthermore, this difference tended to decrease with the heating time, indicating that the material was changing continuously into the stable form. As a test of this hypothesis we have included in the table the result of one combustion on a sample which had been heated for seventy-eight days at 65–70° followed by eighteen hours at 100°. This additional heating caused no change in the mass of the pellet but did cause the combustion value to drop about 28 calories (as determined by comparison with a sample whose history was identical except for treatment at 100°) to agree with that of other samples dehydrated at 100°. The removal of the water of hydration takes place so slowly at room temperature that we have not been able to obtain a completely anhydrous material in this manner. At elevated temperatures the fact that dehydration is accompanied by the transition to the stable form makes it impossible to obtain a reliable combustion value for the high temperature form. We believe, however, that it is probably about 30 calories higher than that of the stable modifications.

To see if this apparent dimorphism persisted in the hydrate two attempts were made to obtain a different crystal type, preparations (i) and (j). The results of the combustions of these two hydrated samples agreed perfectly with those on the hydrate obtained in the usual manner.

Where the hydrated asparagine has been burned the following method was resorted to. The crystalline material protected from contamination by dust particles was allowed to come to equilibrium in the air of the room. Pellets were made and also allowed to equilibrate with the air of the room before burning. At the time of burning, a pellet was also dehydrated at 100° and the amount of hydration determined. In the case of sample (i) the loss in mass corresponded to 99.68% hydrate, hence a suitable correction was applied for the amount of anhydrous material present. In the other cases the material was 100% hydrated within the error ±0.02% of the measurements. Due to the fact that it is impossible to be sure that the substance is free from adsorbed gases or water the mass determinations in this case are probably less reliable than in the other cases.

***l*-Aspartic Acid.**—Material from two commercial sources was treated in the following manner to make three combustion samples.

(a) An Eastman product which had been subjected to seven recrystallizations for use in heat capacity measurements[1] was recrystallized three more times from water by dissolving in hot water and allowing the solution to cool.

(b) A portion of (a) was subjected to two additional crystallizations from water in the same manner.

(c) Material obtained from Hoffmann–LaRoche was once crystallized from water.

The nitrogen content of (a) was found to be theoretical. The rotation of the original material of sample (a) has been given in a previous communication.[1] The ash content of each of the preparations was less than 0.01%.

In addition to the values given in the table combustions on samples of (b) and (c) which had been dried for several days at 100° gave values about 2.5 calories higher than the mean value reported. These pellets showed signs of decomposition and hence the results have been discarded.

***d*-Glutamic Acid.**—A commercial sample from Pfanstiehl and a preparation made from Ajinomoto by the method of Schmidt and Foster[6] were the starting materials for the preparation of five combustion samples.

(a) A large amount of *d*-glutamic acid had been prepared from Ajinomoto and carefully purified for heat capacity measurements.[1] A portion of this material was subjected to two fractional crystallizations from water by solution at 100° and subsequent rapid cooling to zero degrees. This material was discarded when found to contain glass from the sintered glass filters used.

(b) A sample of Pfanstiehl *d*-glutamic acid was subjected to five crystallizations under the same conditions as (a).

(c) The same original material as used in preparation (a) was three times crystallized from water by dissolving at 75° and subsequent cooling rapidly to zero degrees.

(d) A portion of sample (a) was once more crystallized from water by dissolving at 100° and rapidly cooling.

(e) A portion of sample (b) was dissolved in water at 60° and rapidly cooled.

The nitrogen content of samples (a), (b) and (c) was found to be theoretical. The ash content of all of the above samples was negligible. The optical rotation of the original material for (a) has been reported previously.[1]

In addition to the values given in the table, several combustions were made on material dried at 100°. These samples were discolored and the combustion values increased with the time of heating.

Creatine (Anhydrous).—Two commercial products were utilized to prepare three different combustion samples.

(a) Eastman creatine was twice crystallized from water by dissolving in boiling water and cooling the solution.

(b) Creatine from Hoffmann–LaRoche was twice crystallized from water as above.

(d) A portion of sample (a) was dissolved in boiling water and crystallization started by seeding with anhydrous creatine which had been dehydrated at 100°.

The nitrogen content was theoretical and the ash content negligible. It was necessary to use oil to initiate the combustion.

During the course of this investigation of anhydrous creatine we have again found evidence of dimorphism. As in the case of *l*-asparagine different values were obtained for the anhydrous material depending merely on its heat treatment. Thus creatine (samples (a) and (b)) which was crystallized in the usual manner and heated to 100° for dehydrating has a lower combustion value by about five calories than that which has been dehydrated at room temperature. We have included two values obtained on sample (d), dehydrated at room temperature, which agree with combustions on the other samples dehydrated at 100°. We are investigating this phenomenon further and will make a report in a future publication.

These phenomena in the case of *l*-asparagine and creatine serve again to emphasize the necessity for a positive definition of the physical state when reporting physical properties.

[5a] Since submitting this article for publication, the existence of the two polymorphic forms of anhydrous asparagine has been confirmed by x-ray pictures, which were taken for us by Mr. G. Albrecht working in Professor Pauling's laboratory.

(6) Schmidt and Foster, *J. Exptl. Biol. Med.*, **18**, 205 (1920–21).

Creatinine.—Materials from two commercial sources were utilized to prepare four combustion samples.

(a) A sample of Pfanstiehl creatinine purchased in 1931 and extensively purified for heat capacity measurements[1] was dissolved in water at 65° and precipitated with purified acetone according to the method of Edgar and Hinegardner.[7]

(b) A portion of the starting material in (a) was converted to the hydrochloride and neutralized with ammonia according to Edgar and Hinegardner's[7] methods (a) and (b). It was finally washed with ammonia and ethyl alcohol.

(c) A sample from Eastman was dissolved in water and precipitated with acetone as in (a).

(d) A sample of Pfanstiehl creatinine especially purchased for this research (1936) was dissolved in boiling water and immediately placed in an ice-bath to crystallize. The crystals were slightly greenish. This material was again dissolved in hot water and treated with norite. The crystals from the above were again dissolved in hot water and allowed to cool and crystallize.

Nitrogen determinations on (a) gave theoretical values. Sample (c) was found to have a high ash content 0.02–0.03% while that of samples (a) and (d) was negligible. In view of the uncertainty introduced into the combustion values of (c) by the high ash content we have reported the weights only to the nearest 0.1 mg. Sample (b) was discolored and gave low combustion values, hence it was discarded.

Since most of these compounds are more or less hygroscopic the following method was adopted for an accurate determination of the mass. The pelleted samples were kept in open weighing bottles during the desiccation process, after which they were stoppered immediately and kept over phosphorus pentoxide in a desiccator until time for their combustion. The bottle was then transferred to the balance case and allowed to equilibrate for a short time. The bottle plus pellet was weighed and the pellet transferred to the crucible and the empty bottle weighed. As a check on the weight thus obtained the weight was also determined by weighing the crucible plus the pellet.

When these materials were hygroscopic it was observed that the pellet usually gained weight rapidly when first exposed to the air, the rate falling off with time and approaching a steady state. There is of course the possibility that the reaction between the material and water may appreciably change the energy content of the sample. In the case of creatinine we have investigated this possibility by burning a sample in the bomb without having any water present. The sample was transferred as rapidly as possible to the bomb and then evacuated for some time before admitting oxygen which had been passed over drierite. This combustion when corrected in a suitable manner for the initial absence of water agreed exactly with the rest of the combustions in that series. There is some uncertainty in the corrections to be applied as we found that the oxygen still contained a small and unknown amount of water vapor. For this reason we have not included this value in the table but feel that it shows that creatinine values are not appreciably affected by sorbed water.

The use of oil as an auxiliary substance serves also to give at least partial protection against sorption of water. Our feeling is that any energy effect due to this phenomenon is well within the experimental error.

There is, furthermore, the possibility that oil may react with the materials in such a manner as to affect the energy content. In the cases where we have used oil we have either varied the amount of oil or have made combustions in which no oil was used. The results show that this effect if present is negligible.

The experimental results of the combustion on these seven compounds are given in Table I. We have utilized the experimental values to calculate certain other useful data. These appear in Table II along with some auxiliary data which have been used. Finally we have utilized these new values for ΔH_f^0 in conjunction with the entropy data of Huffman and Borsook[1] to calculate new and more reliable values for the free energies of formation. We have used the same values for the entropies of the elements and the heats of formation of water and carbon dioxide as were used by Stiehler and Huffman.[2b]

Discussion of the Results

As in the previous papers in this series we have chosen as our limits of error the extreme deviation from the mean of the experimental results in each case and have also allowed for an additional uncertainty of 10% in the Washburn correction. We have taken numerous precautions to assure ourselves of the purity, dryness and physical state of these compounds so that we feel that absolute errors due to these factors have been largely eliminated. We have not assigned any limits of error to the heats or free energies of formation of these compounds, due to uncertainties in the accuracy of certain of the auxiliary data required. We have included photomicrographs of the crystalline compounds which were burned. In the case where the original material was hydrated, the physical state of the anhydrous material must be defined by the method of dehydration.

All of these compounds have been burned by earlier workers. Wrede[8] has burned *d*-alanine, Fischer and Wrede[9] have burned *l*-aspartic acid and *d*-glutamic acid, Emory and Benedict[10] have burned all of the compounds except anhydrous *l*-asparagine. Stohmann and Langbein[11] have burned anhydrous *l*-asparagine and anhydrous creatine.

With the exception of Wrede[8] none of the above authors include sufficient data for correcting their values in terms of newer thermochemical standards. We have, however, made approximate

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[7] Edgar and Hinegardner, *J. Biol. Chem.*, **56**, 881 (1923).

[8] Wrede, *Z. physik. Chem.*, **75**, 81 (1910).

[9] Fischer and Wrede, *Sitzber. kgl. preuss. Akad. Wiss.*, 687 (1904).

[10] Emory and Benedict, *Am. J. Physiol.*, **28**, 301 (1911).

[11] Stohmann and Langbein, *J. prakt. Chem.*, **44**, 336 (1891).

TABLE I

THE EXPERIMENTAL DATA

Sample	P_2O_5 vac.	Desiccation Vac. 70° hours	Oven 100°	True mass	Total heat evolved, cal.	Cal. from HNO_3	Cal. from oil	Cal. from paper and Elt	$-\Delta U_B/m$, cal. g.$^{-1}$	Deviation
d-Alanine (a)	2232			1.47660	6452.6	18.6		17.1	4345.7	−0.8
d-Alanine (a)	168			1.22765	5845.9	16.7	474.4	17.3	4347.8	1.3
d-Alanine (d)			120	1.35550	6411.9	20.0	484.2	16.5	4346.1	−0.4
Mean									4346.5	±0.8
l-Asparagine (b)			240	1.81750	6385.1	19.4		17.6	3492.8	−0.3
l-Asparagine (b)		1872	18	1.77845	6252.9	21.7		17.8	3493.7	.6
l-Asparagine (c)			120	1.80005	6322.3	19.6		16.5	3492.3	− .8
l-Asparagine (d)			96	1.82520	6414.3	22.0		16.1	3492.9	− .2
l-Asparagine (e)			456	1.80440	6340.7	20.9		16.6	3493.3	.2
l-Asparagine (f)			146	1.80615	6346.6	21.2		16.7	3492.9	− .2
l-Asparagine (g)			116	1.82215	6403.0	20.1		16.9	3493.7	.6
Mean									3493.1	± .4
l-Asparagine hyd. (e)				2.05405	6309.2	16.0		17.8	3055.2	− .5
l-Asparagine hyd. (e)				2.05475	6311.4	16.2		16.8	3055.6	.1
l-Asparagine hyd. (i)				2.08370	6405.0	17.0		16.7	3056.3[a]	.6
l-Asparagine hyd. (j)				2.07860	6385.5	16.0		17.1	3055.6	− .1
Mean									3055.7	± .3
l-Aspartic acid (a)	1008			2.18075	6312.9	12.2		17.0	2881.4	− .5
l-Aspartic acid (a)	1032			2.18255	6318.6	11.9		17.2	2881.7	− .2
l-Aspartic acid (a)		144		2.18315	6322.0	12.1		16.6	2882.7	.8
l-Aspartic acid (a)			96	2.17760	6307.9	12.3		18.5	2882.6	.7
l-Aspartic acid (b)	216	192		2.12940	6164.2	11.9		16.7	2881.4	− .5
l-Aspartic acid (c)	216			2.18060	6310.9	11.6		17.3	2880.8	−1.1
l-Aspartic acid (c)		336		2.16625	6272.9	11.5		17.2	2882.5	0.6
Mean									2881.9	± .7
d-Glutamic acid (b)	216			1.73255	6365.8	13.3		16.4	3657.1	.2
d-Glutamic acid (b)		52		1.65785	6310.9	12.5	218.8	16.5	3657.2	.3
d-Glutamic acid (b)		52		1.65460	6300.9	11.6	223.6	16.6	3655.9	−1.0
d-Glutamic acid (b)		72		1.72440	6556.4	13.4	218.5	17.1	3657.7	0.8
d-Glutamic acid (b)		168		1.67065	6361.6	12.6	222.3	16.4	3657.5	.6
d-Glutamic acid (c)	360			1.71895	6535.9	12.9	220.1	17.4	3656.6	− .3
d-Glutamic acid (c)	192	4		1.65770	6310.3	12.3	221.1	17.4	3655.3	−1.6
d-Glutamic acid (d)	96			1.66820	6354.6	13.1	222.4	17.5	3657.6	0.7
d-Glutamic acid (d)	192	4		1.66365	6338.5	12.6	224.0	17.4	3657.3	.4
d-Glutamic acid (e)		10		1.66830	6343.4	13.2	212.5	17.4	3656.3	− .6
Mean									3656.9	± .6
Creatine (a)			192	1.44350	6324.1	25.2	164.7	17.2	4237.6	− .5
Creatine (a)			192	1.40560	6293.4	24.8	293.0	17.4	4238.9	.8
Creatine (a)	648	96[b]		1.27975	6322.9	24.7	859.4	17.2	4237.5	− .8
Creatine (a + b)	120		168	1.43285	6347.8	25.1	232.0	16.5	4239.2	1.1
Creatine (b)			216	1.44615	6352.5	25.2	181.1	16.6	4237.6	−0.5
Creatine (d)	570			1.36670	6455.3	26.0	620.1	17.1	4238.0	− .1
Creatine (d)	1416			1.31245	6345.4	24.4	740.8	17.6	4238.4	.3
Mean									4238.1	± .6
Creatinine (a)	380			1.27175	6330.2	30.1		17.0	4940.7	.6
Creatinine (a)	48	400		1.27245	6332.8	29.5		16.6	4940.6	.5
Creatinine (a)	48		42	1.27450	6343.1	30.0		17.7	4939.8	− .3
Creatinine (a)	48		72	1.27385	6340.2	30.4		16.9	4940.3	.2
Creatinine (a)	48		72	1.27485	6344.6	29.5		16.2	4940.9	.8
Creatinine (c)	720			1.2747	6345.0	29.9		17.4	4940.4	.3
Creatinine (c)	720			1.2746	6343.6	30.6		17.8	4939.0	−1.1
Creatinine (c)	720			1.2761	6350.1	29.8		16.9	4939.6	−0.5
Creatinine (d)			90	1.27400	6342.1	29.7		19.1	4939.8	− .3
Mean									4940.1	± .5

[a] This value is corrected for the fact that the sample was only 99.68% hydrated.

[b] Temperature of vacuum oven 45–50°.

TABLE II

SUMMARY OF DERIVED DATA

Substance	Formula	Mol. wt.	Density	$-\Delta U_B$, kcal. mole^{-1}	$-\Delta U_R$, kcal. mole^{-1}	$-\Delta H_R$, kcal. mole^{-1}	$-\Delta H_f^0$ kcal. mole^{-1}	$\Delta U_R/dT$ mole^{-1} cal.	$-\Delta F_f^0$ kcal. mole^{-1}
d-Alanine	$C_3H_7O_2N$	89.063	1.38	387.11 ± 0.11	386.86 ± 0.13	387.10 ± 0.13	134.81	38	88.99
l-Asparagine (anhyd.)	$C_4H_8O_3N_2$	132.078	1.44	461.36 ± 0.13	460.93 ± .17	460.63 ± .17	189.58	43	127.58
l-Asparagine (hyd.)	$C_4H_{10}O_4N_2$	150.094	1.54	458.64 ± .15	458.25 ± .19	457.95 ± .19	260.57	50	184.74
l-Aspartic acid	$C_4H_7O_4N$	133.063	1.66	383.47 ± .15	383.01 ± .19	382.57 ± .19	233.49	36	175.59
d-Glutamic acid	$C_5H_9O_4N$	147.078	1.54	537.85 ± .23	537.36 ± .28	537.31 ± .28	241.30	49	174.94
Creatine (anhyd.)	$C_4H_9O_2N_3$	131.094	1.33	555.59 ± .16	555.21 ± .20	555.06 ± .20	129.31	48	64.20
Creatinine	$C_4H_7ON_3$	113.079	1.31	558.62 ± .12	558.26 ± .16	558.11 ± .16	57.94	38	7.89

corrections and these corrected values are compared with our values in Table III. In the case of creatinine Emory and Benedict[10] calculated their result on the basis of the carbon dioxide found. We have corrected their reported value back to the mass basis which brings it into much better agreement with our value.

TABLE III

COMPARISON OF THE PRESENT DATA WITH VALUES FROM THE LITERATURE

	Older data			New value		Difference
Substance	Reference	$-\Delta H_R$, kcal.	mole^{-1}	$-\Delta H_R$, kcal.	mole^{-1}	%
d-Alanine	8	386.87	±0.19	387.10	±0.13	−0.06
d-Alanine	10	390.6	±1.2	387.10	± .13	.90
l-Asparagine (anh.)	11	462.3	±1.2	460.63	± .17	.37
l-Asparagine (hyd.)	10	458.4	±1.2	458.50	± .19	− .01
l-Aspartic acid	10	381.9	±1.1	382.57	± .19	− .18
l-Aspartic acid	9	384.7	±1.3	382.57	± .19	+ .48
d-Glutamic acid	9	541.7	±0.7	537.31	± .28	+ .82
d-Glutamic acid	10	536.6	±1.3	537.31	± .28	− .13
Creatine	11	558.4	±1.5	555.06	± .20	+ .54
Creatine	10	553.8	±1.3	555.06	± .20	− .23
Creatinine	10	556.4	±1.3	558.11	± .16	− .31

In a recent paper Zittle and Schmidt[12] report the heat of hydration of anhydrous *l*-asparagine as 2250 ± 200 calories. This compares favorably with the value of 2680 ± 330 calories as calculated from our combustion data on these two compounds. They do not state how the anhydrous material was obtained but it was very probably by treatment at 100° or above.

Summary

1. The experimental values of the heats of combustion at constant volume and at 25° of seven organic compounds are given.

2. From the experimental values the heat of combustion at constant pressure and the heat of formation have been calculated.

3. These new values for heats of formation have been used with existing entropy data to calculate more reliable free energy data.

[12] Zittle and Schmidt, *J. Biol. Chem.*, **108**, 161 (1935).

PASADENA, CALIF. RECEIVED JUNE 30, 1936

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Coördination Compounds of Platinous Halides with Unsaturated (Ethylene) Substances

BY M. S. KHARASCH AND T. A. ASHFORD[1]

Introduction

Platinum is an unusually versatile element. It has primary valences of two and four, and it forms two series of coördination compounds with both organic and inorganic substances. In these the metal exhibits the coördination numbers of four and six, respectively. Stereoisomers have been obtained in both series. Where the coördination number is six, the accepted view is that the valence bonds of the platinum atom are directed toward the corners of an octahedron; giving rise to the following two stereoisomeric configurations for compounds of the type PtX_4A_2.[2] Some compounds of the type PtX_2A_2 also exist in two stereoisomeric forms: *cis* and *trans*[2] (p. 338).

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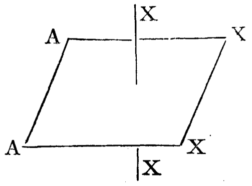
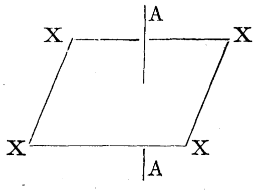
[1] This communication is an abstract of a dissertation submitted by T. A. Ashford in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Chicago.

[2] Werner, "Lehrbuch der Stereochemie," Gustave Fischer, Jena, 1904, p. 350.





Furthermore, Reihlen and Hühn[3] report that they have resolved into optical antipodes platinum compounds of coördination number four. It is still an unsettled question whether the configuration of these compounds is planar, tetrahedral or pyramidal.[4]

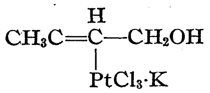
Several classes of coördination compounds of platinum, notably those with ammonia and with the amines, have been studied extensively. However, two important classes, namely, those with unsaturated substances and those with nitriles, have received scant attention because of the lack of satisfactory methods for preparing these complexes.

In the work reported in this paper a particularly simple general method has been developed for the preparation of organo-platinum complexes with unsaturated compounds. This method has been used to prepare a large number of compounds, the properties of which are herein described.

Previous Work

The literature contains references to complex salts of the type $K(Un\cdot PtX_3)$, in which Un is an unsaturated molecule containing an ethylene bond. The first compound of this series was obtained by Zeise,[5] who isolated a substance with the empirical formula $K(C_2H_4\cdot PtCl_3)\cdot H_2O$, from a reaction mixture of chloroplatinic acid and alcohol. Birnbaum[6] prepared similar compounds with propylene and amylene, and Chojnacki[7] obtained $K(C_2H_4\cdot PtBr_3)$, with platinic bromide.

Biilmann and his collaborators[8] have extended the work to unsaturated substances other than hydrocarbons, and they have prepared compounds with unsaturated alcohols, acids and aldehydes. Pfeiffer and Hoyer[9] have prepared similar substances from allyl alcohol, allyl acetate, crotyl alcohol and crotyl aldehyde. The latter workers consider that in these compounds the platinum atom is coördinately bound directly to the carbon atom by a single bond; they propose the following structure.



$$CH_3C{=}\overset{H}{\underset{PtCl_3\cdot K}{C}}{-}CH_2OH$$

This structure indicates that the compounds are derivatives of the metallic chloroplatinates, in which a chloride ion has been replaced by an unsaturated molecule. There is, however, no experimental evidence that the substances are monomolecular.

The series from which the compounds discussed above are derived is obviously $Un\cdot PtX_2$. As will be shown later, however, substances of this type are bimolecular and should be written $(Un\cdot PtX_2)_2$. Recently, Anderson[10] obtained $(C_2H_4PtCl_2)_2$ by refluxing ethyl alcohol with sodium chloroplatinate. This reaction is very complex, presumably involving at least four steps. Preliminary attempts to extend this method to other alcohols have not as yet proved successful.

General Method of Preparation

The most direct method for preparing a compound of the type $(Un\cdot PtCl_2)_2$ or $(Un\cdot PtBr_2)_2$ would be to combine a platinous halide with an unsaturated compound. However, attempts to apply this method have given unsatisfactory results. Platinous halides are very insoluble and inert substances; consequently platinic halides have been used.

The general method here described departs radically from that of Anderson since anhydrous platinic chloride or bromide in an anhydrous solvent is used instead of the metallic haloplatinates. It differs further in that the unsaturated compounds are used instead of the alcohols. The method is rapid as well as general. The reaction is complete in about an hour.

Although the reaction, as outlined above, and described in more detail in the experimental part, appears simple, it is probably more complex than might at first be supposed. Hydrogen halide is usually evolved during the reaction, and in some instances a small quantity of platinum separates. Halogenation of the unsaturated compound also has been demonstrated.

Physical and Chemical Properties

The coördination compounds $(Un\cdot PtCl_2)_2$ are well-defined crystalline substances. When heated

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(3) Reihlen and Hühn, *Ann.*, **489**, 42 (1931).

(4) *Cf.* Dwyer and Mellor, THIS JOURNAL, **56**, 1551 (1934).

(5) Zeise, *Pogg. Ann.*, **21**, 497 (1831).

(6) Birnbaum, *Ann.*, **145**, 67 (1869).

(7) Chojnacki, *Jahresber.*, 510 (1870).

(8) Biilmann, *Ber.*, **33**, 2196 (1900); Biilmann and Anderson, *ibid.*, **36**, 1565 (1903); Biilmann and Hoff, *Chem. Zentr.*, 88, I, 562 (1917).

(9) Pfeiffer and Hoyer, *Z. anorg. allgem Chem.*, **211**, 241 (1933).

(10) Anderson, *J. Chem. Soc.*, 971 (1934).

in a melting-point tube they do not melt sharply, but darken over a range of several degrees. They vary widely in stability. The greatest difference has been observed between the compounds obtained from *trans*-dichloroethylene and from dipentene. The former decomposes in a few days; the latter appears unchanged even after standing in the air for ten months.

The compounds are in general soluble in acetone, chloroform and alcohol; they are less soluble in benzene, and difficultly soluble or insoluble in glacial acetic acid. Those of low molecular weight are soluble in sodium chloride solution, presumably forming compounds analogous to Zeise's salt

$$[(CH_3)_2C{=}CH_2{\cdot}PtCl_2]_2 + 2NaCl \longrightarrow 2Na(CH_3)_2C{=}CH_2{\cdot}PtCl_3$$

When treated with pyridine the substances decompose, liberating the olefin and forming the pyridine platinous chloride.

$$[Un{\cdot}PtCl_2]_2 + 4C_5H_5N \longrightarrow 2Un + 2(C_5H_5N)_2{\cdot}PtCl_2$$

Concentrated hydrochloric acid decomposes them.

$$Un{\cdot}PtCl_2]_2 + 4HCl \longrightarrow 2Un + 2H_2PtCl_4$$

Bromine also decomposes these substances, forming the platinum halides and the bromine addition product of the unsaturated compound.

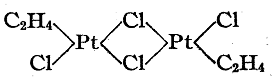
Molecular Weight

The coördination compounds of the series $(Un{\cdot}PtCl_2)_2$ are unstable at higher temperatures; consequently the ebullioscopic method for the determination of their molecular weights is inapplicable. For the same reason the Rast method cannot be used. With the exception of the compound obtained from isobutylene, these substances are also sparingly soluble in benzene. However, the depression of the freezing point of benzene by isobutylene platinous dichloride indicates that the substance is bimolecular, $[(CH_3)_2C{=}CH_2{\cdot}PtCl_2]_2$, and no doubt the other compounds of the same series are likewise.[11]

Structure of the Compounds of the Type $[(Un{\cdot}PtCl_2)]_2$

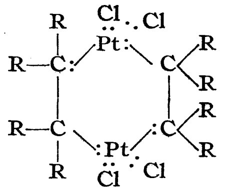
That these compounds are derivatives of platinous chloride seems fairly well established. Their analyses as well as their reactions with pyridine, with concentrated hydrochloric acid, and with bromine point to this conclusion. Furthermore, the compound prepared from dipentene and platinic chloride is the same as the one obtained by treating dipentene with platinous chloride in the presence of dry hydrogen chloride.

Anderson[10] has proposed for ethylene platinous chloride the formula

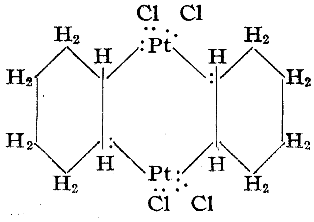


Against this formula, however, may be raised the serious objection that it makes a chlorine atom form two coördination bonds.

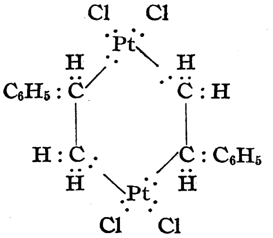
Consideration of the electron arrangement in the substance aids in deriving a structure. The general electronic configuration here proposed for all compounds of the type $(Un{\cdot}PtCl_2)_2$



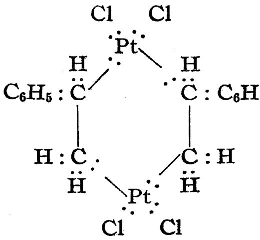
is specifically exemplified in the following formula for cyclohexene platinous chloride



When monosubstituted ethylenes are used, there is a possibility of structural isomerism. For instance, the compound derived from styrene might have either of the two structures shown by the formulas



and



It is interesting to note that each of these structural isomers contains two asymmetric carbon atoms, and can exist in three stereoisomeric forms. With more complex substituted ethylenes, the number of isomers becomes still greater. Further study of these substances is contemplated.

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[11] Anderson[10] has estimated the molecular weight of ethylene platinous chloride by the Barger–Rast method, and his results point to a bimolecular form.

Applicability of the Method

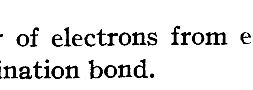
The method described above has been used to prepare coördination compounds from the following unsaturated substances: cyclohexene, dipentene, pinene, ethylene, isobutylene, styrene, stilbene and *trans*-dichloroethylene. No crystalline coördination compounds could be isolated from the following substances: allyl chloride, allyl bromide, allylbenzene, vinyl bromide, tridecene, isostilbene and *cis*-dichloroethylene. The latter substances react with the platinic chloride to give red solutions but no crystals separate. In all these cases red gums are obtained.

It is interesting that crystalline compounds have been isolated from *trans*-dichloroethylene and from *trans*-diphenylethylene, whereas all attempts to obtain crystalline substances from their *cis*-isomers have failed. It would be desirable to extend the work to other pairs of *cis–trans* stereoisomers, to determine how general this relation is. In this connection it should be noted that from cyclohexene, dipentene and pinene (which are *cis* compounds) crystalline substances have been isolated.

The method does not seem to be applicable to unsaturated acids and their esters. All attempts to prepare compounds with maleic anhydride, maleic and fumaric acids and their ethyl esters, and with cinnamic ester have failed. These substances do not appear to react at all with platinic chloride.

Coördination Compound of Platinic Chloride with Azobenzene

It might be expected that azo compounds which contain a double bond between two nitrogen atoms would form coördination compounds similar to those obtained from the olefins. However, the compound obtained from the interaction of platinic chloride and azobenzene has the empirical formula $(C_6H_5N{=}NC_6H_5)_2PtCl_4$. This compound is analogous to the coördination compounds of the type $(RCN)_2PtCl_4$ obtained from platinic chloride and nitriles. It appears that the azo group is equivalent to a nitrile group. For this compound the following formula is proposed



$$\begin{array}{c} \cdot\cdot\,\mathrm{Cl}\ \ \mathrm{Cl}\,\cdot\cdot \\ C_6H_5:\ddot{N}\ \ \ddot{N}:C_6H_5 \\ :\mathrm{Pt}: \\ C_6H_5:\ddot{N}\ \ \ddot{N}:C_6H_5 \\ \cdot\cdot\,\mathrm{Cl}\ \ \mathrm{Cl}\,\cdot\cdot \end{array}$$

Here one pair of electrons from each azo group forms a coördination bond.

Experimental Part

Preparation of Anhydrous Platinic Chloride.—Anhydrous platinic chloride is prepared by a modification of the method of Rosenheim and Löwenstamm.[12] Chloroplatinic acid is prepared by the usual method. The acid melts at about 60° and still contains six molecules of water of crystallization. The melted acid is poured into a porcelain boat and the boat with its contents is placed in a glass tube contained in an electric furnace. A slow current of dry chlorine is passed through the apparatus. The temperature is raised gradually to 275° in the course of two hours; it is kept there for one-half hour and then is allowed to fall gradually. When the apparatus has cooled to about 150°, the boat is removed and the contents are pulverized while hot in an agate mortar. The powdered substance is again placed in the furnace in an atmosphere of chlorine at 275° for one-half hour. It is then allowed to cool and is placed in a glass-stoppered bottle in a desiccator over concentrated sulfuric acid.

Anal. Calcd. for $PtCl_4$: Pt, 57.9. Found: Pt, 57.7.

Platinic chloride thus prepared is a very hygroscopic red-brown substance. It is slightly soluble in nitrobenzene, glacial acetic acid and alcohol, very slightly soluble in chloroform and ether, and insoluble in benzene and in toluene.

Preparation of Platinous Chloride.—Platinous chloride is prepared by a modification of the method of Berzelius.[13] Pure chloroplatinic acid is heated over a free flame to about 150°. The resulting solid is placed in a boat, and the boat with its contents is placed inside the furnace. The temperature is raised to 360–380° for about two hours, while a slow current of air is passed through the apparatus. The greenish solid is then pulverized and is again placed in the furnace at 360° for about one hour. After cooling, the solid is boiled with water containing a few drops of hydrochloric acid to remove any unchanged platinic chloride. The platinous chloride, which is insoluble, is washed twice by decantation and again placed in the furnace at 360° for one-half hour.

Anal. Calcd. for $PtCl_2$: Pt, 73.4. Found: Pt, 73.2.

Platinous chloride is a greenish-gray solid. It is insoluble in benzene, chloroform, glacial acetic acid and alcohol.

General Method of Preparation of Complexes

The most direct method for preparing a compound of the type $(Un{\cdot}PtCl_2)_2$ or $(Un{\cdot}PtBr_2)$ would be to combine a platinous halide with an unsaturated compound. However, attempts to apply this method have given unsatisfactory results. Platinous halides are very insoluble and inert substances; consequently platinic halides have been used.

To prepare the chlorides 0.5 g. of platinic chloride is suspended in 10 cc. of glacial acetic acid and 0.5 cc. (about 2–4 moles) of the unsaturated hydrocarbon is added (in the case of pinene 1 cc. is added). The mixture is warmed in the steam-bath for about ten minutes. During this period the platinic chloride goes into solution and the reaction is completed. Crystals of the chloride

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[12] Rosenheim and Löwenstamm, *Z. anorg. Chem.*, **37**, 403 (1903).

[13] Berzelius, *Schweigger's J.*, **7**, 55 (1813).

separate out from the filtrate with or without cooling and these are collected and washed with additional portions of the solvent. In the case of *cyclohexene* 1 g. of the chloride is triturated with 0.25 g. (1 mole) of the hydrocarbon in 15 cc. of glacial acetic acid and after a few minutes 1 cc. (3 moles) more of the cyclohexene is added, considerable heat being evolved and the reaction going to completion.

In the case of *stilbene* 0.25 g. of the hydrocarbon also is first added and the mixture is heated on the steam-bath, the platinic chloride being completely dissolved in about fifteen minutes to form a red solution. After filtration an additional 0.5 g. (2 moles) of stilbene is added.

Platinic bromide can also be used in place of the chloride and it has the advantage of being more soluble in glacial acetic acid. In the case of *cyclohexene* 0.2 g. of the bromide is dissolved in 5 cc. of glacial acetic acid and 1 cc. of cyclohexene is added. In a few minutes the deep red solution becomes pale orange and long needles separate.

In the case of *styrene* 2 cc. of the hydrocarbon is added to 0.5 g. of the bromide in 10 cc. of glacial acetic acid.

Preparation of Ethylene Platinous Chloride ($(C_2H_4 \cdot PtCl_2)_2$).—About 1 g. of platinic chloride is suspended in about 25 cc. of anhydrous benzene. The suspension is kept at 70° for about one hour, while ethylene from a cylinder is bubbled through it. After standing at room temperature for twenty-four hours, the reaction mixture is again warmed to 70° and treated with ethylene. During these operations most of the platinic chloride goes into solution, and at the same time a considerable quantity of hydrogen chloride is evolved. The hot solution is filtered, and from the filtrate, upon cooling, orange crystals separate. They are crystallized from benzene.

This compound is identical with the one prepared by Anderson[10] by refluxing absolute alcohol with sodium chloroplatinate.

Preparation of Isobutylene Platinous Chloride $[(CH_3)_2C{=}CH_2 \cdot PtCl_2]_2$.—About 0.5 g. of platinic chloride is suspended in 10 cc. of glacial acetic acid and the mixture is warmed to 50°. Isobutylene, prepared by heating *t*-butyl alcohol with oxalic acid, is then bubbled through the suspension. In the course of a few minutes the platinic chloride dissolves, giving a red solution. The solution is filtered. As more isobutylene is bubbled through the filtrate orange crystals separate. The crystals are washed with glacial acetic acid.

Molecular Weight.—The solubility of this compound in benzene permits an accurate determination of its molecular weight. The compound is found to be bimolecular: solute, 0.1330, 0.2406, 0.2406 g.; solvent, 8.742, 8.742, 17.484 g.; average depression, 0.119, 0.223, 0.107°. Calcd. for $(C_4H_8 \cdot PtCl_2)_2$: mol. wt., 644.4. Found: mol. wt., 654, 633, 658.

Reaction of Stilbene Platinous Chloride with Pyridine.—About 0.2 g. of stilbene platinous chloride is dissolved in 2 cc. of chloroform and 10 drops of pyridine added. A yellowish precipitate, presumably pyridine platinous chloride, separates. About 25 cc. of petroleum ether is added, and the filtrate is evaporated to dryness. A crystalline substance melting at 125° is obtained. A mixture of this substance with stilbene also melts at 125°. The reaction evidently proceeds according to the equation

$$(C_6H_5CH{=}CHC_6H_5PtCl_2)_2 + 4C_5H_5N \longrightarrow 2C_6H_5CH{=}CHC_6H_5 + 2(C_5H_5N)_2PtCl_2$$

Reaction of Stilbene Platinous Chloride with Concentrated Hydrochloric Acid.—About 0.1 g. of stilbene platinous chloride is dissolved in 10 cc. of benzene, and 20 cc. of concentrated hydrochloric acid is added. After shaking for about one hour the mixture is allowed to stand overnight. The benzene layer becomes colorless, while the aqueous layer becomes orange. The benzene layer upon evaporation gives colorless crystals, melting at 125°. A mixture of these crystals with stilbene also melts at 125°. The aqueous layer upon evaporation at 100° gives platinous chloride.

Reaction of Stilbene Platinous Chloride with Bromine.—About 0.3 g. of stilbene platinous chloride is dissolved in 20 cc. of chloroform and an excess of bromine in carbon tetrachloride is added. The solution is then evaporated under reduced pressure. The red mass is extracted with petroleum ether, and the solution after filtering is evaporated to dryness. The solid that is obtained and also a mixture with stilbene dibromide melts at 237°. The residue from the extraction is soluble in water, consisting presumably of platinic chloride and platinic bromide.

Cis-Phenylethylene; Isostilbene.—This substance is prepared by hydrogenation of tolane in methyl alcohol solution in the presence of platinum catalyst, until the theoretical amount of hydrogen is absorbed. Upon evaporation of the solvent an oil is obtained. This oil is dissolved in light petroleum ether (b. p. 30–35°), and placed in acetone–carbon dioxide mixture to precipitate any unchanged tolane. The cold solution is then filtered and the filtrate is evaporated, leaving the pure substance in the form of an oil.

All attempts to prepare crystalline coördination compounds with isostilbene have failed. Nitrobenzene, benzene, chloroform and glacial acetic acid have been used as solvents, and the temperature as well as the time of heating have been varied. In all cases the platinic chloride goes into solution while hydrogen chloride is evolved. Under all conditions red gums have been obtained.

Preparation of Trans-Dichloroethylene Platinous Chloride, *trans*-$(C_2H_2Cl_2 \cdot PtCl_2)_2$.—About 0.5 g. of platinic chloride is suspended in 10 cc. of benzene, and 1 cc. of *trans*-dichloroethylene is added. The mixture is warmed to 40–50° for about three hours, during which most of the platinic chloride goes into solution and at the same time a considerable quantity of hydrogen chloride gas is evolved. The reaction mixture is then heated to the boiling point of benzene and filtered. From the filtrate amber crystals separate on cooling.

Cis-Dichloroethylene.—Several attempts to isolate a crystalline compound with *cis*-dichloroethylene have failed. As in the case of *cis*-diphenylethylene gums have been obtained.

Preparation of Di-azobenzene Platinic Chloride $(C_6H_5N{=}NC_6H_5)_2 \cdot PtCl_4$.—About 0.5 g. of platinic chloride is suspended in 10 cc. of glacial acetic acid, a gram of azobenzene added to the mixture and the whole warmed on a steam-bath. After about one hour the platinic chloride goes into solution and at the same time a brick-red solid separates. The compound is purified by washing successively with glacial acetic acid, benzene and petroleum ether.

Anal. Calcd. for $(C_6H_5N{=}NC_6H_5)_2 \cdot PtCl_4$: Pt, 27.84. Found: Pt, 27.5, 27.6.

Table I

Organo Platinum Compounds: Analyses, Chemical, Physical and Optical Properties

Platinous chlorides	Color	Optical data[a] Form	Bire.	Ext. angle	Solubilities[b] CHCl₃	Ether	Bz	EtOH	Glac. HAc	Acetone	Water	NaCl soln.	M.p., °C.	Platinum, % Calcd.	Found	Found
Cyclohexene	sl. or.	l. silky needles[c]	...	par. sym. obl.	s.	s.	sl. s.	v. s.	ins.	v. s.	...	ins.	145–146	56.07	56.0	56.0[i]
Dipentene	f. yel.	biax. pr.[c]	low	34°	v. s.	ins.	v. sl.	ins.	ins.	s.	...	ins.	151–152	48.53	48.4[d]	48.3[e,j]
Pinene	f. yel.	prisms[c]	high	6°	v. s.	sl.	s.	sl.	sl.	s.	...	ins.	138–141	48.53	48.6	48.6
Ethylene	or.	tablets[c]	high	32°	s.	v. s.	s.	v. s.	ins.	v. s.	sl.[g]	sl.	170–180[f]	66.35	65.7	65.7
Isobutylene	or.	rhb. pl.	...	18°	v. s.	v. s.	v. s.	v. s.	sl.	v. s.	ins.[g]	v. s.	144–145	60.59	60.6	60.7
Styrene	or.	hex. pr.[c]	fair	30°	s.	s.	sl.	...	v. sl.	s.	ins.	v. sl.	169–171	52.73	52.6	52.6
Stilbene	or.	sm. hex. pr.[c]	high	30°	v. s.[h]	s.	v. sl.	v. sl.	ins.	v. s.	...	ins.	191–192	43.75	43.7	43.7[k]
trans-Dichloroethylene	or.	cryst.[c]	high	par.	s.[h]	...	s.	...	...	s.	...	...	155–160	53.77	54.6	54.7
Cyclohexene ·PtBr₂	or.	l. sl. need.[c]	fair	par.	s.	ins.	v. sl.	v. sl.	ins.	sl.	...	...	150–151	44.66	44.5	44.7
Styrene·-PtBr₂	rose	hex. pr.[c]	fair	32°	s.	ins.	sl.	ins.	ins.	sl.	...	ins.	153–154	42.52	42.4	42.5

[a] Abbreviations: par., parallel; sym., symmetrical; obl., oblique; ext., extinction; bire., birefringence; or., orange; yel., yellow; f., faint; l., long; sm., small; pl., plates; sl., slender; pr., prisms; hex., hexagonal. [b] Abbreviations: s., soluble; v., very; sl., slightly soluble; ins., insoluble. [c] Anisotropic. [d] Prepared from platinous chloride and dipentene. [e] Prepared from platinic chloride and dipentene. [f] After standing in air for about three weeks it decomposes at 125–130°. [g] Also in petroleum ether. [h] Also in nitrobenzene. [i] % Chlorine calcd.: 20.37. Found: 20.34 and 20.44. [j] % Chlorine calcd.: 17.63. Found: 17.7 and 17.7. [k] % Chlorine calcd.: 15.89. Found: 15.8 and 15.8.

The compound decomposes at 168–170°.

Solubility.—This compound is soluble in acetone, chloroform and ether; and slightly soluble in glacial acetic acid, alcohol and benzene.

Summary

1. It has been shown that anhydrous platinic halides react with ethylenic substances to give coördination compounds of the type $(Un \cdot PtX_2)_2$.

2. The behavior of these coördination compounds with various reagents has been described.

3. A ring formula has been proposed for the coördination compounds.

Chicago, Ill.

Received June 8, 1936

[Contribution from the Chemical Laboratory of Harvard University]

The Orientation of *p*-Methoxydiphenyl in the Friedel and Crafts Reaction

By L. F. Fieser and Charles K. Bradsher

In the course of certain synthetic work the occasion arose to investigate the condensation of *p*-methoxydiphenyl with succinic anhydride in the presence of aluminum chloride, and it was found that the reaction proceeds smoothly in nitrobenzene solution, giving a mixture of two isomers. As the higher melting keto acid forms a sparingly soluble sodium salt by means of which it can be removed from the mixture, a separation is easily accomplished. It was found that about two-thirds of the substitution occurs in the para position of the unsubstituted ring (I) and the remainder ortho to the methoxyl group (II). In establishing the structures the keto acids were first oxidized, best with permanganate in the case of I and with hypobromite for II, to the methoxydiphenyl carboxylic acids III and IV. The hydroxy acids obtained on demethylation corresponded in melting point to substances described in the patent literature, 4-hydroxy-4′-carboxydiphenyl having been obtained through the nitro derivative of the 4-carboxylic acid[1] and 3-carboxy-4-hydroxydiphenyl from the 4-hydroxy compound through the aldehyde[2] and by the Kolbe reaction.[3] In order to establish the structures completely exhaustive oxidations were conducted on the phenol III and the keto acid II. These yielded terephthalic acid and benzoic acid, respectively, in accordance with the formulation.

It was of interest to see whether the solvent in the Friedel and Crafts reaction plays any part in determining the ratio of homo- and hetero-nuclear substitution products, and as the condensation of *p*-methoxydiphenyl with succinic anhy-

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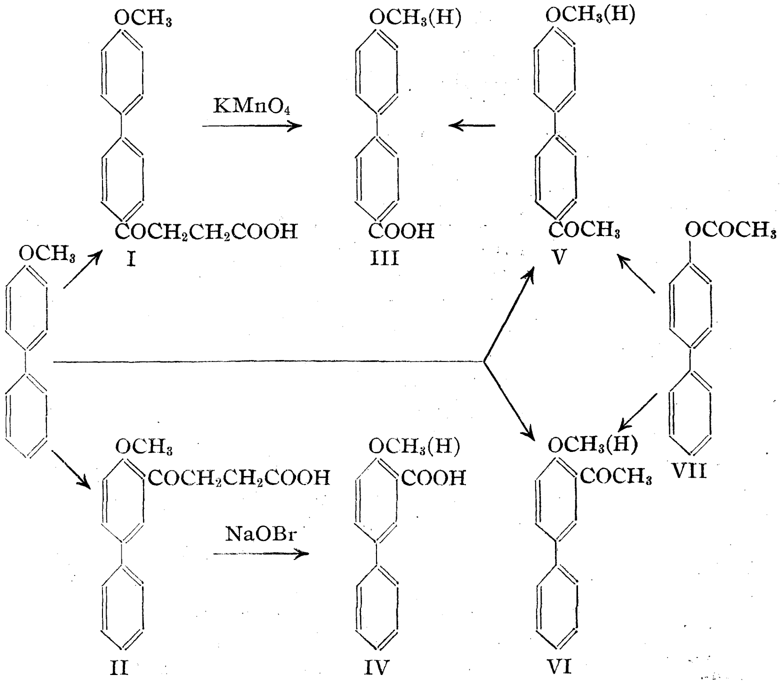
(1) French Patent 735,846; English Patent 390,556.

(2) American Patent 1,839,526.

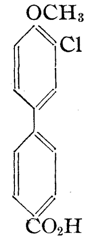
(3) American Patent 1,941,207.



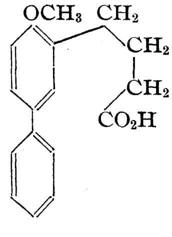
dride did not proceed satisfactorily in solvents other than nitrobenzene the reaction with acetyl chloride was investigated for this purpose. Two isomers were invariably obtained and there was no appreciable difference in the results using nitrobenzene, tetrachloroethane or carbon bisulfide. The isomer formed in larger amounts and having the higher melting point was found to be 4′-aceto-4-methoxydiphenyl (V) for it yielded III (ether) on oxidation with permanganate. In analogy with the above results the second product, isolated from the mother liquor as the semicarbazone, is very probably VI. With the two aceto compounds available it was of interest to investigate the Fries rearrangement of the acetate of *p*-hydroxydiphenyl (VII), for although Blicke and Weinkauff[4] studied the rearrangement of the benzoate they did not establish rigorously the structure of the sole reaction product isolated. In the present case it was found that the acetyl group migrates to both the *o*- and the *p*′-positions.

In general *p*-methoxydiphenyl resembles β-methoxynaphthalene in giving rise to Friedel and Crafts substitutions both ortho to the methoxyl group and at the most remote position of the second nucleus.

An additional observation worthy of note is that on oxidizing β-(4-methoxy-4′-xenoyl)-propionic acid (I) with sodium hypochlorite the product, separated from excess reagent as the sodium salt, was found to contain chlorine. The structure VIII was established by the preparation of the acid from the known[5] 3-chloro-4-methoxydiphenyl by condensation with acetyl chloride and permanganate oxidation. In this Friedel and Crafts reaction the unsubstituted ring alone appears to be attacked. The corresponding 3-bromo compounds also were prepared. Another interesting observation is that all attempts to cyclize the butyric acid derivative IX with sulfuric acid or through the acid chloride were unsuccessful. The ester of IX was also converted into the oxalyl derivative and submitted to the Bougault reaction with sulfuric acid, but a ring closure was not achieved. This evidently constitutes an additional case of the inhibitory influence on cyclizations often exerted by a *m*-methoxyl group.[6]



VIII



IX

Experimental Part

Condensation of *p*-Methoxydiphenyl with Succinic Anhydride.—A solution of 50 g. of the ether and 29.9 g. of succinic anhydride in 500 cc. of nitrobenzene was cooled in an ice-bath and 67.5 g. of aluminum chloride was added in small portions with stirring. The mixture was stirred cold for six hours and at room temperature for an equal period and then treated with ice and acid and the solvent removed with steam. The solid residue was dissolved in 1.5 liters of water containing 40 g. of sodium carbonate and after clarifying the hot solution with Norite and cooling to 0° the sodium salt of **β-(4-methoxy-4′-xenoyl)-propionic acid** (I) separated as a curdy precipitate. The collected salt was suspended in hot water and acidified, giving a light gray precipitate of the free acid, m. p. 192–195°, yield 18.9 g. (24.5%). Crystallized from acetic acid in which it

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(4) Blicke and Weinkauff, THIS JOURNAL, **54**, 330 (1932).

(5) Colbert, Meigs and Mackin, *ibid.*, **56**, 202 (1934).

(6) Compare Graves and Adams, *ibid.*, **45**, 2439 (1923); Gardner and Adams, *ibid.*, **45**, 2455 (1923); Jacobson and Adams, *ibid.*, **46**, 1312 (1924).

is moderately soluble, the acid forms colorless plates or needles melting at 200–201° with slight darkening in contact with the glass.

The mother liquor remaining after removal of the salt was treated at the boiling point with sodium chloride until nearly saturated, and on cooling the sodium salt of **β-(4-methoxy-3-xenoyl)-propionic acid** (II) separated in a crystalline condition. The free acid precipitated from a clarified solution was nearly pure, m. p. 147–148°, yield 46.5 g. (60%). It is much more soluble than the isomer and forms small needles from ether and a microcrystalline powder from alcohol, m. p. (camphor-like) 155°, clear.

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.81; H, 5.67. Found: (I) C, 72.02; H, 5.63; (II) C, 72.05; H, 5.90.

The methyl ester of I, microcrystals from dilute acetic acid, has a camphor-like melting point, liquefaction beginning at 99° and the crystal skeleton disappearing at 110°. **The methyl ester of II** forms small plates from ether–petroleum ether, m. p. 48–49°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.46; H, 6.09. Found: (I-ester) C, 72.31; H, 5.93; (II-ester) C, 72.12; H, 6.06.

Clemmensen Reduction.—The keto acids I and II were reduced in the form of the methyl esters (crude) by the ordinary Clemmensen procedure and the resulting acids were conveniently purified by salting out the sodium salts from the alkaline solutions. **γ-(4-Methoxy-4′-xenyl)-butyric acid,** obtained in a small-scale experiment in 20% yield, formed microcrystals from dilute alcohol, m. p. 148–149° with previous softening. **γ-(4-Methoxy-3-xenyl)-butyric acid** (IX) formed long, colorless needles from dilute alcohol, m. p. (camphor-like) 109°; yield 54–58%.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.56; H, 6.72. Found: (4′-isomer) C, 75.62; H, 6.64; (3-isomer) C, 75.69; H, 6.49.

The acid IX was either sulfonated or unattacked in attempted cyclizations with sulfuric acid of various strengths, and the acid chloride seemed either not to react or to yield polymeric products when treated with condensing agents. Polymerization seemed to occur also in the Bougault condensation of the oxalyl derivative of the ethyl ester, prepared and treated in the usual way.[7]

Oxidation to Methoxydiphenyl Carboxylic Acids.—The keto acid I (2.5 g.) was best oxidized in a solution of potassium hydroxide (2.5 g.) and water (200 cc.) with potassium permanganate (6.6 g.) at the temperature of the steam-bath. The precipitated dioxide was dissolved, after cooling, with sulfur dioxide and the solution was acidified and heated to coagulate the **4-methoxy-4′-carboxydiphenyl** (III) which separated; yield 1.5 g. This formed a microcrystalline powder from glacial acetic acid, m. p. 248–249°.

For the preparation of **3-carboxy-4-methoxydiphenyl** (IV) a solution of 5 g. of the keto acid II and 14 g. of sodium hydroxide in 200 cc. of water was treated at 10° with 14 g. of bromine. After twelve hours the solution was treated with sulfur dioxide, followed by hydrochloric acid. The precipitated acid was coagulated by digestion at the boiling point; yield 3 g. (75%). Distilled in vacuum and crystallized from ether the acid formed slightly yellow plates, m. p. 166–167°.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.65; H, 5.31. Found: (III) C, 73.49; H, 5.66; (IV) C, 73.30; H, 5.59.

The methyl ester of III forms plates from methyl alcohol, m. p. 172–173°.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.35; H, 5.82. Found: C, 74.31; H, 6.15.

Demethylation.—The methoxy acids III and IV were refluxed with glacial acetic acid (20 cc. for a 3-g. lot) and 48% hydrobromic acid (6 cc.) for four hours and the solutions were concentrated and diluted to crystallization. **4-Hydroxy-4′-carboxydiphenyl** was crystallized from dioxane–cyclohexane, forming transparent (solvated) needles, m. p. (dry) 293–294°. **3-Carboxy-4-hydroxydiphenyl** formed needles from ether–cyclohexane, m. p. 212–213°.

Anal. Calcd. for $C_{13}H_{10}O_3$: C, 72.86; H, 4.71. Found: (4′-acid) C, 72.62; H, 5.05; (3-acid) C, 72.73; H, 5.08.

The 4′-methyl ester formed plates from alcohol, m. p. 224–225°; the **3-ester** crystallized from petroleum ether as prismatic needles, m. p. 93–94°.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.65; H, 5.31. Found: (4′-ester) C, 73.97; H, 5.64; (3-ester) C, 73.67; H, 5.42.

Exhaustive Oxidation.—A hot solution of 0.9 g. of 4-hydroxy-4′-carboxydiphenyl and 3 g. of potassium hydroxide in 100 cc. of water was treated in the course of two hours with a solution of 5.75 g. of permanganate. The crude oxidation product was esterified and the ester (0.3 g.) distilled in vacuum and crystallized from methyl alcohol, giving flat needles of dimethyl terephthalate, m. p. 140–141°.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.82; H, 5.19. Found: C, 61.66; H, 5.52.

β-(4-Methoxy-3-xenoyl)-propionic acid on oxidation with excess alkaline permanganate gave benzoic acid, which was extracted with ether from the residue after evaporation, sublimed, and fully identified.

3-Chloro-4-methoxy-4′-carboxydiphenyl (VIII).—(a) β-(4-Methoxy-4′-xenoyl)-propionic acid (5 g.) was heated with 720 cc. of 2.5% sodium hypochlorite solution for several hours on the steam-bath and on nearly saturating the solution with sodium chloride and cooling, the sodium salt of the chlorinated acid separated. It was collected and washed with salt solution, and the free acid was liberated and crystallized from dilute acetic acid; small needles, m. p. 275–276°.

Anal. Calcd. for $C_{14}H_{11}O_3Cl$: C, 63.98; H, 4.23. Found: C, 63.96; H, 4.62.

The methyl ester formed cottony needles from methyl alcohol, m. p. 145–146°.

Anal. Calcd. for $C_{15}H_{13}O_3Cl$: C, 65.08; H, 4.74. Found: C, 65.30; H, 4.82.

(b) 3-Chloro-4-methoxydiphenyl (5 g.) was first converted with acetyl chloride (2 g.) and aluminum chloride (3.4 g.) in carbon bisulfide medium into **3-chloro-4-methoxy-4′-acetodiphenyl,** which was vacuum distilled and crystallized from alcohol; needles, m. p. 109–110°.

Anal. Calcd. for $C_{15}H_{13}O_2Cl$: C, 69.07; H, 5.03. Found: C, 69.17; H, 5.30.

The ketone (1 g.) was oxidized with potassium permanganate (1.21 g.) in a hot, stirred, alkaline medium, and the purified product (0.35 g.) and its methyl ester were com-

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[7] Fieser and Hershberg, This Journal, **57**, 1851 (1935).

pared with the above samples and found to give no depressions in the melting points.

Bromo Compounds.—Using analogous methods the following compounds were prepared: **3-bromo-4-methoxy-4′-acetodiphenyl** (a), plates from methyl alcohol, m. p. 97–98°; **3-bromo-4-methoxy-4′-carboxydiphenyl** (b), needles from tetrachloroethane, m. p. 270–271°; methyl ester (c), long needles from alcohol, m. p. 148–149°.

Anal. Calcd. (a) C, 59.02; H, 4.30; (b) C, 54.72; H, 3.62; (c) C, 56.07; H, 4.08. Found: (a) C, 59.10; H, 4.63; (b) C, 54.66; H, 3.89; (c) C, 55.91; H, 3.95.

Condensation of *p*-Methoxydiphenyl with Acetyl Chloride.—The reaction of the ether (5 g.) and acetyl chloride (2.2 g.) in the presence of aluminum chloride (4 g.) was run in boiling carbon bisulfide, in tetrachloroethane at 0–20°, and in nitrobenzene at 0–20°. There was little difference in the total yield or the ratio of isomers in the three cases, although tetrachloroethane seemed to give slightly better results (65% yield) than the other solvents. A separation is easily accomplished with ether, which readily dissolves the low-melting isomer (VI) and leaves the other ketone (V) as a residue, and in each case the high-melting compound was found to comprise 65–75% of the total. This substance, **4-methoxy-4′-acetodiphenyl** (V), forms microcrystals from methyl alcohol, m. p. 153–154°. On oxidation with alkaline permanganate it gave an acid identical with III. **3-Aceto-4-methoxydiphenyl** (VI) was found in the ether mother liquor contaminated with unchanged *p*-methoxydiphenyl. It was easily separated from this substance and purified through the semicarbazone, which gives plates from alcohol. On hydrolysis with boiling 2 *N* hydrochloric acid the ketone was obtained and crystallized from dilute methyl alcohol; plates, m. p. 62–63°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.61; H, 6.24. Found: (V) C, 79.65; H, 6.34; (VI) C, 79.66; H, 6.43.

Fries Rearrangement.—4-Acetoxydiphenyl (5 g.) was intimately mixed with aluminum chloride (3.5 g.) and carbon disulfide (20 cc.) and heated to evaporate the solvent. The residue was heated in a bath at 140° for thirty minutes and then decomposed with dilute hydrochloric acid and extracted with ether. The rearranged material was extracted from the washed solution with dilute alkali and recovered as a solid by acidification. **4-Hydroxy-4′-acetodiphenyl,** the less soluble isomer, was obtained by crystallization of the crude material to constant melting point from benzene; small needles, m. p. 206–207° (0.2 g.). It gave on methylation a product identical with the ether V described above. The material recovered from the benzene mother liquor was taken up in alcohol (50 cc.) and treated with an aqueous solution of semicarbazide hydrochloride (1.1 g.) and sodium acetate (0.8 g.). On standing yellow crystals of a semicarbazone separated (0.95 g.; m. p. >270°) and this was hydrolyzed with boiling 2 *N* hydrochloric acid. After crystallizing the recovered ketone from petroleum ether **3-aceto-4-hydroxydiphenyl** was obtained as small prisms, m. p. 61–62°, and on methylation it formed an ether, m. p. 62–63°, which did not depress the melting point of 3-aceto-4-methoxydiphenyl.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.21; H, 5.71. Found: (4′-isomer) C, 79.37; H, 6.01; (3-isomer) C, 79.19; H, 5.83.

Summary

In the Friedel and Crafts reaction with succinic anhydride and with acetyl chloride 4-methoxydiphenyl is substituted in both the 3- and the 4′-positions and solvents have little influence on the ratio of the isomers produced. The Fries rearrangement of 4-acetoxydiphenyl also proceeds in these two directions.

The closing of a six-membered ring at the 2-position of diphenyl is inhibited by a *m*-methoxyl group at position 4.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.

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[CONTRIBUTION FROM RÖHM AND HAAS COMPANY, INC.]

The Condensation of Phenols with Ethanolamine and Formaldehyde

BY HERMAN ALEXANDER BRUSON

It has been known for some time that amines catalyze the condensation between phenols and formaldehyde to form resins. The mechanism of this reaction is still obscure.

When phenols are condensed with molecular equivalents each of formaldehyde and secondary amines, such as dimethylamine or piperidine, tertiary amines are formed.[1]

Décombe has shown that the products thus obtained are, without doubt, *o*-hydroxybenzylamino derivatives.[2]

Morpholine is particularly prone to form well-defined, crystalline hydroxybenzylmorpholines with a variety of monohydric or polyhydric phenols and formaldehyde.[3]

In a study of this reaction with other amines, it has now been found that β-aminoethanol can be combined with formaldehyde and phenols to yield hydroxybenzylaminoethanols. The condensation is, however, complicated by the formation of resinous materials which in some cases form the main product. It has been found possible, by intro-

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[1] Bayer, German Patent 89,979, 92,309 (1895).

[2] J. Décombe, *Compt. rend.*, **196**, 866 (1933); **197**, 258 (1933).

[3] H. Bruson, U. S. Patent 2,040,039, 2,040,040 (1936).

ducing various orienting groups into the phenol nucleus and thereby decreasing the number of reactive available nuclear positions, to so arrest resin formation that the intermediate compounds can be isolated in pure crystalline form.

When phenol was mixed with a molecular equivalent quantity each of formaldehyde and ethanolamine, heat was evolved, and a sticky, sirupy mass was formed. After washing with water, this material formed a reddish, viscous, resinous material which was readily soluble in dilute hydrochloric acid or sodium hydroxide solution. It therefore contained an amino group and a free phenolic hydroxyl group. When heated to about 100°, it gradually hardened to a nitrogenous, pale reddish, resin which was still soluble in dilute acid, but which progressively became more and more insoluble as heating was continued. When two molecular equivalents of formaldehyde were used for the condensation, the product resinified faster to an infusible resin. At no stage was it possible to isolate therefrom any crystalline product.

The three isomeric cresols reacted in a similar manner to yield sticky, nitrogenous sirups or resins which could not be crystallized, nor could they be distilled, even in high vacuum, without decomposition.

However, the introduction of a phenyl group *ortho* to the phenolic hydroxyl group, led to the formation of a crystalline compound which could easily be separated from resinous by-products. *o*-Phenylphenol reacted with one mole equivalent each of formaldehyde and ethanolamine to yield a substance crystallizing in colorless needles melting at 116° and corresponding to the empirical formula $C_{15}H_{17}O_2N$. This compound was soluble in aqueous 10% sodium hydroxide solution or phosphoric acid solution, but was insoluble in sodium bicarbonate solution. From its empirical composition and chemical behavior, it would correspond to the probable formula $C_6H_5C_6H_3OHCH_2NHCH_2CH_2OH$ in which the entering group could be ortho or para to the phenolic hydroxyl group.

p-Phenylphenol, on the other hand, formed a crystalline compound containing less nitrogen than that called for by the above empirical formula. It was less soluble in acids or in sodium hydroxide solution and more soluble in alcohol than the *o*-phenyl compound. After repeated crystallizations from benzene, it melted at 102°. Assuming that it is not a mixture, its analysis approximates a possible formula $(C_6H_5C_6H_3OHCH_2)_2NCH_2CH_2OH$.

p-Cyclohexylphenol likewise formed a crystalline compound, m. p. 171°, which contained less nitrogen than that called for by a simple cyclohexylhydroxybenzylaminoethanol, and which approximates a possible structure analogous to the para-phenyl compound.

Well-defined crystalline reaction products were obtained from *p*-*t*-butylphenol, *p*-*t*-amylphenol, *p*-benzoylphenol, *p*-nitrophenol and 3-nitro-4-hydroxytoluene, the analysis and behavior of which indicated the presence of one $—CH_2NHCH_2CH_2OH$ group attached to the aromatic nucleus. In view of the blocking of the para positions in these phenols, the entering $—CH_2NHCH_2CH_2OH$ radical very probably enters the ortho position to the phenolic hydroxyl group. By using 2,4-dichlorophenol and 5-chloro-2-hydroxydiphenyl, which contain one very reactive free ortho position, the corresponding compounds containing the $—CH_2NHCH_2CH_2OH$ group undoubtedly ortho to the phenolic OH group, were obtained.

In the case of *o*-cyclohexylphenol, *p*-benzylphenol, *p*-$\alpha,\alpha,\gamma,\gamma$-tetramethylbutylphenol, *o*- and *p*-chlorophenols, oily, resinous materials were obtained. These products were soluble, however, for the most part in 10% phosphoric acid solution.

Resorcinol, upon treatment with one mole equivalent each of formaldehyde and ethanolamine, gave an amorphous water-insoluble powder which was soluble in dilute hydrochloric acid.

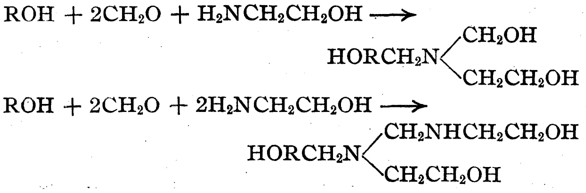
Attempts to introduce two hydroxyethyl aminomethyl groups into those phenols containing two free *ortho* positions to the hydroxyl group, led to the formation of viscous oils which could not be distilled without resinification.

The crystalline hydroxybenzylamino ethanols isolated, react further with formaldehyde to form resins. It is believed that the formaldehyde reacts with the imino group to form a methylol compound which is capable of further condensation with the components present. Various competing reactions may take place. These may be formulated as follows, where R is the phenolic nucleus

$$CH_2O + H_2NCH_2CH_2OH \longrightarrow HOCH_2NHCH_2CH_2OH \quad (A)$$

$$ROH + HOCH_2NHCH_2CH_2OH \longrightarrow HORCH_2NHCH_2CH_2OH \quad (B)$$

The formaldehyde and ethanolamine first combine with evolution of heat to form a methylol derivative (A), which then reacts with a mole of the phenol to form the hydroxyaralkylaminoethanol (B). This compound is usually the main product of the reaction, especially if care is taken to use only one molecular equivalent to each of the three components. If the phenol is suitably oriented, product (B) crystallizes out. However, side reactions also occur, especially if an excess of formaldehyde or of ethanolamine is present, so that a complex mixture of phenolic amino alcohols is formed, among which may be the following



$$ROH + 2CH_2O + H_2NCH_2CH_2OH \longrightarrow HORCH_2N\left\langle\begin{matrix}CH_2OH\\CH_2CH_2OH\end{matrix}\right.$$

$$ROH + 2CH_2O + 2H_2NCH_2CH_2OH \longrightarrow HORCH_2N\left\langle\begin{matrix}CH_2NHCH_2CH_2OH\\CH_2CH_2OH\end{matrix}\right.$$

These can, of course, again react with formaldehyde or with formaldehyde plus ethanolamine, and this can be kept up until all free molecular movement ceases and the end-product becomes a rigid, nitrogenous resin.

Experimental Part

Phenylhydroxybenzylaminoethanol.—(a) To a solution of 51 g. of *o*-phenylphenol (0.3 mol), 50 cc. of methanol, and 30 g. of aqueous 30% formaldehyde (0.3 mol), there was added, while shaking and cooling with tap water, 18.3 g. of β-aminoethanol. The clear, reddish solution was allowed to stand at room temperature (20–25°) for about sixty-five hours, during which time it solidified to a crystalline mass which contained a sticky, resinous material. The yield of the filtered, air-dried, crude crystalline product was 33 g. Upon recrystallization from 50 cc. of absolute ethyl alcohol, 19 g. of product were obtained in the form of colorless needles. The analytical sample melted at 116° (uncorr.) after three recrystallizations from alcohol.

Anal. Calcd. for $C_{15}H_{17}O_2N$: C, 74.03; H, 7.05; N, 5.76. Found: C, 73.72; H, 6.89; N, 5.51.

(b) The same product may be obtained in a much shorter time by the following procedure:

A solution of 60 g. of aqueous 30% formaldehyde (0.6 mole) was added slowly to 36.6 g. of β-aminoethanol (0.6 mole) while cooling and stirring the mixture. The clear solution was allowed to stand for about one hour until the odor of formaldehyde disappeared. It was then added to a solution of 102 g. of *o*-phenylphenol (0.6 mole) in 100 cc. of ethyl alcohol. The solution was boiled under reflux on a steam-bath for one and one-half hours, and allowed to stand overnight in an ice-box. The weight of colorless crystals obtained was 55 g. or 38%.

Condensation of *p*-Phenylphenol, Formaldehyde and Ethanolamine.—To a suspension of 34 g. of *p*-phenylphenol (0.2 mol) in 34 cc. of methanol, 12.2 g. of β-aminoethanol was added and the mixture warmed until it became clear. It was then cooled to 25° and 6 g. of powdered *p*-formaldehyde added. The mixture was shaken for about ten minutes, during which time the *p*-formaldehyde dissolved with heat evolution, the temperature reaching 40°. The clear solution thus obtained was then boiled for one hour under reflux on a steam-bath, cooled and poured slowly into 200 cc. of water with stirring. The white precipitate was filtered by suction, washed thoroughly with water and dried in the air. The somewhat yellowish powder thus obtained was recrystallized twice from benzene with chilling, using Norite to remove the yellow color, until a constant melting point of 102° was obtained; colorless crystals; very soluble in alcohol. Three separate preparations were analyzed in duplicate and averaged.

Anal. Calcd. for $C_{28}H_{27}O_3N$: C, 79.02; H, 6.40; N, 3.30. Found (1): C, 78.54; H, 6.98; N, 3.46. Found (2): C, 78.93; H, 6.92; N, 3.20. Found (3): C, 78.67; H, 6.88; N, 3.26.

***p*-Cyclohexylphenol, Formaldehyde, Ethanolamine Condensation.**—To a solution of 35.2 g. of *p*-cyclohexylphenol, 33 cc. of methanol and 12.2 g. of β-aminoethanol, there was added, with cooling and shaking, 20 g. of aqueous 30% formaldehyde solution. After standing at room temperature for one hour, the mixture was boiled for one and one-half hours under reflux on a steam-bath and placed in a refrigerator at 5° for several weeks. A small quantity (5 g.) of crystalline crusts separated, which were contaminated with a sticky sirup. The crystalline material was dried on porous tile and recrystallized from methanol to a constant melting point; colorless fine crystals, m. p. 170–171°. Four separate preparations were analyzed in duplicate and averaged.

Anal. Calcd. for $C_{15}H_{23}O_2N$: C, 72.23; H, 9.32; N, 5.62. $C_{28}H_{39}O_3N$: C, 76.83; H, 8.99; N, 3.20. Found (1): C, 76.27; H, 9.15; N, 3.21. Found (2): C, 76.71; H, 8.66; N, 3.26. Found (3): C, 76.94; H, 8.84; N, 3.27. Found (4): C, 76.38; H, 9.16; N, 3.38.

Chlorophenylphenol, Formaldehyde, Ethanolamine Condensation.—To a solution consisting of 20.5 g. of 5-chloro-2-hydroxydiphenyl, 27 cc. of methanol, and 10 g. of aqueous 30% formaldehyde, there was added, with cooling and shaking, 6.1 g. of ethanolamine. The mixture was then boiled under reflux for one and one-half hours on a steam-bath. The crystalline mass thus obtained was recrystallized from *n*-butanol. It separated in very fine colorless crystals, m. p. 182–183°; difficultly soluble in alcohol; readily soluble in 10% sodium hydroxide or hydrochloric acid solution.

Anal. Calcd. for $C_{15}H_{16}O_2NCl$: Cl, 12.77; N, 5.04. Found: Cl, 12.80; N, 4.81.

2-Hydroxy-3,5-dichlorobenzylaminoethanol.—To a solution of 16.3 g. of 2,4-dichlorophenol, 16 cc. of methanol, and 6.1 g. of ethanolamine, there was added 3 g. of *p*-formaldehyde. The mixture was shaken for fifteen minutes until the *p*-formaldehyde had dissolved, then boiled under reflux on the steam-bath. After about thirty minutes of boiling, a yellowish crystalline material began to separate. The mixture was cooled and filtered. The yellowish crystals (7 g.) were washed with a little methanol and recrystallized from *n*-butanol for analysis; colorless, fine white needles, m. p. 199–200°.

Anal. Calcd. for $C_9H_{11}O_2NCl_2$: Cl, 30.04; N, 5.93. Found: Cl, 29.80; N, 5.76.

2-Hydroxy-3-nitro-5-methylbenzylaminoethanol.—A mixture of 15.3 g. of 3-nitro-4-hydroxytoluene, 20 cc. of methanol, 6.1 g. of ethanolamine and 3 g. of *p*-formaldehyde, was boiled under reflux for one hour. The clear red solution was cooled and scratched to induce crystallization. The yellow crystals were washed with a little methanol and recrystallized from butanol; yellow needles, m. p. 205–206°.

Anal. Calcd. for $C_{10}H_{14}O_4N_2$: C, 53.07; H, 6.24; N, 12.38. Found: C, 53.26; H, 6.36; N, 12.61.

***p*-*t*-Butylhydroxybenzylaminoethanol.**—To a solution consisting of 30 g. of *p*-*t*-butylphenol, 30 cc. of methanol and 12.2 g. of ethanolamine, there was added, with cooling and shaking, 6 g. of *p*-formaldehyde. After shaking until all heat evolution had ceased, the clear solution obtained was boiled for one hour under reflux on a steam-bath, and then placed in a refrigerator at 5° for several days, during which time it solidified to a colorless, crystalline mass; yield of crude air-dried crystals was 19 g. After recrystallization from methanol by repeated boiling and chilling, 5 g. of the analytically pure, colorless, crystalline product, m. p. 127–128°, was isolated.

Anal. Calcd. for $C_{13}H_{21}O_2N$: C, 69.99; H, 9.49; N, 6.27. Found: C, 69.91; H, 9.63; N, 6.17.

The product dissolved readily in 10% sodium hydroxide solution, as well as in 10% hydrochloric acid.

***p*-*t*-Amylhydroxybenzylaminoethanol.**—To a solution of 49.2 g. of *p*-*t*-amylphenol, 50 cc. of methanol, and 30 g. of aqueous 30% formaldehyde solution, there was added 18.3 g. of ethanolamine, while cooling with tap water and shaking. The solution was then boiled under reflux on a steam-bath for one and one-half hours. The oily layer which separated on cooling was run off and chilled to 0° to induce crystallization. The crystals were dried on porous tile to remove sticky, resinous material, and recrystallized from methanol to a constant melting point of 114° (uncorr.).

Anal. Calcd. for $C_{14}H_{23}O_2N$: C, 70.87; H, 9.77; N, 5.90. Found: C, 70.54; H, 9.44; N, 5.72.

***p*-Nitrohydroxybenzylaminoethanol.**—A solution of 20 g. of 30% formaldehyde and 12.2 g. of ethanolamine was added to a solution of 27.8 g. of *p*-nitrophenol in 30 cc. of methanol. A clear red solution was obtained. After standing for seven days at room temperature, there was no evidence of reaction. The solution was therefore boiled for one and one-half hours under reflux on a steam-bath. Upon cooling, yellow crystals slowly separated. Upon recrystallization from ethyl alcohol to a constant melting point, the product formed yellow needles melting at 195–196° (uncorr.).

Anal. Calcd. for $C_9H_{12}O_4N_2$: C, 50.91; H, 5.75; N, 13.20. Found: C, 50.81; H, 5.77; N, 12.86.

***p*-Benzoylhydroxybenzylaminoethanol.**—To a solution of 19.8 g. of *p*-benzoylphenol in 25 cc. of methanol, there was added a previously prepared solution made by mixing 10 g. of aqueous 30% formaldehyde with 6.1 g. of ethanolamine, with cooling. The mixture was allowed to stand for two hours at room temperature, and was then heated under reflux on a steam-bath for one and one-half hours. The solution thus obtained was allowed to stand at 5° for several days. The crystals which separated were dried on tile, washed with a little alcohol and recrystallized from alcohol to a constant melting point of 188–189°.

Anal. Calcd. for $C_{16}H_{17}O_3N$: C, 70.81; H, 6.32; N, 5.16. Found: C, 70.47; H, 6.38; N, 5.05.

The product was soluble in dilute oxalic or lactic acid. The above analyses were carried out by Dr. C. W. Nash of the Röhm and Haas Company.

Summary

The condensation of formaldehyde and β-aminoethanol with various phenols was investigated. Crystalline compounds were obtained from equimolecular mixtures of formaldehyde and ethanolamine with *o*-phenylphenol, *p*-*t*-butylphenol, *p*-*t*-amylphenol, *p*-nitrophenol, *p*-benzoylphenol, 5-chloro-2-hydroxydiphenyl, 2,4-dichlorophenol and 3-nitro-4-hydroxytoluene. These appear to be substituted hydroxybenzylaminoethanols; *i. e.*, phenols containing one —$CH_2NHCH_2CH_2OH$ group attached to the aromatic nucleus.

p-Phenylphenol and *p*-cyclohexylphenol gave compounds containing less nitrogen per mole of the phenol, indicating the presence of two phenolic nuclei in the products.

Resins containing nitrogen were obtained from phenol, the three cresols and resorcinol.

PHILADELPHIA, PENNA. RECEIVED MARCH 16, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reversibility of the Friedel-Crafts Reaction. Hydrogenation

BY L. L. ALEXANDER AND REYNOLD C. FUSON

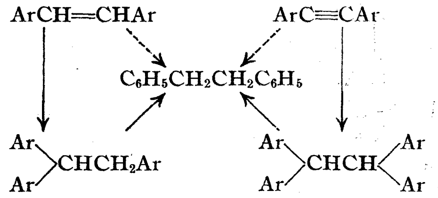
The addition of hydrogen to an ethylenic bond can be accomplished by use of benzene and aluminum chloride at room temperatures.[1] Under these conditions this reaction competes with the addition of benzene to the double bond. However, the latter process is reversible, whereas the former appears to be irreversible. This means that eventually the hydrogenation process will take place to the exclusion of the addition of benzene. Thus, in the case of stilbene the formation of dibenzyl, which is irreversible, must eventually supplant the reaction leading to the production of triphenylethane:[2]

$$(C_6H_5)_2CHCH_2C_6H_5 \overset{C_6H_6}{\rightleftarrows} C_6H_5CH{=}CHC_6H_5 \xrightarrow{H_2} C_6H_5CH_2CH_2C_6H_5$$

Another way of stating the proposition is to say that in aryl ethanes or ethylenes the aryl groups will be replaced by hydrogen atoms. Experiment has shown that this replacement is subject to certain limitations. The end-product under the conditions mentioned above is dibenzyl rather than ethane. Thus, with dibenzyl (or stilbene), ethylbenzene, styrene, 1,1-diphenylethane or 1,1-diphenylethylene, no replacement of aryl groups is observed.

From these facts emerges the following generalization. *The production of dibenzyl by the action of benzene and aluminum chloride is a general phenomenon for acetylene and ethylene derivatives in which each carbon atom bears at least one aryl group, and for similarly constituted tri- and tetraarylethanes.*

These four classes of compounds may in reality be reduced to two, since the ethylenic and acetylenic types are converted to the triarylethane and tetraarylethane types, respectively, under the conditions used. This is indicated in the following chart

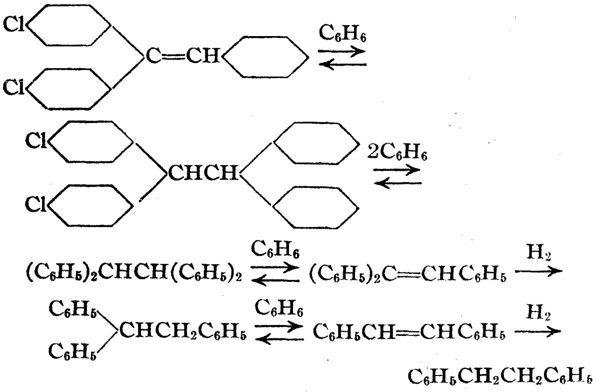


We have found, for example, that stilbene and *p*-bromostilbene give 1,1,2-triphenylethane when treated with benzene in the presence of a limited amount of aluminum chloride.

$$\left.\begin{array}{r} C_6H_5CH{=}CHC_6H_5 \\ BrC_6H_4CH{=}CHC_6H_5 \end{array}\right\} \rightarrow C_6H_5CH_2CH(C_6H_5)_2$$

It seems probable, therefore, that the transformation of these compounds into dibenzyl in the presence of large amounts of aluminum chloride involves the triphenylethane as an intermediate.

Similarly, triphenylethylene and 1,1-di-(*p*-chlorophenyl)-2-phenylethylene could be converted either to *sym*-tetraphenylethane or to dibenzyl, depending on the experimental conditions used. Thus, in the case of triphenylethylene the product is *sym*-tetraphenylethane *when 0.3 mole of aluminum chloride is used.* If four moles of aluminum chloride is employed, the chief product is dibenzyl. The same results were obtained with 1,1-di-(*p*-chlorophenyl)-2-phenylethylene. In the latter case, the mechanism must be the following



$$(C_6H_5)_2CHCH(C_6H_5)_2 \overset{C_6H_6}{\rightleftarrows} (C_6H_5)_2C{=}CHC_6H_5 \xrightarrow{H_2}$$

$$(C_6H_5)_2CHCH_2C_6H_5 \overset{C_6H_6}{\rightleftarrows} C_6H_5CH{=}CHC_6H_5 \xrightarrow{H_2} C_6H_5CH_2CH_2C_6H_5$$

These findings make possible a satisfactory interpretation of the fact that dibenzyl results when certain halogen derivatives of ethane, ethylene or acetylene are treated with benzene and aluminum chloride. It will be obvious that dibenzyl may

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[1] Alexander, Jacoby and Fuson, THIS JOURNAL, **57**, 2208 (1935). It seems probable that a similar explanation might account for the formation of propylbenzene by the action of benzene and aluminum chloride on allyl chloride [Nenitzescu and Isacescu, *Ber.*, **66B**, 1100 (1933)].

[2] Neither the source of the hydrogen nor the mechanism by which it is added have as yet been discovered. It may be, for example, that the process consists of the addition of hydrogen chloride to the ethylenic bond, followed by replacement of the chlorine atom by a hydrogen atom.

be expected from such of these compounds as react to form derivatives in which each of the two carbon atoms bears a phenyl radical. According to the literature, dibenzyl has been obtained in greater or less amounts from a number of such halogen derivatives. The following are illustrative examples: ethylene chloride,[3] ethylene bromide,[3] acetylene dibromide,[4] 1,1,2-trichloroethane,[5] 1,1,2-tribromoethane,[4] 1-phenyl-2-chloroethane,[6] 1-phenyl-1,2-dibromoethane[7] and tolane dibromide.[8]

Experimental Part

***sym*-Tetraphenylethane from Tolane.**—A mixture of 1 g. of tolane, 60 cc. of benzene and 0.5 g. of aluminum chloride was saturated with dry hydrogen chloride, then tightly stoppered and shaken for six hours at room temperature. The color changed from green to brown. The decomposition was carried out in an ice–hydrochloric acid mixture, and the product obtained on removal of the benzene melted, after recrystallization from glacial acetic acid, at 207–208°. There was no depression of a mixed melting point with an authentic sample of *sym*-tetraphenylethane. The yield was 64% of the theoretical amount.

Dibenzyl from Tolane.—A mixture of 1 g. of tolane, 50 cc. of benzene and 4 g. of aluminum chloride was saturated with dry hydrogen chloride. The mixture was placed in a glass-stoppered bottle and shaken at room temperature for twenty hours. The decomposition and the washing of the reaction mixture were effected as described in the other experiments. The brown viscous product was distilled at 4 to 5 mm., and the fraction boiling up to 120° was collected. The distillate crystallized on standing, and melted at 50–51°. It was shown by the method of mixed melting points to be dibenzyl. The yield was 32% of the theoretical amount.

Dibenzyl also has been obtained as a result of the treatment of the following compounds in a manner which was entirely analogous to that described for the production of dibenzyl from tolane.

Starting material	Material, g.	Aluminum chloride, g.	Yield of dibenzyl, %
Triphenylethylene	5	10	28
1,1-Di-(*p*-chlorophenyl)-2-phenylethylene	5	10	27
1,1,2-Triphenylethane	5	10	57
s-Tetraphenylethane	2.5	5	54

1,1,2-Triphenylethane from Stilbene.—A solution of 10 g. of stilbene in 150 cc. of benzene was saturated with hydrogen chloride and shaken for eight hours with 2 g. of aluminum chloride. The decomposition was accomplished with a mixture of ice and hydrochloric acid. The red oil resulting was distilled under reduced pressure. A fraction distilling at 206–210° (12 mm.) was collected, and crystallized on standing. The melting point of the product, as well as the mixed melting point with 1,1,2-triphenylethane (prepared as indicated below), was 51–52.5°. The yield calculated on the basis of triphenylethane was 49% of the theoretical amount.

1,1,2-Triphenylethane from *p*-Bromostilbene.—From 5 g. of *p*-bromostilbene, 100 cc. of benzene, dry hydrogen chloride and 0.5 g. of aluminum chloride, 1,1,2-triphenylethane was prepared in a yield of 37% of the theoretical by a procedure exactly analogous to the conversion of stilbene into 1,1,2-triphenylethane described above.

Synthesis of 1,1,2-Triphenylethane.[9]—A solution of 2 g. of triphenylethylene in 100 cc. of dry ether was freed from oxygen by means of a stream of dry nitrogen gas. Three grams of finely powdered sodium was added, and the mixture was shaken for ten hours at room temperature. The solution was added slowly to 100 cc. of absolute alcohol, and a large part of the ether and alcohol removed. Upon the addition of water and extraction with ether, a liquid residue was obtained which crystallized readily on standing with methyl alcohol. After recrystallization from the same solvent, it melted at 52–53°. The yield was 83% of the theoretical amount.

Synthesis of Di-(*p*-chlorophenyl)-benzylcarbinol.—A Grignard reagent was prepared from 13 g. of magnesium, 63 g. of benzyl chloride and 200 cc. of dry ether. To this solution 85 g. of *p*,*p*′-dichlorobenzophenone was added, and the solution was stirred for two hours. It was then allowed to stand overnight. After decomposition in an ammonium chloride–ice mixture and separation and concentration of the ether solution, a straw-colored liquid remained. When recrystallized from petroleum ether (high-boiling), the product melted at 116–117°. The yield was 68%.

Anal. Calcd. for $C_{20}H_{16}OCl_2$: C, 69.85; H, 4.66. Found: C, 70.02; H, 4.76.

1,1-Di-(*p*-chlorophenyl)-2-phenylethylene.—Fifty grams of di-(*p*-chlorophenyl)-benzylcarbinol dissolved in 600 cc. of glacial acetic acid was heated to boiling as 50 cc. of concentrated sulfuric acid was slowly added. The mixture was heated under reflux for thirty minutes, and then poured into water. The organic material was extracted with ether and obtained in crystalline form by removal of the ether. After recrystallization from methyl alcohol, it melted at 116.5–117.5°; the mixed melting point with the original carbinol was 90–96°. The yield of the ethylenic compound was practically quantitative.

Anal. Calcd. for $C_{20}H_{14}Cl_2$: Cl, 21.87. Found: Cl, 21.80.

***sym*-Tetraphenylethane from Triphenylethylene.**—A solution of 5 g. of triphenylethylene in 150 cc. of benzene was saturated with dry hydrogen chloride and shaken with 1 g. of aluminum chloride for twenty hours. The resulting red solution was decomposed in ice and hydrochloric acid and, after removal of the benzene, the resulting product was treated with norite and crystallized from an acetic acid solution. The melting point was 206–208°, and a mixed melting point with an authentic sample of *sym*-tetraphenylethane showed no depression. The yield was 70% of the theoretical amount.

***sym*-Tetraphenylethane from 1,1-Di-(*p*-chlorophenyl)-2-phenylethylene.**—A yield of 55% of the calculated quan-

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(3) Silva, *Compt. rend.*, **89**, 606 (1879).

(4) Anschütz, *Ann.*, **235**, 153 (1886).

(5) Ravitzer, *Bull. soc. chim.*, [3] **17**, 477 (1877).

(6) Nenitzescu, Isasescu and Ionescu, *Ann.*, **491**, 210 (1931).

(7) Anschütz, *ibid.*, **235**, 338 (1886).

(8) Anschütz, *ibid.*, **235**, 209 (1886).

(9) Schlenk and Bergmann, *ibid.*, **463**, 45 (1928).

tity of tetraphenylethylene was obtained from 5 g. of the ethylene, 1 g. of aluminum chloride and 150 cc. of benzene which had been saturated with hydrogen chloride. The procedure was the same as that used for the conversion of triphenylethylene into *sym*-tetraphenylethane.

Dibenzyl from Tetraphenylethylene.—A solution of 7 g. of tetraphenylethylene in 150 cc. of dry benzene was saturated with dry hydrogen chloride and shaken in contact with 20 g. of aluminum chloride for three days. After decomposition and separation had been completed, the benzene was removed and the residue distilled under reduced pressure. A small amount of distillate was collected at 100–200° (8 mm.). This distillate crystallized from dilute alcohol and melted at 52–53°. It was shown by the method of mixed melting points to be dibenzyl. The residue from the distillation was unchanged tetraphenylethylene.

Summary

The production of dibenzyl by the action of benzene and aluminum chloride is a general phenomenon in the case of acetylene and ethylene derivatives in which each carbon atom bears at least one aryl group, and for similarly constituted tri- and tetraarylethanes. These transformations may be explained by assuming that hydrogen adds irreversibly to the ethylenic bond, whereas aromatic hydrocarbons add reversibly.

URBANA, ILLINOIS RECEIVED JUNE 22, 1936

[CONTRIBUTION NO. 163 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. XXVI. The Reaction of Halogen Ethers with Vinylacetylene

BY HARRY B. DYKSTRA

Isochloroprene (I) and chloroprene (II) are obtained by the addition of hydrogen chloride to

$$CH\equiv CCH{=}CH_2 + HCl \longrightarrow \underset{\text{(I)}}{CH_2{=}C{=}CHCH_2Cl} \longrightarrow \underset{\text{(II)}}{CH_2{=}CClCH{=}CH_2}$$

vinylacetylene.[1] The present paper is concerned with analogous compounds obtained by the addition of alpha chloroethers to vinylacetylene.

$$CH\equiv CCH{=}CH_2 + CH_3OCH_2Cl \longrightarrow \underset{\text{(III)}}{CH_3OCH_2CH{=}C{=}CHCH_2Cl} \longrightarrow \underset{\text{(IV)}}{CH_3OCH_2CH{=}CClCH{=}CH_2}$$

Methoxy-5-chloro-1-pentadiene-2,3 (III) and methoxy-5-chloro-3-pentadiene-1,3 (IV) are formed when vinylacetylene and chloromethyl methyl ether have reacted in ether solution containing bismuth chloride. The initial step appears to be 1,4-addition, for III is the principal product of the reaction. On treatment with hydrochloric acid and cuprous chloride, III rapidly rearranges to IV. The presence of IV in the original reaction mixture probably results from isomerization of III induced by the bismuth chloride.

The addition of alpha halogen ethers to vinylacetylene appears to be a general reaction. Compounds obtained in this manner are listed in Table I. The synthesis is a special application of the olefin–halogen ether reaction developed by Norman D. Scott.[2]

Proof of Structure of Methoxy-5-chloro-1-pentadiene-2,3 (III).—This compound is a colorless liquid having an ethereal odor. Other physical properties are recorded in Table I. Failure of III to react with alkaline mercuric iodide reagent indicates the absence of acetylenic hydrogen. It does not polymerize or react with maleic anhydride as it might be expected to do if it contained a 1,3-diene structure. Its chlorine atom is reactive, for on treatment with alcoholic silver nitrate it rapidly yields a copious precipitate of silver chloride. A substantially quantitative yield of silver chloride is obtained in twenty hours at 25°. On oxidation with potassium permanganate, III yields chloroacetic acid. These data are similar to those reported for isochloroprene[1] and indicate that III is methoxy-5-chloro-1-pentadiene-2,3.

Proof of Structure of Methoxy-5-chloro-3-pentadiene-1,3 (IV).—Physical and analytical data for this compound are given in Table I. It is a colorless liquid having weakly lachrymatory properties. It does not yield a derivative with alkaline mercuric iodide reagent, which shows that it is not a true acetylenic compound. Its chlorine atom must be attached to a carbon bearing a

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(1) Carothers, Berchet and Collins, THIS JOURNAL, **54**, 4066 (1932).

(2) E. I. du Pont de Nemours & Co., U. S. Patent 2,024,749 (1935).

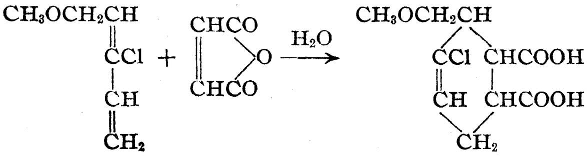
TABLE I

CHLORO ETHER–VINYLACETYLENE CONDENSATION PRODUCTS

Compound	B. p., °C.	B. p., Mm.	d^{20}_4	n^{20}_D	MR Calcd.	MR Found	Cl, % Calcd.	Cl, % Found
$CH_3OCH_2CH{=}CClCH{=}CH_2$	46	10	1.0351	1.4846	35.48	36.68	26.76	26.95
$CH_3OCH_2CH{=}C{=}CHCH_2Cl$	60–61	10	1.0427	1.4893	35.48	36.70	26.76	27.35
$C_2H_5OCH(CH_3)CH{=}CClCH{=}CH_2$[a]	44	4	0.9895	1.4762	44.72	45.78		
$C_2H_5OCH(CH_3)CH{=}C{=}CHCH_2Cl$[a]	56	4	.9991	1.4778	44.72	45.47		
$C_4H_9OCH(CH_3)CH{=}CClCH{=}CH_2$	67	2	.9365	1.4680	53.96	55.98	18.80	17.24
$C_4H_9OCH(CH_3)CH{=}C{=}CHCH_2Cl$	79	2	.9482	1.4705	53.96	56.84	18.80	18.71

[a] Impure.

double bond, for it does not react appreciably with alcoholic silver nitrate. When heated with an equivalent amount of maleic anhydride, it forms a viscous mass from which a chloro acid can be obtained by extraction with hot water. This acid melts at 163–165° and has a neutral equivalent of 123.3 as compared with a calculated value of 124.3 for $C_{10}H_{13}O_5Cl$ (V)



(V)

The reaction with maleic anhydride shows that IV is a 1,3-diene.[3] The 1,3-diene structure is further evidenced by the ease with which IV polymerizes. On oxidation with alkaline potassium permanganate, IV yields carbon dioxide, oxalic acid and methoxyacetic acid. These data indicate that IV has one of the structures

$CH_3OCH_2CH{=}CHCCl{=}CH_2$ (A)
$CH_3OCH_2CH{=}CClCH{=}CH_2$ (B)

The formation of IV from III and the close analogy which these compounds bear to chloroprene and isochloroprene, respectively, strongly favor structure B for compound IV.

Polymerization of Methoxy-5-chloro-3-pentadiene-1,3 (IV).—On standing at room temperature in the presence of air and diffused light, IV polymerizes slowly to a soft, rubber-like resin. The rate of polymerization is accelerated by light, heat and the presence of certain catalysts, *e. g.*, benzoyl peroxide and maleic anhydride. Exposure of IV to ultraviolet light from a mercury arc causes 65% to polymerize in forty-eight hours. When IV is heated in contact with air at 80°, 72% polymerizes in ten hours. In the presence of 1% benzoyl peroxide, a 95% yield of polymer is obtained in five hours at 75°. A comparison of these data with those reported for isoprene[4] and for chloroprene[5] indicates that IV polymerizes about 115 times as fast as isoprene and one-sixth as fast as chloroprene.

Polymers of IV are for the most part light colored resins which are soluble in acetone, ethyl acetate and benzene. Polymers prepared at low temperatures are somewhat rubber-like; they are elastic and resilient but lack the snap and strength of polychloroprene. Similar polymers are obtained from the analogs of IV described in Table I.

Experimental Part

Preparation of Methoxy-5-chloro-1-pentadiene-2,3 (III) and Methoxy-5-chloro-3-pentadiene-1,3 (IV).—During the course of two hours, 156 g. of vinylacetylene and 241 g. of chloromethyl methyl ether were added to a well-stirred mixture of 100 g. of ether, 1 g. of pyrogallol (antioxidant), and 3 g. of bismuth chloride maintained at 5–15°. The stirring was continued at this temperature for nine hours with periodic additions of bismuth chloride until a total of 13 g. had been added. The reaction mixture was then washed with water, dried over magnesium sulfate and distilled under reduced pressure. This yielded 60 g. of impure IV boiling at 46° (10 mm.), 138 g. of III boiling at 60–61° (10 mm.), 21 g. of liquid boiling at 78–85° (2 mm.) (probably resulting from addition of two mols of chloro ether to one of vinylacetylene), and 38 g. of non-volatile resin. Compound IV was obtained in pure form from the fraction boiling at 46° (10 mm.) by shaking with sodium methylate and redistilling. This removed an impurity containing active chlorine.

The analogs of III and IV described in Table I were prepared in a similar manner using alpha-chloroethyl ethyl ether and alpha-chloroethyl butyl ether.

Isomerization of Methoxy-5-chloro-1-pentadiene-2,3 (III).—A mixture of 200 g. of III, 50 g. of ether, 10 g. of cuprous chloride, and 50 g. of 18% hydrochloric acid was stirred at 20–40° for two hours. The ether layer was separated, dried over magnesium sulfate, and distilled. This gave 162 g. of IV boiling at 46° (10 mm.) and corresponding in properties with that separated from the reaction of chloromethyl ether with vinylacetylene.

Reaction of Methoxy-5-chloro-3-pentadiene-1,3 (IV) with Maleic Anhydride.—Twenty-seven grams of IV, 20 g. of maleic anhydride and 30 g. of acetone were heated to-

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(3) Diels and Alder, *Ber.*, **62**, 2337 (1929).

(4) Whitby and Crozier, *Can. J. Research*, **6**, 203 (1932).

(5) Carothers, *Ind. Eng. Chem.*, **26**, 30 (1934).

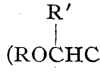
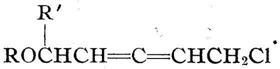
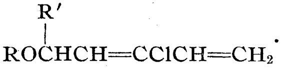
gether at 50° for two hours. The acetone was then removed by distillation and the residue refluxed with water for two hours. The aqueous portion on evaporation yielded 15 g. of chloro acid. After two recrystallizations from hot water, the chloro acid melted at 163–165°. The acid had a neutral equivalent of 123.3 as compared with a calculated value of 124.3 for $C_{10}H_{13}O_5Cl$ (V).

Oxidation of Methoxy-5-chloro-3-pentadiene-1,3 (IV).—To a vigorously stirred mixture of 20 g. of IV, 80 g. of potassium carbonate and 200 g. of water, maintained at 10–25°, 165 g. of potassium permanganate was added during the course of six hours. The mixture was then decolorized with sulfur dioxide, acidified with sulfuric acid and extracted with ether. The ether extract yielded 0.8 g. of oxalic acid and 2 g. of crude methoxyacetic acid, b. p. 70–110° (25 mm.); n^{20}_D 1.4140. The oxalic acid was identified by its melting point (97–101°) and its transformation into oxal-*p*-toluidide (m. p. 266°). The methoxyacetic acid was characterized by conversion into its amide, which melted, after one crystallization from alcohol, at 92–94°, as compared with a recorded value of 92°.[6]

Oxidation of Methoxy-5-chloro-1-pentadiene-2,3 (III).—One hundred and sixty grams of potassium permanganate was added during the course of five hours to a well-stirred mixture of 20 g. of III and 200 g. of water. The mixture was then decolorized with sulfur dioxide, filtered, acidified with sulfuric acid (carbon dioxide evolved) and extracted with ether in the usual way. The ether extract yielded 0.3 g. of oxalic acid (identified by its m. p. of 99–101°, and its *p*-toluidide, m. p. 267–269°) and 6 g. of liquid boiling at 95–110° (25 mm.). On cooling, the liquid fraction deposited chloroacetic acid, m. p. 48–53°. The chloroacetic acid was further identified by conversion into its amide, which melted at 118–120° as compared with a recorded value of 119.5°.[7]

The author wishes to express his thanks to Dr. Wallace H. Carothers for his interest in this work and for his helpful suggestions.

Summary

The reaction between alpha chloro ethers and vinylacetylene is shown to be closely analogous to the addition of hydrogen chloride to vinylacetylene to form isochloroprene and chloroprene. The initial step appears to be 1,4 addition of the chloroethers  $(\mathrm{RO\overset{\overset{R'}{|}}{C}HCl})$ to vinylacetylene with the formation of products of the formula  $\mathrm{RO\overset{\overset{R'}{|}}{C}HCH{=}C{=}CHCH_2Cl}$. In the presence of cuprous chloride and hydrochloric acid these products readily isomerize to compounds of probable structure  $\mathrm{RO\overset{\overset{R'}{|}}{C}HCH{=}CClCH{=}CH_2}$. The latter compounds polymerize to form resins which are somewhat rubber-like.

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(6) Gauthier, *Ann. chim. phys.*, [8] **16**, 307 (1909).

(7) Menschutkin and Jermolajew, *Z. Chem.*, [2] **7**, 5 (1871).

WILMINGTON, DEL.

RECEIVED JULY 16, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS AND SCIENCES OF TEMPLE UNIVERSITY]

The Synthesis of 4-Methyl-6-oxypyrimidine-5-acetic Acid and 4-Methyluracil-5-methylamine

BY WILLIAM T. CALDWELL AND WILLIAM M. ZIEGLER

The first structure[1] for vitamin B_1 proposed by Williams contained an ethyl group in the pyrimidine nucleus. Later, Windaus, Tschesche and Grewe[2] expressed the opinion that the existence of two methyl groups rather than that of a single ethyl group in the primidine nucleus was in better harmony with their experimental results. Cleavage of the vitamin by sulfite[3] formed an amino sulfonic acid from which a corresponding hydroxy acid was obtained in which the sulfonic acid group presumably would be attached to the pyrimidine nucleus in position 5, in accord with the hypothesis of the existence of two free methyl groups in the nucleus.

A search of the literature, however, failed to disclose to us a case in which a pyrimidine with sulfonic acid group in position 5 had been isolated, and although this was no proof that a substance of the latter type was not formed by the sulfite cleavage, it nevertheless led us to consider the synthesis of compounds containing an amino methyl group in position 5.

The formula proposed by Makino and Imai[4] expresses the same conclusion as to the likelihood of an amino methyl group in this position. We set about, accordingly, to synthesize a compound of the structure

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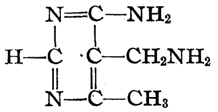
(1) Williams, THIS JOURNAL, **57**, 229 (1935).

(2) Windaus, Tschesche and Grewe, *Z. physiol. Chem.*, **237**, 98 (1935).

(3) Williams, Buchman and Ruehle, THIS JOURNAL, **57**, 1093 (1935).

(4) Makino and Imai, *Z. physiol. Chem.*, **239**, I, 7 (1936).



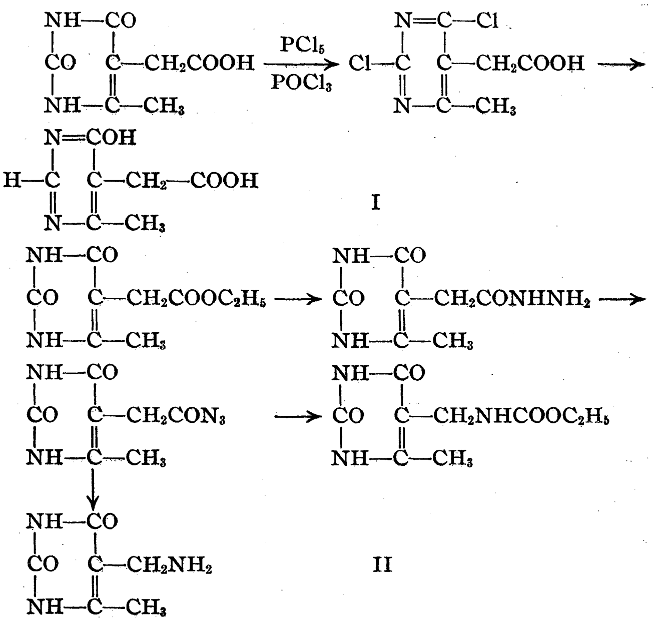
I

in the hope that it might prove to be identical with the compound $C_6H_{10}N_4$ isolated by Windaus as picrate. There has appeared quite recently, however, a report of further work by Williams[5] on the basis of which he proposes a new formula for vitamin B_1 from which it is quite clear that, although one amino group should be found in the side chain in position 5, the nuclear methyl group is in position 2 and not 4 as in the compound we hoped to prepare.

As a result of this new evidence, we have abandoned our original intention of preparing a compound represented by structure I, and are therefore reporting the synthesis of several new pyrimidine derivatives obtained as intermediates for the preparation of the diamine which we had thought might be identical with Windaus' $C_6H_{10}N_4$ but which Williams has shown now could be only an isomer thereof.

One plan of procedure involved the preparation of 4-methyl-6-oxypyrimidine-5-acetic acid from which, by means of the Curtius reaction which Johnson and Litzinger[6] had used successfully for an analogous reaction, we hoped to obtain a desired intermediate in good yield. Unfortunately, preliminary experiments gave little promise of satisfactory yields in our hands, so that we abandoned this path temporarily in the hope of securing more promising results by preparing first 4-methyluracil-5-methylamine. Although we have succeeded in preparing this compound, both as free base and as acetate, the yield is far from good. In fact, we have been unable to hydrolyze the urethan to the amine as yet; heating in a sealed tube at 130° for several hours produced a white, extremely insoluble compound but no amine. After a number of attempts to hydrolyze the urethan had yielded us only white solids that did not melt below 320° and which were insoluble in water or alcohol, we decided to attempt the direct conversion of the azide into the amine by the method described by Lindemann.[7] In this way we were able to obtain a small amount of the desired free base by liberating it from the acetate. This method appears to be more likely to give improved yields than the hydrolysis of the urethan.

The reactions that we shall describe are summarized by the following formulas



Experimental Part

2,6 - Dichloro - 4 - methylpyrimidine - 5 - acetic Acid.— This compound was prepared from the corresponding 4-methyluracil-5-acetic acid which was obtained readily by the method described by Johnson and Heyl.[8] Phosphorus oxychloride (460 g.) was poured upon 4-methyluracil-5-acetic acid (63 g.). Hydrogen chloride was evolved but the solid apparently did not go into solution. Phosphorus pentachloride (350 g.) was then added to the ice-cooled mixture, and then this was heated for six hours on a boiling water-bath. By the end of this time, practically all of the material appeared to have dissolved, forming a very dark brown solution. Phosphorus oxychloride (443 g.) was removed under diminished pressure on the steam-bath, leaving a dark, resinous residue. This was cooled in ice, treated with ether and ice in portions until all had either gone into solution or broken up into small particles so that the material could be poured from the flask. This aqueous suspension and ether extract (both very dark brown or black) upon filtration with suction left a small residue of tarry material upon the filter paper. After separating the ether layer from the aqueous one, and re-extracting the latter with ether, the ether extract (about 2000 cc. in all) was set aside and allowed to evaporate slowly in such a way that the temperature did not rise above 25°. After several days, dark colored crystals (21.4 g.) separated. They were insoluble in benzene and in petroleum ether, but soluble in absolute ether, from which they were recrystallized, separating as pale yellow crystals, melting at 156–157°.

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(5) Williams, THIS JOURNAL, **58**, 1063 (1936).

(6) Johnson and Litzinger, *ibid.*, **57**, 1139 (1935).

(7) Lindemann, *Helv. Chim. Acta*, **11**, 1028 (1928).

(8) Johnson and Heyl, *Am. Chem. J.*, **38**, 659 (1907).

Anal. Calcd. for $C_7H_6O_2N_2Cl_2$: Cl, 32.09. Found: Cl, 30.93.

4 - Methyl - 6 - oxypyrimidine - 5 - acetic Acid.—The above dichloro compound (11.8 g.) was reduced by the method of Gabriel and Colman.[9] The free acid, after liberation from its potassium salt with acetic acid, extraction with benzene and recrystallization from the latter, was obtained as snow-white crystals, melting at 147–149° and giving no Beilstein test; yield 3.5 g.

Anal. Calcd. for $C_7H_8O_3N_2$: N, 16.66. Found: N, 16.38.

4 - Methyluracil - 5 - carbethoxymethylamine.—The ethyl ester of 4-methyluracil-5-acetic acid (22 g.), m. p. 221–222°, was converted into the hydrazide in the usual way. From these white crystals that darkened slightly above 320° but did not melt by 375°, the azide was obtained easily and was converted into the urethan by heating with an excess of absolute alcohol. After the vigorous evolution of gas had ceased, the hot liquid was filtered from considerable insoluble white solid and concentrated. The urethan, which was soluble in water and in alcohol, was obtained as fine white crystals of m. p. 214–215° from absolute alcohol; yield, 12 g. of urethan from 20 g. of hydrazide.

Anal. Calcd. for $C_9H_{13}O_4N_3$: N, 18.50. Found: N, 18.48.

Our attempts to hydrolyze this urethan by heating with concentrated hydrochloric acid either at atmospheric pressure or in a sealed tube for a day at 130–140° failed to yield any of the desired 5-aminomethyl compound. The product was a white solid that did not melt or decompose by 320°, and which was insoluble in all organic solvents that we tried.

4-Methyluracil-5-methylamine.—In view of the unexpected difficulty encountered in the hydrolysis of the above urethan, we made use of Lindemann's method[7] for the conversion of an azide into an amine. By heating the azide with 50% acetic acid, the substance dissolved with evolution of gas. After a few minutes, white solid began to appear and was removed from time to time as the liquid was concentrated. This material was insoluble in water and did not melt below 310°. The filtrate was evaporated to dryness, the residue dissolved in water, filtered, and again concentrated. The white crystals obtained in this way, when dissolved in water, turned red litmus slowly, but distinctly, blue. With a drop of concentrated sulfuric acid the odor of acetic acid became easily perceptible, and the analysis also indicated that the product was the acetate of the amine. The yield from 12 g. of the azide was 2.8 g.

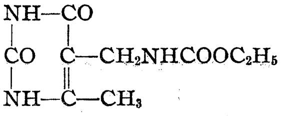
Anal. Calcd. for $C_6H_9O_2N_3 \cdot C_2H_4O_2$: N, 19.53. Found: N, 19.55.

The white salt turned to a very pale yellow material at 227–229°, but on further heating to 360° merely became progressively darker. On adding a solution of potassium hydroxide to a solution of the acetate there soon separated, upon scratching with glass, a finely crystalline white solid—fine needles under the microscope. After washing well with absolute alcohol, they were recrystallized from water in which they were easily soluble. The free base is a strong one, turning red litmus blue. On heating, it became brown by 335° but did not melt; yield 0.5 g.

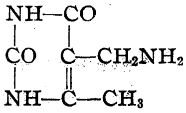
Anal. Calcd. for $C_6H_9O_2N_3$: C, 46.45; H, 5.85; N, 27.09. Found: C, 46.50; H, 6.50; N, 27.27.

Summary

Several new pyrimidines, whose preparation was stimulated by the work of Williams and others on vitamin B, are reported. Attention is called to the difficulty met in the attempt to hydrolyze the urethan



to the amine



PHILADELPHIA, PENNA. RECEIVED JULY 13, 1936

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[9] Gabriel and Colman, *Ber.*, **32**, 1533–1534 (1899).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEW HAMPSHIRE]

A New Method for the Separation of Yttrium from the Yttrium Earths

BY H. C. FOGG AND LEWIS HESS

The use of urea as a precipitant for aluminum in the presence of calcium, barium, magnesium, manganese, zinc, cobalt, nickel, iron, cadmium and copper was the subject of an investigation by Willard and Tang,[1] and its use as a precipitant for gallium in the quantitative determination of that element was studied by Willard and Fogg.[2] Since the decomposition of urea[3] results in the formation of ammonia at a slow and uniform rate throughout the homogeneous solution, it may advantageously be applied to the fractionation of the yttrium earths.

Method of Separation

The mixed earths, in the form of their oxides, are dissolved in nitric acid, and the solution is nearly neutralized with ammonia and diluted. Ammonium sulfate is added in amount just insufficient to cause precipitation, followed by one- to two-tenths of an equivalent of urea. The solution is heated with stirring to 90–95°, and

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[1] H. H. Willard and N. K. Tang, unpublished work.

[2] H. H. Willard and H. C. Fogg, unpublished work.

[3] E. A. Werner, *J. Chem. Soc.*, **113**, 84 (1918).

kept at this temperature for six to eight hours, during which time a precipitate gradually forms. This is filtered off, more urea is added, and the filtrate is again treated in the same manner, fractionation being continued until examination of the absorption spectrum indicates that the solution is nearly free of erbium.

Control of Fractionation

The materials subjected to fractionation were of two types, one a mixture of yttrium and erbium oxides containing very small amounts of the other yttrium earths, and the other a mixture of the hydroxides of the yttrium earths containing 2–3% of thorium. The separation was followed by means of the equivalent weight of the rare earth mixture, which was determined by conversion of oxide to sulfate.

Results of Fractionation

The results of two typical series of fractionations are given below.

TABLE I

FRACTIONATION OF YTTRIUM–ERBIUM MIXTURE

	At. wt.	% Er_2O_3	Weight, g.
Original material	134.6	58.0	100.6
Fraction 1	147.0	73.8	21.3
Fraction 3	141.3	66.5	11.3
Fraction 5	139.9	64.8	5.3
Fraction 7	135.9	59.7	8.2
Fraction 10[a]	107.8	24.0	18.7

[a] Represented the material remaining after the precipitation with urea, and was precipitated as oxalate.

TABLE II

FRACTIONATION OF MIXTURE CONTAINING THORIUM

	At. wt.	Equivalent % Er_2O_3,	Weight, g.
Original material	110.9	27.9	540.0
Fraction 2	131.9	54.6	18.3
Fraction 3	129.6	51.7	22.7
Fraction 5	120.1	39.6	49.7
Fraction 7	114.7	32.8	35.8
Fraction 9	107.2	23.2	31.7
Fraction 11[a]	98.2	11.8	211.3

[a] Represented the material remaining after the precipitation with urea, and was precipitated as oxalate.

The equivalent percentages in Tables II and III are computed upon the admittedly false assumption that the original material was a mixture of yttria and erbia only. The equivalent weight of fraction 1 of the series described in Table II was not determined as, due to its high thorium content, it was not soluble in hydrochloric acid. The thorium content of this fraction (as ThO_2) was found to be 36.4%. It was determined by the method of Carney and Campbell,[4] the solution of the sample being prepared by fusion with potassium pyrosulfate and extraction with water.

Several series of fractionations were carried out using a full equivalent of ammonium sulfate per equivalent of rare earth. This method was found to have no greater efficiency than the one recommended and to have a definite disadvantage, due to the limited solubility of yttrium sulfate. This made it necessary to use a dilute solution of the mixed nitrates with consequent increase in the volume and decrease in the quantity of material which could be handled conveniently. With the method described above, it was possible to use a relatively concentrated solution, say of the order of 5 to 6 per cent. Tables III and IV are representative of data obtained with the use of a full equivalent.

TABLE III

FRACTIONATION OF MATERIAL CONTAINING THORIUM

	At. wt.	Equivalent % Er	Weight, g.
Original material	112.8	30.3	101.1
Fraction 3	136.3	60.2	4.5
Fraction 5	125.4	46.3	5.8
Fraction 7	115.0	33.1	6.8
Fraction 9	108.5	24.9	6.7
Fraction 11	101.3	15.7	7.7
Fraction 13[a]	93.5	5.8	17.8

[a] Represented the material remaining after the precipitation with urea, and was precipitated as oxalate.

TABLE IV

FRACTIONATION OF YTTRIUM–ERBIUM MIXTURE

	At. wt.	% Er	Wt., g.
Original material	132.0	54.7	50.0
Fraction 1	144.7	70.9	3.9
Fraction 4	141.3	66.5	3.2
Fraction 7	136.8	60.8	2.9
Fraction 10	127.9	49.5	3.6
Fraction 14	110.9	27.9	1.2
Fraction 15[a]	101.7	16.2	3.8

[a] Represented the material remaining after the precipitation with urea, and was precipitated as oxalate.

Discussion

A comparison of the new method with those previously used may be of interest. The more important of the earlier methods include the fractional crystallization of the bromates,[5] the fractional decomposition of the nitrates by fusion,[6] and the fractional precipitation of the chromates,[7]

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[4] R. J. Carney and E. D. Campbell, THIS JOURNAL, **36**, 1140 (1914).

[5] C. James, *ibid.*, **30**, 182 (1908).

[6] C. James, *ibid.*, **34**, 757 (1912).

[7] W. Muthmann and R. Böhm, *Ber.*, **33**, 42 (1900).

the basic nitrites,[8] the cobalticyanides[9] and the ferricyanides.[10] The bromate method is the standard one for the fractionation of the yttrium earths, but is not particularly effective for the preparation of pure yttrium. The new method compares favorably in efficiency with the nitrate fusion, chromate and basic nitrite methods. It appears to be superior to the ferricyanide and cobalticyanide methods. Grant and James[10] report a very high efficiency for the ferricyanide method, but no supporting data have been published.

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[8] H. C. Holden and C. James, THIS JOURNAL, **36**, 1418 (1914).

[9] J. P. Bonardi and C. James, *ibid.*, **37**, 2642 (1915).

[10] A. J. Grant and C. James, *ibid.*, **39**, 933 (1917).

Summary

A new method for the separation of yttrium from the yttrium earths has been proposed, and has been found to compare favorably in efficiency with the methods now in use.

DURHAM, NEW HAMPSHIRE RECEIVED MAY 1, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Activated Adsorption of Hydrogen and Carbon Monoxide on Zinc Oxide. The Effect of Water Vapor

BY ROBERT L. BURWELL, JR., AND HUGH S. TAYLOR

Poisons such as water vapor have been presumed to effect the retardation of catalytic processes by being adsorbed on the "active spots," thus blocking access of the reactants to such catalytically effective sections of the surface.[1] This access of reactants to catalytically effective sections of the surface consists according to Taylor[2] of an activated adsorption of the reactants on such regions of the surface. Reversible poisoning would accordingly result from an activated adsorption of the poison on the active sections of the surface, an adsorption possessed of energy relations such that the activation energy of desorption would be large compared with that of the other components of the system. In this fashion the activated adsorption of the reactants may be hindered.

Taylor and Sickman[3] and Taylor and Strother[4] investigated the activated adsorption of hydrogen on zinc oxide. The former investigators further reported that water vapor exerted an inhibitory influence on a catalytic action which they studied, the decomposition of propanol-2 on zinc oxide. It thus appeared of interest to study the effects of water vapor on the activated adsorption of hydrogen on zinc oxide.

Experimental

Rates of the activated adsorption of hydrogen on zinc oxide were determined by means of an apparatus and method similar to that described by Taylor and Strother.[4] The purified hydrogen could be saturated with water vapor at any desired temperature between 0° and room temperature by diverting it through a spiral bubbling column filled with distilled water and maintained at the desired temperature. Carbon monoxide was prepared by dropping formic acid on hot sulfuric acid. It was purified by passage over copper heated to 450°, soda lime, calcium chloride and phosphorus pentoxide. To supply water vapor to the adsorbent preliminary to rate runs, the apparatus was further provided with a buret of 410-cc. capacity. The zinc oxide was prepared from zinc oxalate as described by the above authors.

All gas volumes reported have been corrected to N. T. P. All the experiments described in this paper were performed on two samples of the same batch of zinc oxide. These samples were 3B, weight 16.5 g., and 3C, weight 22.7 g.

Before the start of these researches these adsorbents had been subjected to a series of determinations of the rates of activated adsorption, first of carbon monoxide and then of hydrogen. During the course of these adsorption measurements the activity of the surface had fallen slowly but steadily.

Results and Discussion

After a number of runs with hydrogen at 184 to 302°, it was observed that, at the completion of the adsorption, the preparations, notably 3B, had

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[1] See, for example, Armstrong and Hilditch, *Proc. Roy. Soc.* (London), **A97**, 262 (1920); Dohse and Kälberer, *Z. physik. Chem.*, **5B**, 131 (1929).

[2] Taylor, THIS JOURNAL, **53**, 578 (1931).

[3] Taylor and Sickman, *ibid.*, **54**, 602 (1932).

[4] Taylor and Strother, *ibid.*, **56**, 586 (1934).

a distinctly grayish appearance. On evacuation at 400° the original color of the preparation reappeared. A dark gray condensate gradually appeared above the furnace level on the walls of the capillary tube leading from the catalyst bulb.

It appears that, by reduction, there is formed a certain quantity of metallic zinc which subsequently distils from the catalyst bulb during evacuation. Only a small portion of the adsorbed hydrogen reduces the zinc oxide. Thus in 32 runs on preparation 3C, over 334 cc. of hydrogen was adsorbed. One gram of zinc would have been formed if all of this had led to reduction; actually less than 0.05 g. appeared. The diminution of the activity of the zinc oxide preparation probably resulted from destruction of the more active spots by reduction.

For bulk zinc oxide a very small pressure of water vapor would thermodynamically render reduction impossible at these temperatures. Even at 419° this pressure is only 0.0033 mm.[5] There are two factors which may enter into the observed reduction: (a) thermodynamic considerations applying to bulk material will not apply to surface molecules of different energy characteristics; (b) water vapor is adsorbed so tenaciously as to reduce its vapor pressure below the critical level.

If the surface of the adsorbents be saturated with water vapor after the evacuation but before the start of the determination of the rate of hydrogen adsorption, then the catalyst remains white.

If hydrogen saturated with water at 17° be adsorbed on a freshly evacuated preparation, a fraction of the material at the top of the bulb near the supply tube remains white but that at the bottom turns gray. Thus, during run 51 on preparation 3B at 254°, gas pressure 360 mm., water vapor pressure 7.2 mm., the upper fifth of the zinc oxide remained white, while in run 52 under similar conditions, the upper seventh remained white.

The explanation of this phenomenon is clear. Water vapor is adsorbed so strongly by zinc oxide that the first sections of zinc oxide completely remove the water vapor from the entering gas. Those sections with adsorbed water vapor are protected from attack.

This phenomenon is closely related to one recorded by Russell and Ghering[6] in a study of the effect of oxygen poisoning upon the rate of the hydrogenation of ethylene on copper. There the oxygen was adsorbed tenaciously by the first sections of copper with which it came in contact and portions farther from the inlet tube were supplied only as the nearer portions approached saturation. As a result, progressive additions of oxygen reduced the rate of hydrogenation in a linear manner. As Russell and Ghering emphasize, such a linear relation is not an argument for a uniform surface. From the evidence presented by the present authors, it is clear that similar consideration would prevail in poisoning zinc oxide surfaces with water vapor. In spite of the non-uniformity of zinc oxide surfaces, the reduction of the rate of reaction would bear a linear relation to the quantity of water vapor introduced.

Effect of Water Vapor on the Rate of Activated Adsorption.—Experiments were performed which permit comparison of the rates of activated adsorption of hydrogen and carbon monoxide on zinc oxide surfaces previously saturated with water vapor with those obtained on the ordinarily evacuated catalyst. Adsorption measurements were made at 1 atm. pressure on preparation 3C.

As Taylor and Sickman[3] found, the first portions of water vapor are adsorbed on zinc oxide with great rapidity, the later portions more slowly. Thus, at 218°, preparation 3C, after evacuation for five hours at 410°, adsorbed 7.4 cc. (N. T. P.) of water vapor under 14.5 mm. pressure within two minutes. Another 7.4 cc. was adsorbed in an hour. The final pressure of water vapor was 6 mm.

Table I exhibits the effect of water vapor on the rate of activated adsorption of hydrogen and carbon monoxide on preparation 3C.

TABLE I

EFFECT OF WATER VAPOR ON THE RATE OF ADSORPTION OF HYDROGEN AND CARBON MONOXIDE ON PREPARATION 3C AT 218°

	Adsorption in cc. of								
Time,	Hydrogen						Carbon monoxide		
min.	Run 52	54	55	56	58	59	62	64	65
1	2.35	2.70	2.80		0.40	1.95	0.80	0.90	0.50
2	2.70	3.00	3.10	3.60		2.25	1.10	1.15	.55
4	3.00	3.35	3.30	3.90		2.50	1.65	1.60	.65
8	3.40	3.75	3.60	4.25		2.85	2.30	2.15	.85
12	3.60	4.00	3.85	4.40		3.00	2.80	2.55	1.00
20	3.95	4.30	4.25	4.70	.45	3.30	3.50	3.05	1.15
40	4.35	4.85	4.65	5.05	.50	3.70	4.55	4.10	1.55
60	4.65	5.05	4.90	5.30		3.95	5.20	4.70	1.75
100	4.95	5.45	5.15		.60	4.20	6.00	5.45	2.10

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[5] G. B. Taylor and Starkweather, THIS JOURNAL, **52**, 2323 (1930). This paper deals thoroughly with the problem of reduction of zinc oxide by hydrogen.

[6] Russell and Ghering, *ibid.*, **57**, 2544 (1935).

Adsorption runs 58 and 65 on preparation 3C were performed on zinc oxide surfaces which had been saturated with water vapor in the manner just described. The other runs were made on freshly evacuated surfaces. The gases employed in runs 52, 54, 58, 59, 62, 64 and 65 were free from water vapor. The hydrogen employed in run 55 contained 4.5 mm. of water vapor and that in run 56, 14.5 mm.

It is observed that rates of adsorption of both hydrogen and carbon monoxide are markedly smaller on surfaces saturated with water vapor. On the other hand, partial pressures of water vapor up to 14.5 mm. may be introduced with hydrogen without sensibly affecting the rate of adsorption. At 218° the dead space in the catalyst bulb of preparation 3C amounts to about 20 cc. In run 56, this 20 cc. of gas contains 0.4 cc. (N. T. P.) of water vapor. In the light of earlier considerations this entire quantity would be adsorbed immediately but only by those portions of zinc oxide very near the inlet tube. Since about 7.4 cc. of water vapor can be absorbed with great tenacity, from 5 to 10% of the surface is in the condition of the whole surface in run 58, whereas the remainder of the surface is unaffected. Such variation is within the experimental error set by the reproducibility of the surface.

Similar results were obtained on preparation 3B in regard to the effect of water vapor on the rate of adsorption of hydrogen. At 254° and 0.5 atm. pressure, preliminary saturation of the surface with water vapor reduced the rate of adsorption by 75%.

Because, in the presence of nickel, deuterium exchanges very much more rapidly with benzene than does deuterium oxide, Horiuti and Polanyi[7] consider that the exchange does not proceed by dissociative adsorption succeeded by recombination of the fragments, unless equilibrium conditions on the surface are upset by a change from deuterium to deuterium oxide.

On the basis of common examples of poisoning and on the basis of the researches presented in the paper, the authors consider that water vapor in quantity may reduce reaction rates by reducing the rate of the activated adsorption of the reactants if such adsorption be rate determining, or by making unavailable a certain fraction of the catalytically effective surface if some succeeding step be rate determining. Thus the authors believe that the consideration whereby Horiuti and Polanyi reject the mechanism of exchange via dissociative adsorption is not valid.

Summary

1. Water vapor has been shown to minimize surface reduction of zinc oxide catalysts at lower temperatures.

2. Water vapor has been shown to be strongly adsorbed from gas mixtures containing this vapor by those fractions of zinc oxide surfaces to which the mixture of gases first has access.

3. Saturation of zinc oxide surfaces with water vapor has been shown markedly to inhibit the activated adsorption of hydrogen and carbon monoxide.

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[7] Horiuti and Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

PRINCETON, N. J. RECEIVED JUNE 8, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Behavior of Iodine in Some Sensitized Decompositions of Gaseous Organic Compounds

BY R. FRANCIS FAULL AND G. K. ROLLEFSON

Introduction

It has been shown by Hinshelwood and others[1-3] that the decomposition rates of a number of organic substances are greatly increased by the addition of relatively small amounts of iodine. In discussing their results they have discarded chemical mechanisms for the action of iodine in favor of a hypothesis involving collisions between iodine and the organic molecules. Recently, while preparing to test these reactions for photosensitivity, we have discovered that under the same conditions as prevailed in Hinshelwood's work little or no free iodine can be detected by spectroscopic methods during the course of the reactions. This result leads to the conclusion that these reactions actually proceed by chemical mechan-

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[1] Bairstow and Hinshelwood, *Proc. Roy. Soc.* (London), **A142**, 77 (1933).

[2] Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford Univ. Press, London, 1933, p. 225.

[3] Bairstow, *Trans. Faraday Soc.*, **29**, 1227 (1933).

isms and in this paper we wish to present evidence for three types of behavior.

Apparatus and Experimental Details

The apparatus consisted of a Pyrex reaction vessel of approximately 350-cc. capacity within an electric furnace. The reaction vessel was connected to an external vacuum system and to an iodine storage bulb, each through a heated glass valve.[4]

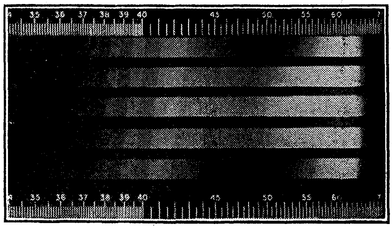


Plate I.—Propionaldehyde at 394°.

The glass valves eliminated troubles caused by ordinary grease stopcocks and were found to operate very satisfactorily in individual ovens, whereby the temperature could be maintained as high as 150°. The iodine storage bulb was immersed in a small oil-bath that could be heated to distil iodine into the reaction vessel. The pressure was measured by a click gage[5] and a mercury manometer. All connecting tubing was capillary glass, wound with resistance wire and electrically heated. The temperature was measured by a chromel–alumel thermocouple which was imbedded in a well extending into the center of the reaction vessel and could be regulated within one degree. The light source was a 500-watt tungsten projection lamp. By utilizing windows in the ends of the furnace the beam could be directed along a 15-cm. path through the reaction vessel into a Hilger E3 spectrograph.

The organic materials used were taken from the center fractions of redistillations of Eastman Kodak Co. stock and stored in three-liter bulbs connected to the vacuum line. The iodine was Merck reagent. In each experiment the iodine, at 1.5 cm. pressure, was introduced from the heated reservoir, the pressure measured and then the organic gas in question, at approximately 25 cm. pressure, was allowed to enter the reaction vessel.

Observations and Spectrograms

Acetaldehyde.—At 400° acetaldehyde removes the iodine color immediately upon entering the reaction vessel. The restoration of the color begins in about three minutes and is complete after five minutes. At 350° the reaction is slower, but at 300° the iodine color never completely disappears. All attempts to isolate an intermediate state failed because the iodine was liberated rapidly on cooling the reaction mixture. The reaction at 300° is photosensitive, the rate measured by pressure change being approximately doubled upon intense illumination with a 500-watt tungsten lamp.

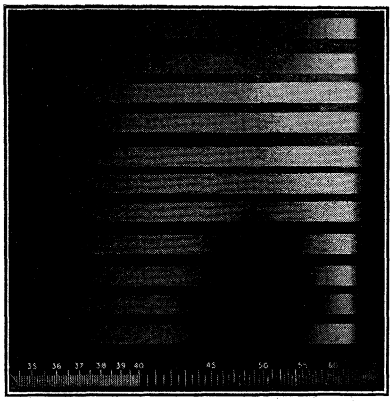
Propionaldehyde.—The same characteristics that are shown by acetaldehyde are exhibited by propionaldehyde (see Plate I). At 394° the color of the iodine disappears and returns within four minutes. At 340° the rate of reaction was increased by strong illumination as measured by pressure change.

Diethyl Ether.—At 440° the color of iodine disappears almost immediately and is completely restored after thirty or forty minutes.

Ethylene Oxide.—The behavior of ethylene oxide resembled closely that of acetaldehyde.

Methyl Alcohol.—At 470° methyl alcohol decolorized iodine within one minute. The color does not begin to return until after four hours have elapsed. The colorless reaction mixture can be removed without the liberation of iodine and can be shown to contain hydrogen iodide.

Methyl Formate.—At 460° methyl formate requires about fifteen minutes to decolorize the iodine (see Plate II). The color begins to return after three hours and is almost completely restored within five hours.



Methyl Formate at 460°.

Plate II.—Spectrograms of different stages of iodine sensitized decompositions. The exposures are ten seconds, with a 500-watt lamp as a light source. Elapsed times are given from the beginning of the reactions. Scale units are in hundreds of Ångströms.

Formaldehyde.—At 450° the color disappears immediately and begins to reappear in about two hours. It is completely restored after five hours.

Diethylamine.—Diethylamine shows no decolorization of iodine over a wide temperature range within which it decomposes.

Discussion

The substances investigated fall into three distinct classes. The first consists of acetaldehyde, propionaldehyde, diethyl ether and ethylene oxide. The characteristics shown by these may be listed as follows: (1) the color of iodine disappears and returns within a short time; (2) no hydrogen iodide can be isolated during the course of the reaction; (3) the iodine absorption band disappears completely on the spectrograms

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(4) The glass valves were of a design supplied to one of us (G. K. R.) by Professor G. B. Kistiakowsky. They are similar to those which have been described by Bodenstein except that they have silver chloride on the valve seat which eliminates the necessity for grinding the movable parts very exactly.

(5) Smith and Taylor, This Journal, **46**, 1393 (1924).

in some experiments; and (4) the decomposition products are the same in both the sensitized and unsensitized reactions.

The second class includes methyl alcohol, methyl formate and formaldehyde. The principal characteristics exhibited by these are as follows: (1) the color disappears rapidly but does not return for a relatively long period of time although the temperature is much higher than in Class I; (2) hydrogen iodide is present and can be isolated during the reaction; (3) the iodine absorption band is never completely removed from the spectrograms; and (4) the products in the iodine sensitized decompositions, except formaldehyde, are different from those in the unsensitized reactions.

The third class, which includes diethylamine, shows no decolorization of the iodine, which may be due to the conditions being such that a high concentration of iodine exists at the steady state.

In both cases where the color of iodine disappears, the reaction is much too fast to be accounted for by a decomposition of the organic substance into hydrogen and a subsequent reaction between iodine and hydrogen.[6] The disappearance of the iodine therefore must be due to the formation of hydrogen iodide or an alkyl iodide.[7] On this basis the following equations for the first two classes may be proposed

CLASS I

$$(C_2H_5)_2O + I_2 = C_2H_5I + HI + CH_3CHO$$

$$RCHO + I_2 = RI + HI + CO$$

$$RI + HI = RH + I_2$$

CLASS II

$$CH_3OH + I_2 = 2HI + HCHO$$

$$HCHO + I_2 = 2HI + CO$$

$$2HI + CH_3OH = H_2O + CH_4 + I_2$$

$$2HI = H_2 + I_2$$

These equations account for the difference in the rate of reappearance of the iodine, because the reaction between an alkyl iodide and hydrogen iodide is rapid, whereas the decomposition of hydrogen iodide is slow.[6] A test of this is given by the rapid appearance of iodine color where methyl iodide is introduced into a reaction mixture containing hydrogen iodide at 365°. Methyl iodide itself does not begin to decompose appreciably until the temperature is well above 400°. A test reaction between hydrogen and iodine was found to be very slow at 450°, showing the absence of any catalytic effect in the apparatus. Therefore the essential difference between the two classes lies in the steps that produce iodine. Also the actual products present in the decomposition are accounted for by the equation.[8]

In any case it seems apparent that the sensitized decomposition takes place through definite chemical reactions rather than a collision activation process that was proposed by Hinshelwood.[1–3] In regard to Class I, it is known that acetaldehyde exists as an intermediate in the thermal decomposition of diethyl ether[9] and ethylene oxide,[10,11] and hence it is not unlikely that the sensitized decompositions go through an aldehyde stage. Even in Class II the formaldehyde intermediate has been reported in some of the thermal decompositions. In comparing the behavior of the two classes it appears that in Class II the course of reaction may go through a formaldehyde step rather than through any other aldehyde, the resulting slowness of the return of iodine color being due to the lack of formation of alkyl iodide from formaldehyde, as would have been the case if the decomposition had gone through any other aldehyde.

Our attention has been called to the work of Ogg [THIS JOURNAL, **56**, 526 (1934)] which makes it possible to calculate the rate of such a reaction as that between methyl iodide and hydrogen iodide under conditions such as prevail in the experiments referred to in this paper. According to the mechanism we have presented after the iodine color has disappeared the rate of decomposition of acetaldehyde is determined by the rate of the reaction between methyl iodide and hydrogen iodide. Using Ogg's equation for the rate as a function of temperature we calculate for one particular experiment at 420° [Hinshelwood, *Proc. Roy Soc.* (London) **A128**, 89 (1930)] a rate of 1.83×10^{-8} mol./cc./sec. whereas the observed rate was 3.47×10^{-8} mol./cc./sec. when the reaction was approximately forty per cent.

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[6] Bodenstein, *Z. physik. Chem.*, **29**, 295 (1899).

[7] The possibility of an addition compound between the organic substances and iodine may be ruled out by the following consideration. The entropy change in an addition reaction is always negative and from the change in the residual iodine concentration with temperature we must consider that ΔH for the formation of an addition product as an intermediate is positive. Therefore if we calculate $\Delta F^\circ_T = \Delta H - T\Delta S$ we find that the free energy change is positive and the equilibrium constant is less than one, which means that such an equilibrium could not account for the disappearance of the iodine.

[8] Bairstow and Hinshelwood, *J. Chem. Soc.*, 1147 (1933).

[9] Newitt and Vernon, *Proc. Roy. Soc.* (London), **A135**, 307 (1932).

[10] Heckert and Mack, THIS JOURNAL, **51**, 2706 (1929).

[11] Fletcher, *ibid.*, **58**, 539 (1936).

complete. This is as close agreement as could be expected.

Summary

The iodine concentration during a sensitized decomposition of gaseous diethyl ether, acetaldehyde, propionaldehyde, ethylene oxide, methyl alcohol, methyl formate, formaldehyde and probably many others, is very low.

The decompositions proceed through definite chemical reactions rather than collision activation processes.

BERKELEY, CALIF. RECEIVED JULY 9, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity and Entropy of Barium Chloride Dihydrate from 15 to 300°K. The Heat of Solution of Barium Chloride Dihydrate. The Entropy of Barium Ion

BY OLIVER L. I. BROWN, WENDELL V. SMITH AND WENDELL M. LATIMER

The method of calculating the entropy of barium ion which has been used up to the present[1] involves directly the entropies of chloride, thallous and nitrate ions, and indirectly the entropies of silver, bromide and iodide ions. Since the entropy of chloride ion is known with greater precision than that of thallous and nitrate ions, a method of calculating barium ion directly from chloride ion has long been considered desirable. The recent careful work of Tippetts and Newton[2] on the thermodynamics of aqueous barium chloride solutions has now made such a calculation feasible. In the present paper we have determined the following properties of barium chloride dihydrate: (1) the entropy, (2) the heat of solution in water, and (3) the solubility in water. Combining these data we have calculated the entropy of barium ion in aqueous solution.

Material.—A C. P. grade of barium chloride was crystallized three times from redistilled water. It was then dried in a desiccator over partially dehydrated barium chloride dihydrate. Since the sample was found by analysis to have more than the theoretical amount of water, it was dried at 105°, then rehydrated in a desiccator containing water. After analysis showed that the sample had taken up more than the theoretical amount of water, the sample was again dried over partially dehydrated barium chloride dihydrate. This cycle was repeated once again before a sample containing the theoretical amount of water was obtained.

Heat Capacity Measurements.—The experimental method was that of Latimer and Greensfelder.[3] The apparatus was slightly modified from that used in previous work. The block employed to ensure a uniform temperature environment for the calorimeter was replaced by a new block, which was machined very carefully so as to provide better contact between the two halves of the block. The inner surface of the block was gold plated and polished, and reduced considerably the corrections necessary for heat interchange due to radiation. The approximate values of ΔT used in the measurements were: 1.2° up to 20°K., 2–3° up to 50°K., 3–6° up to 180°K, and 6–9° up to 300°K. In calculating the heat capacities one calorie was taken equal to 4.1833 int. joules, and the molecular weight of barium chloride diphydrate was taken as 244.317. Measurements were made on a sample of 192.845 g. (weight *in vacuo*). The results are given in Table I and shown as a function of temperature in Fig. 1.

TABLE I

MOLAL HEAT CAPACITY OF BARIUM CHLORIDE DIHYDRATE

T., °K.	C_p Cal./mole/deg.	T., °K.	C_p Cal./mole/deg.
14.87	1.06	112.10	22.87
16.18	1.27	117.92	23.53
17.24	1.49	123.62	24.16
20.00	2.04	129.49	24.94
23.16	2.73	135.64	25.81
25.69	3.36	141.68	26.46
28.14	3.97	147.84	27.09
30.21	4.51	153.76	27.65
32.13	5.05	160.01	28.21
34.87	5.89	166.86	28.77
37.98	6.82	173.45	29.34
40.45	7.39	180.25	29.95
42.91	8.26	187.15	30.63
48.02	9.63	193.41	31.06
51.15	10.57	200.27	31.63
54.60	11.54	207.32	32.11
58.06	12.51	214.06	32.57
61.78	13.38	221.02	32.97
66.12	14.45	229.72	33.45
69.82	15.35	236.41	33.78
70.78	15.58	244.76	34.58
73.92	16.31	254.54	35.02
78.67	17.33	263.58	35.33
83.68	18.31	272.18	36.01
89.08	19.30	281.17	36.48
94.72	20.26	287.97	36.65
100.61	21.21	297.07	37.09
106.37	22.00	301.28	37.13

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[1] Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1933).

[2] Tippetts and Newton, THIS JOURNAL, **56**, 1675 (1934); Newton and Tippetts, *ibid.*, **58**, 280 (1936).

[3] Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928).

Entropy of Barium Chloride Dihydrate.—The entropy was calculated by graphical integration of a plot of C_p against log T, combined with an extrapolation at low temperatures using the Debye specific heat equation. The calculation is summarized in Table II.

TABLE II

MOLAL ENTROPY OF BARIUM CHLORIDE DIHYDRATE

0–14.87°K.	Debye extrapolation	0.39
14.87–298.1°K.	Graphical from data	48.19 ± 0.1
	Entropy at 298.1°K.	48.58 E. U.

Heat of Solution of Barium Chloride Dihydrate.—The measurements of the heat of solution were made in a calorimeter which consisted of a vacuum-walled flask of about one-liter capacity fitted with a stirrer, resistance thermometer, and device for introducing a weighed quantity of salt into the water by breaking two gold foil seals. The resistance thermometer consisted of about 45 ohms of platinum wire and also served as a heater for determining the heat capacity of the calorimeter and contents. The values obtained for the heat of solution of one mole of barium chloride dihydrate in 400 moles of water at 298.1°K. were 4412 and 4427 cal. If we combine the average value, 4420 cal., with the known heat of dilution of barium chloride solutions at 298.1°K.[4,5] we obtain for the heat of solution at infinite dilution, $\Delta H^\circ = 3955$ cal./mole.

Free Energy and Entropy of Solution of Barium Chloride Dihydrate.—The solubility of barium chloride at 298.1°K. was determined by evaporating weighed portions of the saturated solution to dryness and weighing the anhydrous barium chloride, after heating to constant weight at 150°. Equilibrium in the saturated solution was approached from both sides by saturating at higher temperatures and at lower temperatures than 298.1°K. The solubility in moles of anhydrous salt per 1000 g. of water was found to be 1.788. The activity coefficient of barium chloride has been determined by Tippetts and Newton[2] from both e. m. f. measurements and vapor pressure measurements. Using their results we find for the saturated solution $\gamma = 0.4418$ and $a_1 = 0.9021$ (a_1 = activity of water). For the reaction

$$BaCl_2{\cdot}2H_2O(s) = Ba^{++} + 2Cl^- + 2H_2O(l) \quad \text{(hypothetical one molal solution)} \qquad (1)$$

$\Delta F^\circ = -1363.8 \log 4(\gamma m)^3 a_1^2 = -280$ cal. $\Delta H^\circ = 3955$ cal. $\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T = 14.20$ E. U.

Entropy of Barium Ion.—The entropy of chloride ion is 13.5 E .U.[1] The entropy of water calculated from the spectroscopic value for the perfect gas[6] and the entropy of condensation of the perfect gas to liquid water[7] is 16.77 E. U. The entropy of barium ion is given by the expression

$$S^\circ_{Ba^{++}} = S_{BaCl_2\cdot 2H_2O} + \Delta S^\circ - 2S^\circ_{Cl^-} - 2S_{H_2O} = 48.58 + 14.20 - 27.0 - 33.54 = 2.2 \text{ E. U.}$$

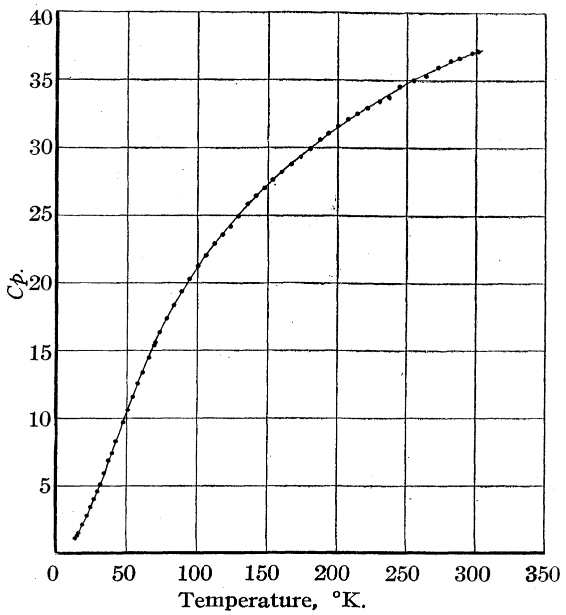

Fig. 1.—Molal heat capacity of barium chloride dihydrate.

Summary

The heat capacity of barium chloride dihydrate has been measured from 15 to 300°K., and the entropy of the salt determined by graphical integration. The solubility and heat of solution of barium chloride dihydrate in water has been determined at 298.1°K. Combining these data with other data already available, the entropy of barium ion has been determined.

BERKELEY, CALIFORNIA RECEIVED JUNE 23, 1936

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(4) Richards and Dole, THIS JOURNAL, **51**, 794 (1929).

(5) Lange and Streeck, *Z. physik. Chem.*, **A152**, 1 (1931).

(6) Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

(7) Giauque and Stout, THIS JOURNAL, **58**, 1144 (1936). The value here quoted is consistent with that selected by these authors after a review of the existing data.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Kinetic and Equilibrium Measurements of the Reaction $2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$

BY ALLEN V. HERSHEY AND WILLIAM C. BRAY

The reaction

$$2Fe^{+++} + 2I^- \rightleftharpoons 2Fe^{++} + I_2 \qquad (1)$$

furnishes an example in which the rates of both the forward and reverse reactions may be measured conveniently, and in which the kinetic results may be checked by comparison between values of the equilibrium quotient

$$K = (Fe^{++})^2(I_2)/(Fe^{+++})^2(I^-)^2 \qquad (2)$$

based on measurements of rate, electromotive force and equilibrium concentrations. Wagner[1] in 1924 suggested the complete rate law

$$\frac{d(Fe^{++})}{dt} = \frac{k_1(Fe^{+++})(I^-)^2}{1 + (Fe^{++})/(Fe^{+++})\epsilon_4} - \frac{k_4(Fe^{++})(I_2)}{1 + (Fe^{+++})\epsilon_4/(Fe^{++})} \qquad (3)$$

which corresponds to a single path with two rate determining steps. Application of the condition that $d(Fe^{++})/dt$ is equal to zero at equlibrium leads to the relation $K = k_1\epsilon_4/k_4$. A check of equation 3 is thus furnished by the calculation of K from experimental values of k_1, k_4 and ϵ_4, provided all measurements are made at the same temperature and the same ionic strength.

Wagner's evidence for the rate law of the forward reaction

$$\frac{d(Fe^{++})}{dt} = \frac{k_1(Fe^{+++})(I^-)^2}{1 + (Fe^{++})/(Fe^{+++})\epsilon_4} \qquad (3a)$$

comprised the early work of Schukarew[2] showing that the initial rate depends on the third order reaction $Fe^{+++} + 2I^- \longrightarrow$, the retarding effect of ferrous ion, and the identity of this rate law with that demonstrated by Wagner himself for the analogous reaction between ferricyanide ion and iodide ion. He gives one pair of values of k_1 and ϵ_4 at 15° and a single ionic strength. As evidence that the first step of the reverse reaction is $Fe^{++} + I_2 \longrightarrow$, Wagner refers to the results of Banerji and Dhar.[3a] However, we were not able to calculate values of k_4 in conventional units from the published data.[3] Additional experimental work was therefore necessary before the above mentioned test could be applied to equation 3.

Our measurements were made at 25° in dilute acid solutions having an ionic strength of 0.09, and are in agreement with a rate law of the form

$$\frac{d(Fe^{++})}{dt} = \frac{k_1(Fe^{+++})(I^-)^2}{1 + (Fe^{++})/(Fe^{+++})[\epsilon_4 + \epsilon_6(I^-)]} - \frac{k_4(Fe^{++})(I_2) + k_6(Fe^{++})(I_3^-)}{1 + (Fe^{+++})[\epsilon_4 + \epsilon_6(I^-)]/(Fe^{++})}\ \mathrm{I}$$
$$+ \frac{k_1'(Fe^{+++})(I^-)}{1 + (Fe^{++})(H^+)/(Fe^{+++})\epsilon'} - \frac{k_4'(Fe^{++})(I_2)/(H^+)(I^-)}{1 + (Fe^{+++})\epsilon'/(Fe^{++})(H^+)}\ \mathrm{II} \qquad (4)$$

The two parts, I and II, correspond to two paths, each with two rate determining steps. If the terms containing ϵ_6 and k_6 are omitted, I is the rate law suggested by Wagner. II is dominant only at low concentrations of iodide ion. Setting $d(Fe^{++})/dt$ equal to zero in equation 4 gives the relations

$$k_1\epsilon_4/k_4 = K_{I_3^-}k_1\epsilon_6/k_6 = k_1'\epsilon'/k_4' = K \qquad (5)$$

where $K_{I_3^-}$ is the equilibrium quotient of the reaction $I_3^- = I_2 + I^-$.

Equation 4 was constructed by combining into one rate law the results of rate measurements on both sides of equilibrium. The two positive terms of the rate law were derived from an analysis of the data for the forward reaction between ferric ion and iodide ion, and the sum of the numerators of the negative terms was in agreement with the data for the reverse reaction between ferrous ion and iodine. The denominators of the negative terms were included in the rate law to make it consistent with the equilibrium law, 2. They did not exceed unity by an amount significant in comparison with the experimental errors. Equations 5 were checked by comparison with the results of equilibrium determinations.

The specific rates and equilibrium quotients of ferric reactions vary rapidly with changing ionic strength. According to the Debye–Hückel theory, the relationship between any equilibrium quotient, K, the ionic strength, μ, and the charge of each ion, z, may be expressed in the form

$$\log_{10}(K/K^0) = -(\Delta z^2)f(\gamma)$$

where $f(\gamma)$ is a function of the activity coefficients of the ions, and at 25° approaches the limit $-0.5\ \mu^{1/2}$ as $\mu^{1/2}$ approaches zero.

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(1) Wagner, *Z. physik. Chem.*, **113**, 269 (1924).

(2) Schukarew, *ibid.*, **38**, 353 (1901).

(3) (a) Banerji and Dhar, *Z. anorg. Chem.*, **134**, 172 (1924); (b) Bhattacharya and Dhar, *J. Ind. Chem. Soc.*, **6**, 455 (1929); *Z. anorg. allgem. Chem.*, **196**, 28 (1931).

Randall[4] has shown that, when Δz^2 is not zero, the $-(1/\Delta z^2)\log K/K^0$ curve in a $\mu^{1/2}$ diagram may be represented by the log γ curve for some one of the strong electrolytes. Bray and Hershey[5a] adopted this method of plotting in their study of certain equilibria involving ferric ion, and their values of $f(\gamma)$ have been used in this investigation. Thus at $\mu = 0.09, f(\gamma) = -0.097$; in reaction 1, $\Delta z^2 = -12$, $\log (K/K^0) = -12\,(0.097)$, and $K/K^0 = 0.0685$.

In applying these ideas to the specific rates in equation 4 the value $\Delta z^2 = -12$ must be distributed among the specific rates in each part of the rate law. The following values are based upon the Brönsted rule and equation 5.

	k_1	ϵ_4	k_4	ϵ_6	k_6	k_1'	ϵ'	k_4'
Δz^2	-10	-2	0	-6	-4	-6	-4	$+2$

In each case $f(\gamma)$ was assumed to be -0.097 at $\mu = 0.09$.

Allowance was made for the formation of the complex ferric iodide ion, FeI^{++}, by comparing two sets of calculations, the first based on the complete ionization of ferric iodide, the second on the assumption that, at $\mu = 0.09$, $K_{FeI^{++}} = (FeI^{++})/(Fe^{+++})(I^-) = 20$.

$$Fe^{+++} + I^- = FeI^{++} \quad \Delta z^2 = -6 \tag{6}$$

The corresponding value of $K_{FeI^{++}}$ at $\mu = 0$ is 75.

Corrections for the hydrolysis of ferric ion were based on the results of Bray and Hershey.[5a]

$$Fe^{+++} + H_2O = FeOH^{++} + H^+ \quad \Delta z^2 = -4 \tag{7}$$

$K^0_{FeOH^{++}} = 60(10^{-4})$. At $\mu = 0.09$, $K_{FeOH^{++}} = 24.6(10^{-4})$. The hydrolysis ranged from 10 to 30% and was controlled by the addition of nitric acid. We believe that the hydrolysis corrections are at least approximately correct since the values of the hydrolysis quotients[5a] were determined from a study of equilibria involving ferric ion. The calculation of ferric ion concentrations is the reverse step, and may be accepted as an empirical method even if the values of $K_{FeOH^{++}}$ are incorrect.[5b]

The concentrations of triiodide ion were calculated by means of the equilibrium constant $K_{I_3^-} = (I_2)(I^-)/(I_3^-) = 0.00141$[6]

$$I_3^- = I_2 + I^- \quad \Delta z^2 = 0 \tag{8}$$

Similarly, in one group of experiments in which bromide ion was present, the concentrations of I_2Br^- were calculated by means of the constant $K_{I_2Br^-} = 0.08$.[7]

The standard potentials used in calculating the equilibrium constant of reaction 1 were

$$Fe^{+++} + E^- = Fe^{++} \quad \Delta z^2 = -5 \quad E^0 = 0.772^{5a} \tag{9}$$

and

$${}^1/_2\,I_2 + E^- = I^- \quad \Delta z^2 = 1 \quad E^0 = 0.534 \tag{10}$$

To determine the latter value, the correction recommended by Randall and Young[8] was applied to the value, 0.5357, chosen by Lewis and Randall.[9]

The solubility product of silver iodide

$$AgI = Ag^+ + I^- \quad \Delta z^2 = +2$$
$$K^0_{AgI} = (9.0 \pm 0.5)(10^{-17}) \tag{11}$$

was calculated by combining the standard iodine potential (equation 10) with the results of Jones and Kaplan[6] for the reaction

$$Ag + {}^1/_2 I_2(s) = AgI \quad E^0_{298} = 0.6845$$

and the silver electrode potential[5a]

$$Ag^+ + E^- = Ag \quad E^0_{298} = 0.7985$$

The solubility product of silver bromide

$$AgBr = Ag^+ + Br^- \quad K^0_{AgBr} = (5.3 \pm 0.3)(10^{-13}) \tag{12}$$

was determined by combining the silver electrode potential with the silver bromide electrode potential

$$AgBr + E^- = Ag + Br^- \quad E^0_{298} = 0.0723 \pm 0.0002$$

The latter was obtained by plotting in a $\mu^{1/2}$ diagram the results of Lewis and Storch[10] for the reaction $AgBr + {}^1/_2H_2 = Ag + H^+ + Br^-$. This potential is in agreement with the value 0.072 ± 0.001 obtained by combining the measurements of Afanasiev[11] for the reaction $AgCl + Br^- = AgBr + Cl^-$ with the silver chloride potential of Randall and Young.[8]

On account of the great tendency of ferric ion to form addition compounds, the presence of chloride and sulfate ions is to be avoided, but ferric nitrate may be assumed to be completely ionized. The ionic strength was controlled by the addition of potassium nitrate. C. P. chemicals were used without further purification. Ferrous

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(4) (a) Randall and Vietti, THIS JOURNAL, **50,** 1526 (1928); (b) Randall, *J. Chem. Education*, **8,** 1062 (1931).

(5) (a) Bray and Hershey, THIS JOURNAL, **56,** 1889 (1934).

(5) (b) In our previous calculations (Ref. 5a) we assumed that the hydrolysis of $FeOH^{++}$ is negligible in comparison with that of Fe^{+++}. If this assumption is in error our values of $K_{FeOH^{++}}$ are too large. Also, methods which are based on the determination of hydrogen ion concentrations should yield higher values of $K_{FeOH^{++}}$ than we obtained. This may explain the higher results of Brönsted and Volqvartz, *Z. physik. Chem.*, **134,** 127, 133 (1928), which we unwittingly overlooked in 1934. Their value of $K^0_{FeOH^{++}}$ at 15° is nearly the same as ours at 25°.

(6) Jones and Kaplan, THIS JOURNAL, **50,** 1845 (1928).

(7) Jakowkin, *Z. physik. Chem.*, **20,** 31 (1896).

(8) Randall and Young, THIS JOURNAL, **50,** 1003 (1928).

(9) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York City, 1923, p. 430.

(10) Lewis and Storch, THIS JOURNAL, **39,** 2544 (1917).

(11) Afanasiev, *ibid.*, **52,** 3477 (1930).

TABLE I

INITIAL RATES OF THE REACTION BETWEEN FERRIC ION AND IODIDE ION AT 0.09 IONIC STRENGTH AND 25°

Expt.	$Fe(NO_3)_3$	KI	HNO_3	$Fe(NO_3)_2$	(Fe^{+++})	(I^-)	(H^+)	$10^6d(Fe^{++})/dt$	
								Obsd.	Calcd.
1	0.0112	0.01	0.0188		0.0087	0.0085	0.0198	3850	3330
2	.0056	.01	.0194		.0043	.0092	.0199	1870	1930
3	.0112	.003	.0188		.0096	.0025	.0200	345	333
4	.0124	.01	.0076		.0088	.0085	.0098	3550	3350
5	.0124	.01	.0076		.0088	.0085	.0098	3450	3350
6	.0062	.01	.0088		.00435	.0092	.0099	1825	1950
7	.00124	.01	.0098		.00086	.0098	.0100	485	440
8	.0124	.003	.0076		.0096	.0025	.0099	310	334
9	.0124	.003	.0076		.0096	.0025	.0099	285	334
10	.00124	.003	.0098		.00096	.00295	.0100	43.5	45
11	.0148	.01	.0002		.0088	.0085	.0047	3250	3370
12	.00148	.01	.0045		.00088	.0098	.0050	440	448
13	.0148	.003	.0002		.0096	.0025	.0049	305	334
14	.00148	.003	.0045		.00096	.00295	.0050	41	45
15	.0148	.001	.0002	0.001	.0099	.00084	.0050	13.25	13.4
16	.0148	.0005	.0002	.001	.0099	.00042	.0050	4.07	4.01
17	.0074	.01	.0026	.001	.0044	.0092	.0048	950	931
18	.0062	.01	.0088	.001	.00435	.0092	.0099	950	921
19	.0062	.008	.0088	.001	.0045	.0073	.0099	535	539
20	.0062	.005	.0088	.001	.0046	.0046	.0099	155	177
21	.0062	.003	.0088	.001	.0048	.00275	.0100	46	52
22	.0074	.003	.0026	.001	.0048	.00275	.0050	47	54
23	.0062	.001	.0088	.001	.0049	.00091	.0100	5.0	4.6
24	.0062	.001	.0088	.001	.0049	.00091	.0100	4.8	4.6
25	.0074	.001	.0026	.001	.0049	.00091	.0050	5.05	5.05
26	.0074	.0005	.0026	.001	.0050	.00046	.0050	1.5	1.56
27	.0062	.0005	.0088	.001	.0050	.00046	.0100	1.4	1.29
28	.00248	.01	.0095	.001	.00173	.0097	.0100	225	228
29	.00248	.003	.0095	.001	.00191	.0029	.0100	9.6	11.4
30	.00124	.01	.0098	.001	.00086	.0098	.0100	68	69
31	.00124	.003	.0098	.001	.00096	.00295	.0100	3.25	3.2
32	.00062	.01	.0099	.001	.00043	.0099	.0100	21.5	18.8
33	.00062	.003	.0099	.001	.00048	.0030	.0100	1.0	0.87
34	.0074	.01	.0026	.002	.0044	.0092	.0048	622	610
35	.0074	.003	.0026	.002	.0048	.00275	.0050	31	32
36	.0074	.0005	.0026	.002	.0050	.00046	.0050	0.965	0.99
37	.0062	.0005	.0088	.002	.0050	.00046	.0100	.735	.75
38	.0074	.0005	.0026	.003	.0050	.00046	.0050	.725	.74
39	.0062	.0005	.0088	.003	.0050	.00046	.0100	.51	.53
40	.0074	.01	.0026	.01	.0044	.0092	.0048	150	161
41	.0074	.003	.0026	.01	.0048	.00274	.0050	6.7	7.4
42	.0074	.001	.0026	.01	.0049	.00091	.0050	0.62	0.76
43	.0074	.0005	.0026	.01	.0050	.00046	.0050	.25	.27
44	.0062	.0005	.0088	.01	.0050	.00046	.0100	.18	.175

nitrate solutions were prepared by mixing barium nitrate and ferrous sulfate solutions in equivalent amounts and filtering off the precipitated barium sulfate. Atmospheric oxidation of the ferrous salt was closely watched, and fresh solutions were prepared when the ferric iron content exceeded 3% of the total iron. To diminish the oxygen concentration the solutions and reaction systems were shaken with carbon dioxide. Although the effect of the diffuse daylight of the laboratory on the rates was found to be negligible, the precaution was taken to shield the reaction vessels from light in the rate measurements with iodine and ferrous salts and in the equilibrium determinations. All concentrations were measured in moles per liter, and time intervals in minutes.

Rate Measurements of the Reaction between Ferric Ion and Iodide Ion

Sasaki[12] and Kiss and Bossányi[13] have studied the reaction in low ferrous ion concentration. To

[12] Sasaki, *Z. anorg. allgem Chem.*, **137**, 181, 291 (1924).

[13] Kiss and Bossányi, *ibid.*, **191**, 289 (1930).

measure the initial rate they added starch and a small known quantity of sodium thiosulfate to the reaction system, and observed the interval of time from the start of the reaction to the appearance of the blue color of starch–iodine. Ferric ion reacts directly with thiosulfate ion, however, and the method is subject to error. Increasing the quantity of the thiosulfate increases the amount lost by direct reaction with ferric ion, but there is then a greater average concentration of ferrous ion and the reaction between ferric ion and iodide ion is retarded. The two effects cancel and the rate appears to be independent of the quantity of thiosulfate used. The specific rate in low ferrous ion concentration was redetermined, therefore, by a more direct method.

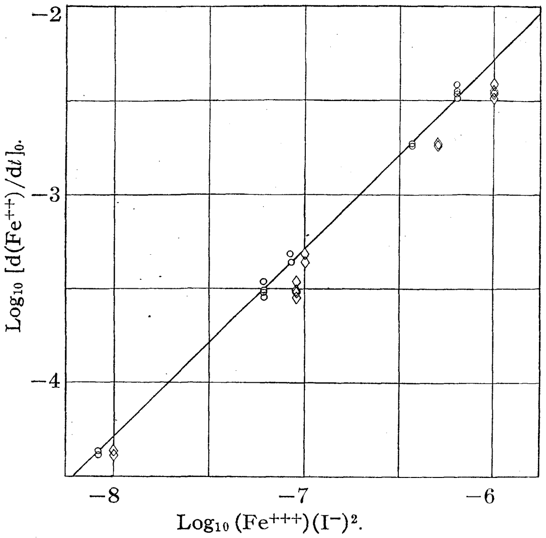

Fig. 1.—Rate measurements in low (Fe^{++}), Expts. 1 to 14: ○, concentrations based on $K_{\text{FeI}^{++}} = (\text{FeI}^{++})/(\text{Fe}^{+++})(\text{I}^-) = 20$; ◇, concentrations based on $K_{\text{FeI}^{++}} = 0$.

Control experiments showed that when iodine is in excess it can be titrated with sodium thiosulfate in the presence of ferric ion without loss of accuracy. Ten-cc. samples of the reaction system were quenched in about 0.075 *M* FeSO_4, and the iodine was titrated without delay. The effectiveness of the quenching was indicated by the slowness with which the blue color reappeared after the starch end-point had been reached.

The results are summarized in Table I. The initial concentrations of ferric nitrate, potassium iodide, nitric acid and ferrous nitrate, composing the reaction systems, are listed in the second, third, fourth and fifth columns. The initial concentrations of ferric ion, iodide ion and hydrogen ion, corrected for the complex ion, FeI^{++}, by means of $K_{\text{FeI}^{++}} = 20$, are listed in the sixth, seventh and eighth columns.

The "observed" initial rates listed in the ninth column were determined from the experimental data by the following method. An approximate rate law was formulated, and values of the rate were calculated at convenient values of (Fe^{++}), the concentration of ferrous ion. For each experiment the reciprocal of the rate, $dt/d(\text{Fe}^{++})$ was plotted against (Fe^{++}). By graphically integrating $[dt/d(\text{Fe}^{++})]d(\text{Fe}^{++})$ from the initial value of (Fe^{++}), time intervals were determined, and compared with those found experimentally. The rate law was modified and the calculations repeated until these two sets of time intervals were brought into agreement. This procedure made certain that the initial rate chosen in each experiment is consistent with the rates during the experiment. The points in Figs. 1 to 4 below correspond to these observed initial rates.

The method of calculating the initial rates listed in the last column is explained at the end of the section.

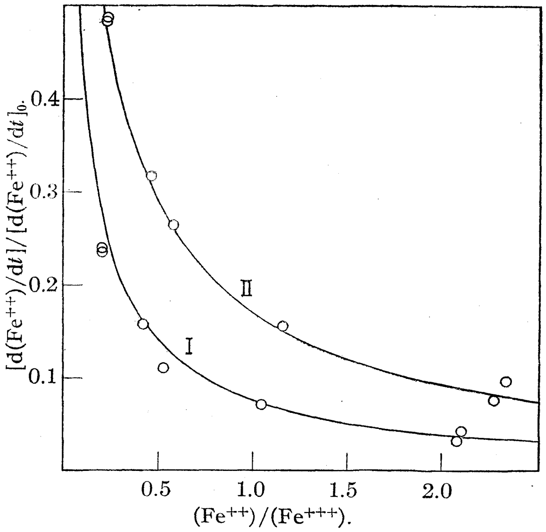

Fig. 2.—The retarding effect of ferrous ion. Curve I, 0.003 *M* KI, Expts; 21, 22, 29, 31, 33, 35 and 41; Curve II, 0.01 *M* KI; Expts. 17, 18, 28, 30, 32, 34 and 40.

The rate is proportional to the concentration product $(\text{Fe}^{+++})(\text{I}^-)^2$ when the concentration of ferrous ion is small and that of iodide ion is not less than about 0.003 molal. This is shown in Fig. 1, where, for the experiments with zero initial ferrous salt, the logarithm of the initial rate is plotted against $\log(\text{Fe}^{+++})(\text{I}^-)^2$. The results obtained without correcting for FeI^{++} are also included in Fig. 1 (but not in Figs. 2, 3 and 4 below). The two values of the specific rate, k_1, determined from the two sets of data are listed at the end of the section.

The retarding effect of ferrous ion is shown in Figs. 2 and 3, where the ratio of the initial rate in each experiment to the rate at zero concentration of ferrous ion, $[d(Fe^{++})/dt]_0$, is plotted against the ratio $(Fe^{++})/(Fe^{+++})$. If equation 3a were the correct rate law, a single curve would be obtained starting at unity on the ordinate axis and approaching zero at high values of $(Fe^{++})/(Fe^{+++})$. The incompleteness of this rate law is therefore shown at once by the existence of two curves in Fig. 2 when the concentration of potassium iodide is varied from 0.01 to 0.003 *M* KI; and in Fig. 3 when, at a much lower iodide concentration, the concentration of hydrogen ion is varied from approximately 0.005 to 0.01 *M* H^+.

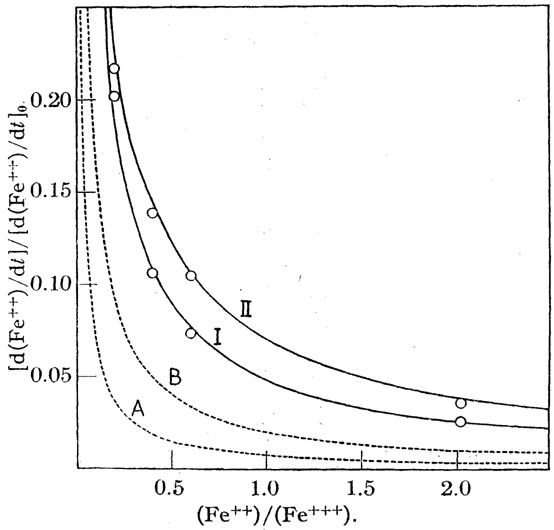

Fig. 3.—The retarding effect of ferrous ion at 0.0005 *M* KI. Curve I, approximately 0.01 *M* H^+; Expts. 27, 37, 39 and 44; Curve II, approximately 0.005 *M* H^+; Expts. 26, 36, 38 and 43.

In Fig. 2, as $(Fe^{++})/(Fe^{+++})$ is increased, the ordinate becomes nearly proportional to (I^-), indicating a rate law of the form

$$\frac{d(Fe^{++})}{dt} = \frac{k_1(Fe^{+++})(I^-)^2}{1 + (Fe^{++})/(Fe^{+++})(I^-)\epsilon_6} \tag{13a}$$

However, when this equation and the data in Fig. 2 are used to calculate the curve for 0.0005 *M* KI, Curve A in Fig. 3 is obtained, and the ratio $[d(Fe^{++})/dt]/[d(Fe^{++})/dt]_0$ is much too small. Some of the discrepancy may be removed by introducing another constant, ϵ_4, in equation 13a

$$\frac{d(Fe^{++})}{dt} = \frac{k_1(Fe^{+++})(I^-)^2}{1 + (Fe^{++})/(Fe^{+++})[\epsilon_4 + \epsilon_6(I^-)]} \tag{13b}$$

which raises Curve A to Curve B. The retarding action of hydrogen ion at low (I^-) and high $(Fe^{++})/(Fe^{+++})$, as shown in Fig. 3, suggests the presence of an additional term in the rate law which is important only at low (I^-), and is therefore of less than the second degree in (I^-)

$$\frac{d(Fe^{++})}{dt} = \frac{k_1'(Fe^{+++})(I^-)}{1 + (Fe^{++})(H^+)/(Fe^{+++})\epsilon'} \tag{13c}$$

The effect of changing (I^-) at constant (Fe^{++}) is shown in Fig. 4. Curves B and B′ are based on equation 13b. At low iodide concentration B is much lower than Curves I and II, and B′ is lower than III; which again shows the need for an added term, such as 13c, in the rate law. Were this added term of the form

$$\frac{d(Fe^{++})}{dt} = \frac{k_1'(Fe^{+++})(I^-)}{(H^+)[1 + (Fe^{++})/(Fe^{+++})\epsilon']}$$

Curve B would have been raised to C, instead of to II, by halving the concentration of hydrogen ion. Were it of the form

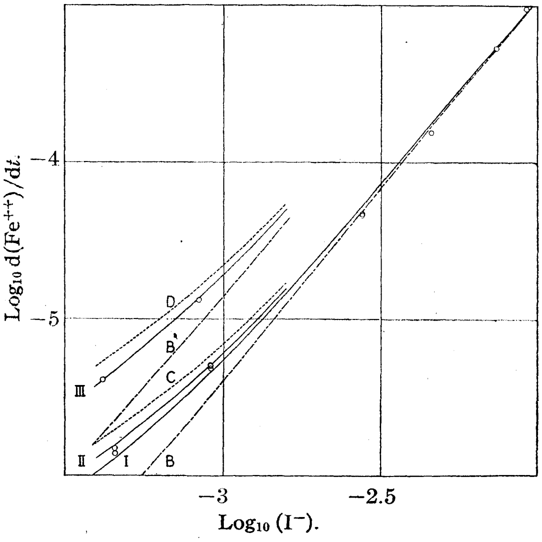

Fig. 4.—Rate measurements at 0.001 *M* Fe^{++}, Expts. 15 to 27: Curve I, 0.0062 *M* $Fe(NO_3)_3$, approximately 0.01 *M* H^+; Curve II, 0.0074 *M* $Fe(NO_3)_3$, approximately 0.005 *M* H^+; Curve III, 0.0148 *M* $Fe(NO_3)_3$, approximately 0.005 *M* H^+.

$$\frac{d(Fe^{++})}{dt} = \frac{k_1'(Fe^{+++})^2(I^-)}{1 + (H^+)(Fe^{++})/\epsilon'}$$

Curve B′ would have been raised to D, instead of to III, by doubling the concentration of ferric ion.

Our experimental data on the rate of interaction of ferric ion and iodide ion are therefore in agreement with the rate law

$$\frac{d(\mathrm{Fe}^{++})}{dt} = \frac{k_1(\mathrm{Fe}^{+++})(\mathrm{I}^-)^2}{1 + (\mathrm{Fe}^{++})/(\mathrm{Fe}^{+++})[\epsilon_4 + \epsilon_6(\mathrm{I}^-)]} + \frac{k_1'(\mathrm{Fe}^{+++})(\mathrm{I}^-)}{1 + (\mathrm{Fe}^{++})(\mathrm{H}^+)/(\mathrm{Fe}^{+++})\epsilon'} \qquad (13)$$

Equation 13 is the sum of 13b and 13c and consists of the positive terms of equation 4. The solid curves in Figs. 1 to 4 and the initial rates in the last column of Table I were calculated by means of equation 13 and the specific rates listed below for $K_{\mathrm{FeI}^{++}} = 20$. When no correction for FeI^{++} was applied, satisfactory agreement between observed and calculated data was also obtained with the same rate law, but with different specific rates.

The values of the specific rates at $\mu = 0.09$ are

	k_1	ϵ_4	ϵ_6	k_1'	ϵ'
$K_{\mathrm{FeI}^{++}} = 20$	5200 ± 500	0.018 ± 0.002	20 ± 1	0.70 ± 0.05	1/(700 ± 50)
$K_{\mathrm{FeI}^{++}} = 0$	3800	.02	17	.55	1/600

Rate Measurements of the Reaction between Ferrous Ion and Iodine

In Homogeneous Solutions at 25°.—Solutions of iodine and ferrous nitrate were mixed and the subsequent changes in the concentration of total iodine, $(\Sigma \mathrm{I}_2)$, were determined by titration against sodium thiosulfate. Since the time required for analysis was negligible in comparison with the time intervals between analyses, no quenching was necessary. The initial concentrations of the substances affecting the rate, corrected for the complex ion, FeI^{++}, are listed in Table II. The ferric iron concentration, $(\Sigma \mathrm{Fe}^{+++})$, was determined iodimetrically. On account of the atmospheric oxidation of some of the ferrous salt, the hydrogen ion concentration is less than that corresponding to the amount of nitric acid added to the reaction system. The iodine solution contained a trace of iodide, which was determined by the permanganate method.[14]

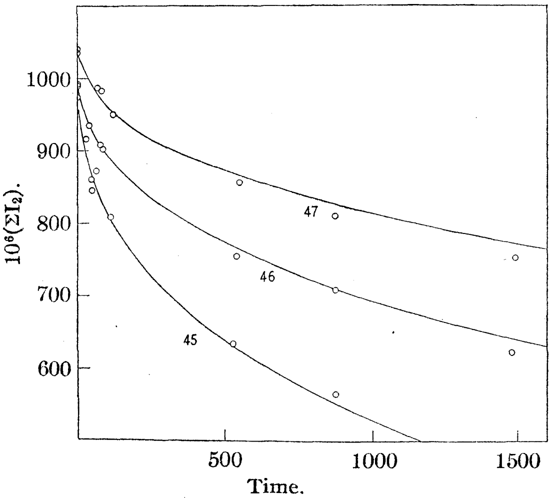

Fig. 5.—The reaction between ferrous ion and iodide ion at 0.005 M $\mathrm{HNO_3}$: Expt. 45, 0.025 M $\mathrm{Fe(NO_3)_2}$; Expt. 46, 0.01 M $\mathrm{Fe(NO_3)_2}$; Expt. 47, 0.005 M $\mathrm{Fe(NO_3)_2}$.

TABLE II

INITIAL CONCENTRATIONS

Expt.	(Fe^{++})	10^6 $(\Sigma\mathrm{Fe}^{+++})$	(H^+)	10^6 $(\Sigma\mathrm{I}_2)$	10^6 (I_3^-)	10^6 (I^-)	10^6 (I_2)	μ
45	0.0244	620	0.0046	974	24	36	950	0.09
46	.0098	250	.0048	992	24	36	968	.09
47	.0049	125	.0049	1035	25	35	1010	.09
48	.0244	620	.0046	997	201	356	796	.09
49	.0244	620	.0046	992	335	719	657	.09
50	.0244	620	.0095	930	23	37	907	.09
51	.0244	620	.0195	920	23	37	897	.09
52	.0245	500	.0196	6170	4830	5130	1340	.107

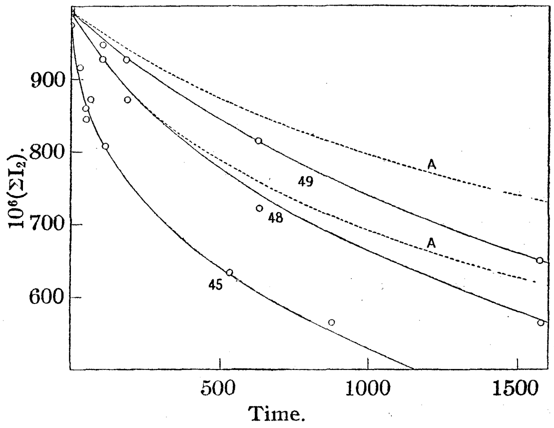

Fig. 6.—The retarding effect of iodide ion at 0.025 M $\mathrm{Fe(NO_3)_2}$ and 0.005 M $\mathrm{HNO_3}$. Initial concentrations of iodide: Expt. 45, $60(10^{-6})$ M; Expt. 48, 0.0005 M; Expt. 49, 0.001 M.

The experimental results are represented by points in Figs. 5 to 8, where the total iodine concentration is plotted against the time in minutes.

In the analysis of these results, various rate laws were tested by a method similar to that described in the preceding section. The reciprocal of the rate, $-dt/d(\Sigma \mathrm{I}_2)$, was calculated at convenient values of $(\Sigma \mathrm{I}_2)$ by means of the assumed rate law, and plotted against $(\Sigma \mathrm{I}_2)$. The time interval to any selected value of $(\Sigma \mathrm{I}_2)$ was calcu-

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[14] Bray and MacKay, THIS JOURNAL, **32**, 1193 (1910).

lated by graphical integration of $-[dt/d(\Sigma I_2)]$ $d(\Sigma I_2)$ from the initial value of (ΣI_2).

In experiments 45 to 51 ferrous nitrate was present in sufficient excess to make the proportionate change in the concentration of ferrous ion during each experiment small in comparison with that of iodine or iodide ion. The results of experiments 45 to 47, which differ only in the concentration of ferrous ion, are given in Fig. 5. At any selected concentration of total iodine the time intervals are inversely proportional to the concentration of ferrous ion. The rate is therefore directly proportional to the concentration of this ion.

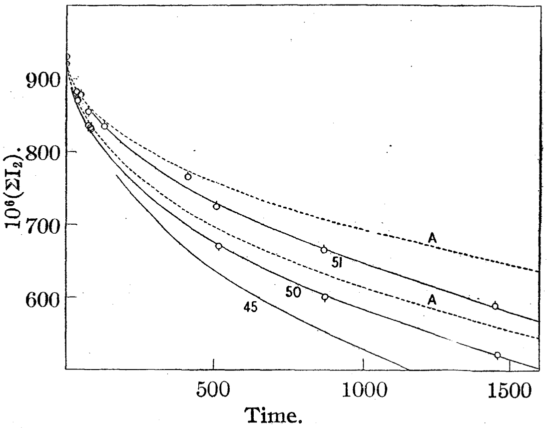

Fig. 7.—The retarding effect of hydrogen ion at 0.025 *M* $Fe(NO_3)_2$: concentrations of HNO_3: Expt. 45, 0.005 *M;* Expt. 50, 0.01 *M;* Expt. 51, 0.02 *M*.

The retarding action of iodide ion is illustrated in Fig. 6, where in three experiments the initial concentration of iodide is varied from a small value in 45 to 0.001 molal in 49. Similarly the retarding action of hydrogen ion is shown in Fig. 7, where the concentration of hydrogen ion is varied from approximately 0.005 molal in 45 to 0.02 molal in 51.

These results indicate a rate law of the form

$$\frac{-d(Fe^{++})}{dt} = \frac{-2d(\Sigma I_2)}{dt} = \frac{k_4'(Fe^{++})(I_2)}{(H^+)(I^-)} \quad (14a)$$

This rate law is in agreement with the results of experiment 45. However, when it is used to calculate the results of the other experiments in Figs. 6 and 7, the curves labeled A are obtained; and the agreement is not satisfactory. The actual rate is greater than that given by equation 14a and the discrepancy increases rapidly as the product $(H^+)(I^-)$ is increased. The discrepancy may be removed, in these experiments, by including in the rate law an added term, which is independent of $(H^+)(I^-)$

$$-d(Fe^{++})/dt = k_4(Fe^{++})(I_2) \quad (14b)$$

That there is a third term in the rate law

$$-d(Fe^{++})/dt = k_6(Fe^{++})(I_3^-) \quad (14c)$$

is indicated by the results of experiment 52, Fig. 8, in which the concentration of triiodide ion was much greater than in the other experiments. Were the rate given by the sum of equations 14a and 14b alone, the measurements would have been represented by Curve B.

Our experimental data on the rate of interaction of ferrous ion and iodine are therefore in agreement with the rate law

$$-d(Fe^{++})/dt = k_4(Fe^{++})(I_2) + k_6(Fe^{++})(I_3^-) + k_4'(Fe^{++})(I_2)/(H^+)(I^-) \quad (14)$$

Equation 14 is the sum of 14a, 14b and 14c, and consists of the numerators of the negative terms of equation 4. The solid curves in Figs. 5 to 8 were calculated by means of equation 4, the specific rates listed below and the specific rates listed at the end of the preceding section. In evaluating k_6 it is necessary to allow for the rate of reaction between ferric ion and iodide ion, which was relatively large only in experiment 52. The magnitude of this effect is illustrated in Fig. 8 by the difference between Curve C, based on equation 14, and the actual data. The values of the specific rates obtained when the complex ion FeI^{++} was neglected were not changed when the correction was applied.

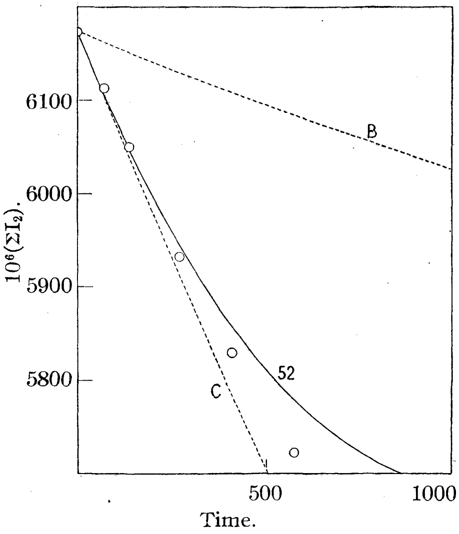

Fig. 8.—The reaction between ferrous ion and triiodide ion at 0.02 *M* HNO_3.

The values of the specific rates at $\mu = 0.09$ are

$$k_4 = 0.009 \pm 0.001$$
$$k_6 = 0.0145 \pm 0.001$$
$$k_4' = (10.0 \pm 0.5)(10^{-8})$$

Rate Measurements in the Presence of Silver Iodide, Silver Bromide and Bromide Ion.—Rate measurements were made also at very low concentrations of iodide ion, maintained by a buffer of silver iodide and silver bromide in a solution containing bromide ion. The ratio $(I^-)/(Br^-)$, which is constant when the system is in equilibrium, is equal to $K_{AgI}/K_{AgBr} = 1.7(10^{-4})$ (*cf.* equations 11 and 12). The ionic strength was 0.055 in these experiments.

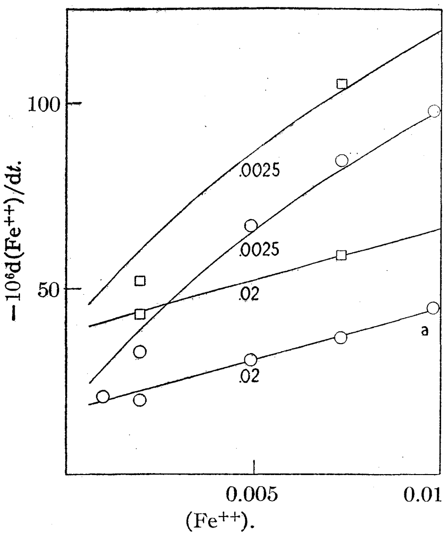

Fig. 9.—Variation of initial rates with the concentration of ferrous ion: ○, 0.005; □, 0.01 mole per liter of AgI and of AgBr; 0.0006 M I_2; 0.01 M Br^-; 0.02 and 0.0025 M H^+; stirring rate, 2000 r. p. m.

An equimolal mixture of the silver halides was precipitated in the reaction vessel before each experiment by adding the calculated amount of a known silver nitrate solution to a solution containing hydrogen ion, potassium ion, iodide ion and bromide ion. After the addition of the ferrous salt solution the reaction was started by adding to the mixture a measured volume of nearly saturated iodine solution (at 25°). The precipitate was kept from settling by vigorously stirring the reaction mixture at a rate of 2000 revolutions per minute, except when otherwise stated. This stirring rate was found to be high enough to bring the reaction rate to within a few per cent. of its maximum value (*cf.* Fig. 11). The results were reproducible when a definite procedure was followed, but they depended on the order in which the reagents were mixed, and are therefore not presented in detail.

The concentration of iodine during the course of the reaction was determined by extraction with carbon tetrachloride and titration with sodium thiosulfate. Since carbon tetrachloride is emulsified by the silver halide precipitate, the latter was first filtered out rapidly on a loosely packed asbestos filter. Some iodine was volatilized in this procedure, and control experiments were made to determine the loss.

(ΣI_2) or $(I_2) + (I_2Br^-)$ could be expressed as a function of the time, t, to within the precision of analysis, by the empirical equation

$$\log [(\Sigma I_2) - \alpha] = -\beta t + \gamma \qquad (15)$$

where α, β and γ were constant during an experiment, but varied from experiment to experiment.

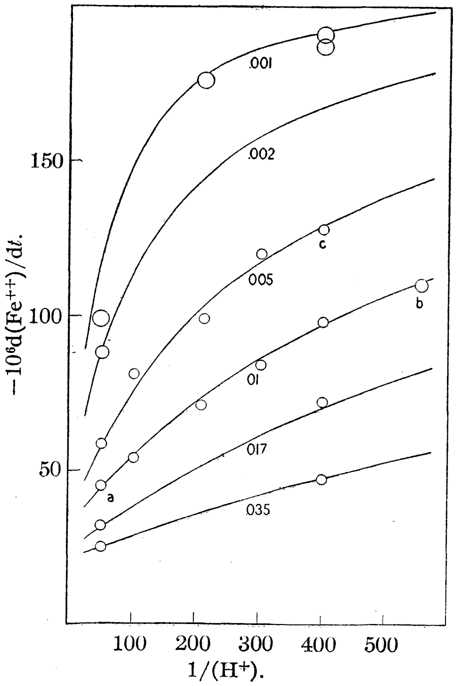

Fig. 10.—Initial rates at various concentrations of hydrogen ion and bromide ion: 0.005 mole per liter of AgI and of AgBr; 0.0006 M I_2; 0.0098 M Fe^{++}; 0.001 to 0.035 M Br^-.

Differentiation of equation 15 gave the rate at any time during the experiment.

$$-d(\Sigma I_2)/dt = -\tfrac{1}{2}d(Fe^{++})/dt = \beta[(\Sigma I_2) - \alpha] \qquad (16)$$

By substituting $t = 0$ in equation 15, the initial value of $(\Sigma I_2) - \alpha$ was calculated, and the initial rate was obtained by substituting this value in equation 16.

The results are presented graphically in Figs. 9, 10 and 11, where the ordinates are the initial rates, reduced to the same iodine concentration, 0.0006 M I_2.

The experimental results can be explained only by assuming two simultaneous reactions, one a homogeneous reaction whose rate is retarded by hydrogen ion and iodide ion (*cf.* equation 14a), and the other a reaction at the surface of the silver halides. As the homogeneous reaction is slow at 0.02 M H^+, the observed rates in the experiments at this concentration, shown in Fig. 9, are due mainly to the heterogeneous reaction. A two-fold increase in the surface, which should double the rate of the heterogeneous reaction, increased the observed rate by the same amount at the two concentrations of hydrogen ion. This result suggests that the rate of the heterogeneous reaction was not altered by an eight-fold change in the concentration of hydrogen ion. A study of all the data supported this result, and led to the additional conclusions that the rate of the heterogeneous reaction was approximately proportional to the concentration of iodine, increased slightly when the concentration of ferrous ion was increased from 0.001 to 0.01 molal, and decreased slightly when the concentration of bromide ion was increased.

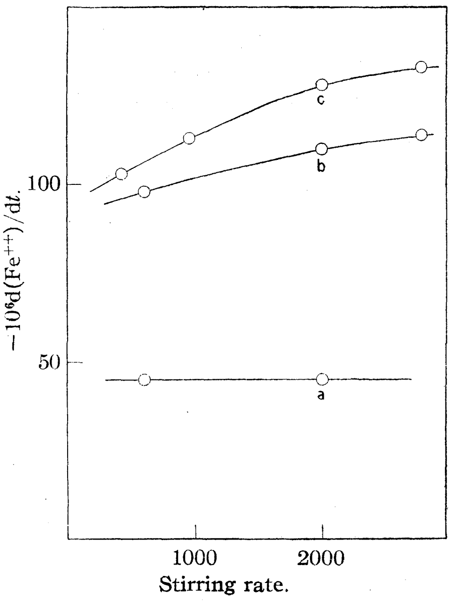

Fig. 11.—Effect of varying the stirring rate in Experiments a, b and c, Fig. 10.

The retarding effects of hydrogen ion and bromide ion (and therefore iodide ion) are illustrated by the data in Fig. 10—and especially by those at low concentrations of hydrogen ion and bromide ion, where the observed rate is due mainly to the homogeneous reaction. When a consistent set of corrections for the heterogeneous reaction were applied to the observed rates, the homogeneous reaction was found to obey rate law 14a at the lowest rates. With increasing values of the quotient $(Fe^{++})/(H^+)(Br^-)$, it approached a value independent of the concentrations of ferrous ion, hydrogen ion and bromide ion. The rates of the homogeneous reaction could therefore be represented by the equation

$$\frac{-d(Fe^{++})}{dt} = \frac{-2d(\Sigma I_2)}{dt} = \frac{k_4'(Fe^{++})(I_2)/(H^+)(I^-)}{1 + \sigma(Fe^{++})/(H^+)(I^-)} \quad (17)$$

The curves in Figs. 9 and 10 represent the sum of the rates calculated by means of this equation and the assumed rates of the heterogeneous reaction. The concentration of iodide ion was assumed to have its equilibrium value, $1.7(10^{-4})$ (Br^-). The corresponding values of σ and k_4' are $28(10^{-8})$ and $8(10^{-8})$ at $\mu = 0.055$.

This value of k_4' corresponds to $8.5(10^{-8})$ at $\mu = 0.09$ and is to be compared with the more accurate value, $10(10^{-8})$, obtained at higher concentrations of iodide ion. The difference could have been eliminated by a small decrease in the corrections for the heterogeneous reaction.

The differential equation, 17, signifies that there are two rate determining steps in series, the first of which is the hydrolysis of iodine. This will become dominant only at high velocities. Thus when the quotient $(Fe^{++})/(H^+)(I^-)$ is increased the equation approaches the limit

$$-d(I_2)/dt = (k_4'/2\sigma)(I_2)$$

$k_4'/2\sigma$ is equal to 0.14, which is of the same order of magnitude as 0.25, the specific rate derived by Abel[15] for the hydrolysis of iodine at 25°. However, this agreement may not be significant, as Liebhafsky[16] has concluded that the specific rate of the iodine hydrolysis has a much higher value. Such a value would require σ to be much smaller than $28(10^{-8})$, and the denominator in 17 would then not be large enough to account for the observed retardations at high reaction rates.

Some or all of the departure of the homogeneous rate from direct proportionality to $(Fe^{++})(I_2)/(H^+)(Br^-)$ may be explained in another way if the steady state concentration of iodide ion is

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[15] Abel, *Z. physik. Chem.*, **136**, 161 (1928).

[16] Liebhafsky, *ibid.*, **A155**, 289 (1931); THIS JOURNAL, **56**, 2372 (1934). *Cf.* Skrabal, *Z. Elektrochem.*, **42**, 244 (1936).

assumed to have exceeded its equilibrium concentration by an amount which increased rapidly with increasing speed of reaction. This assumption receives some support from the decrease in rate observed when the stirring rate was decreased in experiments b and c, Fig. 11. In order to test this explanation the total reaction rate was assumed to be equal to $\kappa[(I^-) - 1.7(10^{-4})\ (Br^-)]$, where κ is a constant of proportionality. Steady state concentrations of iodide ion were calculated by means of this relation and substituted for (I^-) in equation 14a. Comparison of these rates with the data showed that the homogeneous rate could be represented approximately by equation 14a

$$-2d(\Sigma I_2)/dt = k_4'(Fe^{++})(I_2)/(H^+)(I^-) \quad (14a)$$

if the corrections for the heterogeneous reaction were much larger than before, and if κ and k_4' were equal to 250 and $6(10^{-8})$.

TABLE III

MEASUREMENTS OF THE EQUILIBRIUM $2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$ AT 25°

Expt.	53	54	55
	Initial Concentrations		
KI	0.01916	0.00766	0.0100
$Fe(NO_3)_3$	.01022	.00511	....
HNO_3	.02	.02	.0191
KNO_3	....	.042	....
	Final Concentrations		
$10^6(\Sigma I_2)$	4845 ± 10	2140 ± 7	5360 ± 30
$10^6(\Sigma Fe^{+++})$	598 ± 5	752 ± 7	1530 ± 20
(Fe^{++})	0.00962	0.00436	0.0235
(ΣI^-)	.00950	.00334	.01060
μ	.0715	.087	.108
	Results Based on $K^0_{FeI^{++}} = 75$		
(I^-)	0.00558	0.00205	0.00611
$10^6(I_2)$	977	873	1010
$10^6(Fe^{+++})$	478	646	1240
K	12,800 ± 600	9500 ± 1000	9700 ± 1000
	Results Based on $K^0_{FeI^{++}} = 0$		
(I^-)	0.00563	0.00206	0.00623
$10^6(I_2)$	970	870	990
$10^6(Fe^{+++})$	530	670	1365
K	10,100 ± 600	8700 ± 1000	7600 ± 1000

In spite of the uncertainties with regard to the magnitude of the corrections for the heterogeneous reaction, the specific rate of the iodine hydrolysis and the amount of supersaturation of iodide ion, the rate measurements at very low concentrations of iodide ion confirm the presence in the rate law of the term represented by equation 14a, and the order of magnitude of the specific rate, $k_4' = 10^{-7}$.

Equilibrium Determinations

After dilute solutions of ferric nitrate and potassium iodide had been allowed to react for nine days, the concentration of iodine was determined by titration with sodium thiosulfate, and the ferric iron concentration was determined iodimetrically. Equilibrium was approached also from the reverse side by allowing ferrous nitrate and iodine to react.

The results are summarized in Table III. The amounts of potassium iodide, ferric nitrate, nitric acid and potassium nitrate composing the reaction systems are listed in the second to fifth rows. The total iodine, (ΣI_2), and the total ferric iron concentration, (ΣFe^{+++}), obtained by analysis at equilibrium, are given in the sixth and seventh rows. In experiments 53 and 54, the total iodide ion concentration, $(\Sigma I^-) = (FeI^{++}) + (I_3^-) + (I^-)$, can be calculated from the data by subtracting either (Fe^{++}) or $2(\Sigma I_2)$ from the concentration of potassium iodide initially added, and the values of (ΣI^-) given in the ninth row of Table III are the averages of these two values. In the remaining rows are given the ionic strengths, and values of the equilibrium quotient, K, calculated with and without correction for the complex ion FeI^{++}.

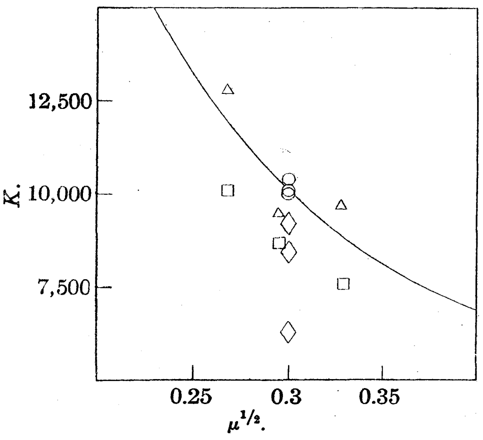

Fig. 12.—$2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$; equilibrium quotients: △, □, from analysis at equilibrium, Table III, assuming $K^0_{FeI^{++}} = 75$ and zero, respectively; ○, ◇, from rate measurements assuming $K^0_{FeI^{++}} = 75$ and zero, respectively; the curve is based on the standard potentials of the ferric–ferrous and iodine–iodide electrodes.

Combination of the standard potentials of the ferric–ferrous and iodine–iodide electrodes, equations 9 and 10, with the solubility of iodine, 0.00132 mole per liter, gives the value of the equilibrium constant, $K^0 = 148{,}000 \pm 2000$ at 25°. This result and the corresponding values of the equilibrium quotients at various ionic strengths, calculated by the method outlined in the introduction, are independent of any assumption regarding the stability of FeI^{++}. At $\mu = 0.09$, $K = 10{,}100$.

The equilibrium quotients at $\mu = 0.09$, calculated from the experimentally determined specific rates by means of equations 5, are

	$K = k_1\epsilon_4/k_4$	$K = K_{I_3^-}k_1\epsilon_6/k_6$	$K = k_1'\epsilon'/k_4'$
$K_{FeI^{++}} = 20$	10,400	10,100	10,000
$K_{FeI^{++}} = 0$	8,450	6,300	9,200

The various values for the equilibrium quotients are compared in Fig. 12. The agreement between the equilibrium quotients calculated from kinetic data, and those determined from measurements of equilibrium concentrations, is fairly close even when no correction for the complex ion FeI^{++} is applied. These "experimental" results are brought into much better agreement with each other, and with the "theoretical" results, represented by the curve in Fig. 12, by correcting for the complex ion, FeI^{++}. This improved agreement may not deserve much weight, since it is the chief basis for the choice of $K_{FeI^{++}} = 20 \pm 5$ at $\mu = 0.09$ and $K^0_{FeI^{++}} = 75 \pm 25$. Regardless of the value of $K_{FeI^{++}}$, however, the results of the various determinations of the equilibrium quotient of reaction 1 confirm the complete rate law, equation 4.

Intermediate Compounds

The rate law expressed by equation 4 signifies that ferric ion may react with either two or one iodide ions in the first rate determining steps of the forward reaction, and that ferrous ion may react with iodine, triiodide ion or hypoiodous acid in the first steps of the reverse reaction. Many reactions are known in which hypoiodous acid is the reactive oxidizing agent in aqueous iodine solutions, and very few in which the iodine itself reacts directly with the reducing agent. This is probably the first example of the direct action of triiodide ion as an oxidizing agent.

To explain part I of the rate law, Wagner[1] advocated intermediate formation of I_2^-, which may be regarded as an addition compound of atomic iodine and iodide ion. Strong supporting evidence is furnished by his more detailed study of the analogous reaction between ferricyanide ion and iodide ion. His theory is a necessary consequence of the assumption that ferrous ion is formed in the rate determining reaction

$$Fe^{+++} + 2I^- \longrightarrow Fe^{++} + I_2^-$$

since there is then only one unit change in the valence of the iron. The same theory may also be used to explain the kinetic results of Yost and Zabaro[17] for the reaction between trivalent titanium and iodine. The rate determining step is then $TiOH^{++} + I_2 \longrightarrow I_2^- + TiO^{++} + H^+$. It seems to be impossible in this case for the titanium to increase its valence by more than one unit. The analogous theory for part II of our rate law requires the formation of IOH^-, an addition compound of atomic iodine and hydroxide ion. If this substance exists at all, it is probably in equilibrium with I_2^-

$$IOH^- + I^- + H^+ = I_2^- + H_2O$$

and therefore is not likely to play a significant role at high concentrations of hydrogen and iodide ions.

The following systems of reactions are in agreement with the rate law:

I

$$Fe^{+++} + I^- \overset{K_2}{Z} FeI^{++}$$

$$FeI^{++} + I^- \underset{k_2}{\overset{^1/_2k_1/K_2}{\rightleftarrows}} Fe^{++} + I_2^-$$

$$\left\{\begin{array}{l} I_2^- + Fe^{+++} \underset{^1/_2k_4}{\overset{k_3}{\rightleftarrows}} Fe^{++} + I_2 \\ I_2^- + FeI^{++} \underset{^1/_2k_6}{\overset{k_5/k_2}{\rightleftarrows}} Fe^{++} + I_3 \end{array}\right.$$

II

$$Fe^{+++} + I^- \overset{K_2}{Z} FeI^{++}$$

$$FeI^{++} + H_2O \underset{k_2'}{\overset{^1/_2k_1'/K_2}{\rightleftarrows}} Fe^{++} + IOH^- + H^+$$

$$IOH^- + Fe^{+++} \underset{^1/_2k_4'/K_3}{\overset{k_3'}{\rightleftarrows}} Fe^{++} + IOH$$

$$IOH + I^- + H^+ \overset{1/K_3}{Z} I_2 + H_2O$$

$$\epsilon_4 = k_3/k_2$$
$$\epsilon_6 = k_5/k_2$$
$$\epsilon' = k_3'/k_2'$$

Each arrow designates a rate determining reaction, and the symbol[18] Z denotes that equilibrium is established relatively rapidly. In deriving the

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(17) Yost and Zabaro, THIS JOURNAL, **48**, 1181 (1926).

(18) Skrabal, *Z. Elektrochem.*, **40**, 235 (1934).

rate law, the concentrations of I_2^- and IOH^- are assumed to be so small that the rate of change of their concentrations may be set equal to zero.

It has usually been assumed that hypohalous acid is reduced to halide in one step, which requires the valence of the element oxidized to increase by two units. For this reason, our preliminary results at low concentrations of iodide and hydrogen ions were cited by Bray and Gorin[19] as one of several items of evidence for the formation of a +4 iron compound as an intermediate.

The following systems of reactions, which involve tetravalent iron compounds as intermediates, are also in agreement with the rate law:

I

$$Fe^{+++} + I^- \overset{K_2}{Z} FeI^{++}$$

$$FeI^{++} + I^- \underset{k_2}{\overset{^1/_2k_1/K_2}{\rightleftarrows}} FeI_2^+$$

$$FeI_2^+ + Fe^{+++} \overset{K_1}{Z} Fe^{++} + FeI_2^{++}$$

$$\left\{\begin{array}{l} FeI_2^{++} \quad \underset{^1/_2k_4}{\overset{k_3}{\rightleftarrows}} Fe^{++} + I_2 \\ FeI_2^{++} + I^- \underset{^1/_2k_6}{\overset{k_5}{\rightleftarrows}} Fe^{++} + I_3^- \end{array}\right.$$

II

$$Fe^{+++} + I^- \overset{K_2}{Z} FeI^{++}$$

$$FeI^{++} + H_2O \underset{k_2'}{\overset{^1/_2k_1'/K_2}{\rightleftarrows}} FeI(OH)^+ + H^+$$

$$FeI(OH)^+ + Fe^{+++} \overset{K_1'}{Z} Fe^{++} + FeI(OH)^{++}$$

$$FeI(OH)^{++} \underset{^1/_2k_4'/K_3}{\overset{k_3'}{\rightleftarrows}} Fe^{++} + IOH$$

$$IOH + I^- + H^+ \overset{1/K_3}{Z} I_2 + H_2O$$

$$\epsilon_4 = k_3K_1/k_2$$
$$\epsilon_6 = k_5K_1/k_2$$
$$\epsilon' = k_3'K_1'/k_2'$$

An ultimate choice between the two theories will depend upon the results of future investigations of other halogen–halide and other ferric–ferrous reactions. At the present time there is definite supporting evidence for the existence of I_2^- as an intermediate, some less definite evidence for tetravalent iron, and no other evidence for IOH^-. The available evidence thus favors Wagner's theory for part I of the rate law, and the tetravalent iron theory for part II.

Summary

Rate measurements at 25° and at an ionic strength of 0.09 in aqueous solutions containing H^+, Fe^{+++}, Fe^{++}, I^-, I_2, K^+ and NO_3^- were found to be in agreement with the rate law

$$\frac{d(Fe^{++})}{dt} = \frac{k_1(Fe^{+++})(I^-)^2}{1 + (Fe^{++})/(Fe^{+++})[\epsilon_4 + \epsilon_6(I^-)]} - \frac{k_4(Fe^{++})(I_2) + k_6(Fe^{++})(I_3^-)}{1 + (Fe^{+++})[\epsilon_4 + \epsilon_6(I^-)]/(Fe^{++})} \quad \text{I}$$

$$+ \frac{k_1'(Fe^{+++})(I^-)}{1 + (Fe^{++})(H^+)/(Fe^{+++})\epsilon'} - \frac{k_4'(Fe^{++})(I_2)/(H^+)(I^-)}{1 + (Fe^{+++})\epsilon'/(Fe^{++})(H^+)} \quad \text{II}$$

The two parts, I and II, correspond to two paths, each with two rate determining steps. The intermediate compounds involved are either derivatives of zero valent iodine, I_2^- and IOH^-, or derivatives of tetravalent iron, FeI_2^{++} and $FeI(OH)^{++}$. I_2^- and a rate law similar to I were suggested by Wagner in 1924.

Rate measurements of the reaction between ferrous ion and iodine in the presence of silver iodide, silver bromide and bromide ion confirmed the $k_4'(Fe^{++})(I_2)/(H^+)(I^-)$ term of the rate law. The homogeneous reaction was accompanied by reaction between ferrous ion and iodine at the surface of the silver halides.

The equilibrium quotient was calculated from the specific rates by means of the following relations

$$\frac{(Fe^{++})^2(I_2)}{(Fe^{+++})^2(I^-)^2} = K = \frac{\epsilon_4k_1}{k_4} = \frac{K_{I_3^-}\epsilon_6k_1}{k_6} = \frac{\epsilon'k_1'}{k_4'}$$

where $K_{I_3^-}$ is the equilibrium quotient of the reaction, $I^-_3 = I_2 + I^-$.

The quotient, K, was determined in the range $\mu = 0.07$ to 0.11 by analyzing equilibrium solutions. The value at $\mu = 0.09$ was also calculated from the value of $K°$ at $\mu = 0$ based on the standard potentials of the ferric–ferrous and iodine–iodide electrodes.

The several values of K at $\mu = 0.09$ were in fair agreement when ferric iodide was assumed to be completely ionized, and became almost identical when $K_{FeI^{++}} = (FeI^{++})/(Fe^{+++})(I^-)$ was assumed to be 20 ± 5 at $\mu = 0.09$ which corresponds to 75 ± 25 at $\mu = 0$. Corrections for the hydrolysis of ferric ion, and extrapolations to zero ionic strength were made by the method outlined by Bray and Hershey; changing the method of extrapolation would change the results at $\mu = 0$, but would not affect the conclusions at $\mu = 0.09$.

The following values of the specific rates and of the equilibrium quotient were chosen:

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[19] Bray and Gorin, THIS JOURNAL, **54**, 2124 (1932).

	k_1	ϵ_4	ϵ_6	k_4	k_6
At $\mu = 0.09$	5200 ± 500	0.018 ± 0.002	20 ± 1	0.009 ± 0.001	0.0145 ± 0.001
At $\mu = 0$	48,500	0.028	75	0.009	0.035

	k_1'	ϵ'	k_4'	K
At $\mu = 0.09$	0.70 ± 0.05	$1/(700 \pm 50)$	$(10.0 \pm 0.5)(10^{-8})$	$10{,}000 \pm 1000$
At $\mu = 0$	2.7	1/290	$6.4\,(10^{-8})$	$148{,}000 \pm 20{,}000$

Concentrations are expressed in moles per liter and time intervals in minutes.

BERKELEY, CALIF.

RECEIVED JULY 6, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Use of Certain Amines for Distinguishing Geometrically Isomeric Aldoximes and their Acyl Derivatives

BY CHARLES R. HAUSER AND EARL JORDAN

A pair of geometrically isomeric aldoximes was originally distinguished by Hantzsch[1] by the reactions of their acetyl derivatives with cold sodium carbonate solution; with this reagent the derivative prepared from the β-aldoxime gave mainly nitrile,[2] whereas the one obtained from the α-isomer was unaffected. In an extensive investigation of this field, Brady and co-workers have found that three acetyl-β-aldoximes,[3] similar to their α-isomers, are unaffected by cold sodium carbonate.[4] These three acetyl-β-aldoximes, however, are readily decomposed by 2 N sodium hydroxide to give nitrile, but, as was shown recently, this reagent decomposes acetyl-β-aldoximes to form oxime in addition to nitrile, the relative yields of these products being dependent upon the temperature of the reaction.[5] The use of sodium hydroxide for distinguishing acylaldoximes is further complicated by the fact that certain acetyl-α-aldoximes are decomposed by hot alkali to give some nitrile (or corresponding acid) in addition to oxime;[5] moreover, certain carbethoxy-α-aldoximes, with this reagent, give even more nitrile than oxime.[6]

Obviously, it would be desirable to find a reagent or a combination of reagents which would react with acyl-β-aldoximes to give only nitrile, but which would either not react with the corresponding α-isomers, or form only aldoxime; pyridine, especially when used in connection with n-butylamine, apparently meets these requirements.

In a previous paper[7] it has been shown that the acetyl-β-3,4-methylenedioxybenzaldoxime is readily decomposed by pyridine to form only nitrile, whereas the corresponding α-isomer is stable in pyridine solution even at 100°. These isomers are distinguished, also, by their reactions with n-butylamine;[8] with this reagent the α-isomer dissolves without noticeable rise of temperature to give only the corresponding aldoxime, but the β-isomer reacts vigorously with this amine to form both β-aldoxime[9] and nitrile, the yield of the latter being almost quantitative when n-butylamine[8] is added, in one cubic centimeter portions, to a gram sample of the acetyl-β-aldoxime.

These reactions have now been carried out with a series of representative acetyl-α- and acetyl-β-aldoximes. In Table I are given the yields of

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(1) Hantzsch, *Ber.*, **24**, 21 (1891).

(2) Recently, it has been found that at least certain acetyl-β-aldoximes with sodium carbonate give small amounts of aldoxime in addition to nitrile. See Hauser and Jordan, THIS JOURNAL, **57**, 2450 (1935).

(3) Acetyl-3,4-dimethoxy-5-bromobenzaldoxime, Wentworth and Brady, *J. Chem. Soc.*, **117**, 1045 (1920); acetyl-3,4-dimethoxybenzaldoxime, Brady and Dunn, *ibid.*, **123**, 1800 (1923); acetyl-2-methoxycinnamaldoxime, Brady and Grayson, *ibid.*, **125**, 1419 (1924). See also Brady, *Science Progress*, **29**, 485 (1935).

(4) Whether or not these particular acetyl-β-aldoximes would give nitrile with hot sodium carbonate apparently has not been determined.

(5) Nevertheless, it is possible to distinguish geometrically isomeric acetyl-aldoximes by means of alkali, since, at the same temperature, the β-isomers give much higher yields of nitrile than the corresponding α-isomers; at 30°, the latter generally give only traces of nitrile or corresponding acid. See especially the reference in Note 2.

(6) Hauser, Jordan and O'Connor, THIS JOURNAL, **57**, 2456 (1935).

(7) See Hauser and Jordan, *ibid.*, **58**, 1419 (1936).

(8) Piperidine and diethylamine react in a similar manner; see ref. 7.

(9) It should be pointed out that when the acetyl-β-aldoxime was added in small portions to n-butylamine kept at room temperature or below, mainly β-oxime was obtained, but when the reaction was carried out at the boiling point of the amine (78°), only nitrile could be isolated; see ref. 7.

Table I

Percentage Yields of Products from the Acetyl Derivatives of Substituted Benzaldoximes with Pyridine

		Nitrile			Recovered acetate		
Substituent	Isomer	Yield, %	M. p., °C. Crude prod.[a]	Literature m. p., °C.	Yield, %	M. p., °C. Crude prod.[a]	Literature m. p., °C.
Benzal-	α				96	Oil	14–15
Benzal-	β	87	Oil	−13			
3-Nitro-	α				99	126–127	128
3-Nitro-	β	96	114–115	117–118			
4-Methoxy-	α				99	48	48
4-Methoxy-	β	96	56–57	60			
3,4-Methylenedioxy-	α				92	105	105
3,4-Methylenedioxy-	β	99	92–94	94–95			
2-Chloro-[b]	α				94	85–87	88
2-Nitro-[b]	α				86	66	66
4-Dimethylamino-	α				87	108	108

[a] The melting points of these products were raised by recrystallization to those reported in the literature. [b] This reaction was carried out at 97–100°.

Table II

Percentage Yields of Products Obtained by Adding 5 Cc. of *n*-Butylamine in 1-Cc. Portions to 1–2 G. Samples of Acetyl Derivatives of Substituted Benzaldoximes

		Corresponding oxime			Nitrile		
Substituent	Isomer	Yield, %	M. p., °C. Crude prod.[a]	Literature m. p., °C.	Yield, %	M. p., °C. Crude prod.[a]	Literature m. p., °C.
Benzal-	α	95	Oil	35			
Benzal-	β				86	Oil	−13
3-Nitro-	α	99	123	123			
3-Nitro-	β				89	115	117–118
4-Methoxy-	α	91	63–64	64			
4-Methoxy-	β				84	52–55	60
3,4-Methylenedioxy-	α	91	108–110	110			
3,4-Methylenedioxy-	β				99	91–93	94–95
2-Chloro-	α	97	72–74	75–76			
2-Nitro-	α	99	102–103	102–103			
4-Dimethylamino-	α	86	143–144	144			

[a] The melting points of these products were raised by recrystallization to those reported in the literature.

nitrile and recovered acetyl-α-aldoxime from the reactions with pyridine, and in Table II, those of nitrile and α-aldoxime from the reactions with *n*-butylamine. The reactions with pyridine were carried out at room temperatures unless otherwise stated; in these cases the yields of products presumably are not affected by a variation of temperature from 0 to 100°. The reactions with *n*-butylamine were carried out by adding the amine, which was at room temperature, to the acetyl-aldoximes as indicated in Table II. In the case of the acetyl-β-aldoximes, the mixtures became hot immediately, producing high yields of nitrile, no aldoxime being found. On the other hand, the α-isomers merely dissolved in the amine without noticeable rise of temperature, giving only α-aldoxime.[10] It should be pointed out that the products of these reactions are readily isolated from the amine solutions; the addition of crushed ice precipitates nitrile, unchanged acetyl-α-aldoxime, or part of the α-oxime, the remainder of the latter being obtained from the filtrate in the usual manner.

These reactions with pyridine and *n*-butylamine may thus be used to distinguish the pairs of geometrically isomeric acetyl-aldoximes listed in Tables I and II; in the cases in which only one geometrical isomer has been studied, their reactions with amines indicate that they have the α- or *syn*-configuration.[11] Since these acetyl derivatives are readily prepared from the corresponding aldoximes, the latter also may be distinguished by this method, but whether or not this method is applicable in all cases remains to be determined by experiment. On this basis α-aldoximes[12] would be those whose acetyl derivatives are stable in pyridine, but react with

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(10) It should be mentioned that even when acetyl-α-3,4-methylenedioxybenzaldoxime was added to *n*-butylamine at 97–100°, only oxime was obtained; see ref. 7.

(11) Contrary to the older view, α-aldoximes are now considered to have the "*syn*" configuration, and the β-aldoximes, the "*anti*" configuration. For references see Hauser and Jordan.[2]

(12) In this connection see note of paper by Brady and McHugh, *J. Chem. Soc.*, 2415 (1925).

TABLE III

PERCENTAGE YIELDS OF PRODUCTS FROM CARBANILINO DERIVATIVES OF SUBSTITUTED BENZALDOXIMES WITH PYRIDINE

Substituent	Isomer	Nitrile Yield, %	Nitrile M. p., °C. Crude prod.[a]	Nitrile Literature m. p., °C.	Recovered product Yield, %	Recovered product M. p., °C. Crude prod.[a]	Recovered product Literature m. p., °C.
3,4-Methylenedioxy-	α				91	103–104	104
3,4-Methylenedioxy-	β	98	94–95	94–95			
3-Nitro-	α				99	145–147	148
3-Nitro-	β	97	112–114	117–118			

[a] The melting points of these products were raised by recrystallization to those reported in the literature.

TABLE IV

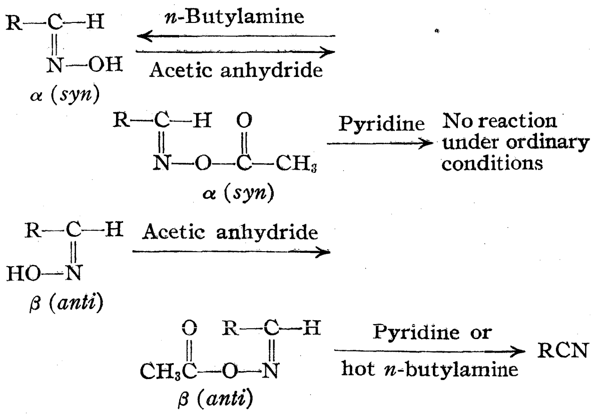
PERCENTAGE YIELDS OF PRODUCTS OBTAINED BY ADDING 5 CC. OF *n*-BUTYLAMINE IN 1-CC. PORTIONS TO 1–2 G. SAMPLES OF CARBANILINO DERIVATIVES OF SUBSTITUTED BENZALDOXIMES

Substituent	Isomer	Corresponding oxime Yield, %	Corresponding oxime M. p., °C. Crude prod.[a]	Corresponding oxime Literature m. p., °C.	Nitrile Yield, %	Nitrile M. p., °C. Crude prod.[a]	Nitrile Literature m. p., °C.
3,4-Methylenedioxy-	α[b,c]	81	109–110	110			
3,4-Methylenedioxy-	β				90	94–95	94–95
3-Nitro-	α[c]	89	120–121	123			
3-Nitro-	β				99	110–112	117–118

[a] The melting points of these products were raised by recrystallization to those reported in the literature. [b] In this case the carbanilino derivative was added to boiling *n*-butylamine. [c] N-Phenyl-N′-*n*-butylurea was obtained in a yield of 98%.

n-butylamine to regenerate the original aldoxime, whereas the β-aldoximes[12] would be those whose acetyl derivatives are decomposed by pyridine or by hot *n*-butylamine to form the corresponding nitrile. Although pure acetyl-aldoximes have generally been used in this work, similar results have been obtained when α-, and β-3,4-methylenedioxybenzaldoximes were treated with acetic anhydride, and, without isolating the acetyl derivatives, the mixtures treated with pyridine or *n*-butylamine.

Using the newer configurations[11] for aldoximes and their acetyl derivatives, these reactions may be represented as follows



$$\underset{\alpha\ (syn)}{\mathrm{R{-}CH{=}N{-}OH}} \underset{\text{Acetic anhydride}}{\overset{n\text{-Butylamine}}{\rightleftarrows}} \underset{\alpha\ (syn)}{\mathrm{R{-}CH{=}N{-}O{-}CO{-}CH_3}} \xrightarrow{\text{Pyridine}} \text{No reaction under ordinary conditions}$$

$$\underset{\beta\ (anti)}{\mathrm{R{-}CH{=}N{-}OH}} \xrightarrow{\text{Acetic anhydride}} \underset{\beta\ (anti)}{\mathrm{CH_3CO{-}O{-}N{=}CH{-}R}} \xrightarrow[\text{hot } n\text{-butylamine}]{\text{Pyridine or}} \mathrm{RCN}$$

This method may be used also for distinguishing certain other acyl-aldoximes. It has been found that carbanilino-β-3-nitro- and carbanilino-β-3,4-methylenedioxybenzaldoximes react with pyridine to give only nitrile whereas the corresponding α-isomers are stable in pyridine solution. Moreover, when *n*-butylamine is added to the β-isomers vigorous reactions occur giving high yields of nitrile, whereas the corresponding α-isomers with this amine give only α-aldoxime. The yields of these products are given in Tables III and IV. It should be pointed out that from the α-isomers with *n*-butylamine high yields of N-phenyl-N′-*n*-butylurea were obtained.

For comparison with these results the yields of products obtained from the reactions of the carbanilino-aldoximes with alkali are given in Table V. It can be seen that, similar to the acetyl-β-aldoximes, these carbanilino-β-aldoximes with alkali give both nitrile and β-aldoxime, although the yield of the latter from the 3-nitro derivative at 25–30° is very small. Alcoholic alkali was used in these cases since these carbanilino derivatives are relatively insoluble in cold aqueous alkali. The reactions with the carbanilino-α-aldoximes give the corresponding oxime as previously reported by others.[13]

It has been shown also that the carbethoxy and benzoyl derivatives of α-aldoximes are stable in pyridine, but are decomposed readily by *n*-butylamine to regenerate the original aldoxime. The yields of recovered acyl-aldoxime and of α-aldoxime obtained in these cases are given in Tables VI and VII.

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[13] See especially Brady and Dunn, *J. Chem. Soc.*, **109**, 650 (1916).

TABLE V

PERCENTAGE YIELDS OF PRODUCTS FROM CERTAIN CARBANILINO DERIVATIVES OF SUBSTITUTED BENZALDOXIMES WITH 2 *N* SODIUM HYDROXIDE

Substituent	Isomer	Base	Temp., °C.	Corresponding oxime Yield, %	Corresponding oxime M. p., °C. Crude prod.[a]	Corresponding oxime Lit. m. p., °C.	Nitrile Yield, %	Nitrile M. p., °C. Crude prod.[a]	Nitrile Lit. m. p., °C.	Acid Yield, %	Acid M. p., °C. Crude prod.[a]	Acid Lit. m. p., °C.
3,4-Methylenedioxy-	α	Aq. NaOH	97–100	83	110	110				3	210–212	228
3,4-Methylenedioxy-	β	Alc. NaOH	0	45	145–146	146	46	94–95	94–95			
3,4-Methylenedioxy-	β	Alc. NaOH	25–30	29	145–146	146	21	158–160	166[b]	30	220–221	228
3,4-Methylenedioxy-	β	Aq. NaOH	97–100	Trace						96	225	228
3-Nitro-	α	Aq. NaOH	97–100	94	121–122	123				Trace		
3-Nitro-	α	Alc. NaOH	25–30	95	121–122	123				3	134–136	140
3-Nitro-	β	Aq. NaOH	97–100				54	114–115	117–118	38	134–136	140
3-Nitro-	β	Alc. NaOH	25–30	5	118–120	123				93	138–139	140

[a] The melting points of these products were raised by recrystallization to those reported in the literature. [b] This is the melting point of the corresponding amide.

TABLE VI

PERCENTAGE YIELDS OF PRODUCTS FROM CARBETHOXY DERIVATIVES OF SUBSTITUTED α-BENZALDOXIMES WITH *n*-BUTYLAMINE AND PYRIDINE

Substituent	Amine	Temp., °C.	Oxime Yield, %	Oxime M. p., °C. Crude prod.[a]	Oxime Literature m. p., °C.	Recovered derivatives Yield, %	Recovered derivatives M. p., °C. Crude prod.[a]	Recovered derivatives Literature m. p., °C.
4-Methoxy-	*n*-Butylamine	25–30	90	64	64			
4-Methoxy-	Pyridine	97–100				87	72–74	74
2-Chloro-	*n*-Butylamine	25–30	85	75–76	75–76			
2-Chloro-	Pyridine	97–100				72	46–47	47
3-Nitro-	*n*-Butylamine	25–30	94	118–120	123			
3-Nitro-	Pyridine	97–100				70	96–97	97–98
3,4-Methylenedioxy-	*n*-Butylamine	25–30	99	104–106	110			
3,4-Methylenedioxy-	Pyridine	25–30				94	78	78
3,4-Methylenedioxy-	Pyridine	97–100				95	73–75	78

[a] The melting points of these products were raised by recrystallization to those reported in the literature.

TABLE VII

PERCENTAGE YIELDS OF PRODUCTS FROM BENZOYL DERIVATIVES OF SUBSTITUTED α-BENZALDOXIMES WITH *n*-BUTYLAMINE AND PYRIDINE

Substituent	Amine	Temp., °C.	Oxime Yield, %	Oxime M. p., °C. Crude prod.[a]	Oxime Literature m. p., °C.	Recovered derivatives Yield, %	Recovered derivatives M. p., °C. Crude prod.[a]	Recovered derivatives Literature m. p., °C.
3-Nitro-	*n*-Butylamine	25–30	98	119–120	123			
3-Nitro-	Pyridine	97–100				99	162–163	164
3,4-Methylenedioxy-	*n*-Butylamine	25–30	90	109–110	110			
3,4-Methylenedioxy-	Pyridine	97–100				99	167–168	168

[a] The melting points of these products were raised by recrystallization to those reported in the literature.

These results are of especial significance in connection with the configuration of the carbethoxy-aldoximes which have been isolated in only one geometrical form. Certain of these compounds, although prepared from the corresponding α-aldoximes, were originally assigned the β-configuration by Brady and McHugh,[14] because with hot alkali, nitrile or the corresponding acid was obtained. Recently, however, it has been shown that these carbethoxy-aldoximes react with alkali to give both nitrile and α-aldoximes,[6] the yields of the latter predominating in most cases at 30° or below. Since the aldoximes obtained had been assigned previously the α-configuration as determined by the reactions of their acetyl derivatives with alkali, it was concluded that these carbethoxy derivatives should likewise be assigned the α-configuration; this conclusion is now supported by the fact that, like the acetyl-α-aldoximes, these carbethoxy derivatives are stable in pyridine solution, but are readily decomposed by *n*-butylamine to give the corresponding α-aldoxime.

In conclusion, it should be pointed out that, although the method for distinguishing geometri-

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(14) Brady and McHugh, *J. Chem. Soc.*, **123**, 1190 (1923). These workers assigned the α-configuration to certain other carbethoxy-aldoximes because with alkali the original aldoxime was obtained. At the time of their work the effect of temperature on the relative yields of nitrile and oxime produced by these reactions was presumably not known; see ref. 6.

cally isomeric acyl-aldoximes described in this paper is very satisfactory for the compounds studied, it is possible that certain types of acyl-α-aldoximes, as well as their β-isomers, might be decomposed by pyridine or *n*-butylamine to give nitrile, especially if there is present in these compounds an activated aldehydic hydrogen atom, or groups that would hinder the aminolysis[7] to aldoxime. Even in these cases, however, it should be possible to distinguish the α- and β-isomers, since the latter would probably form nitrile more readily.[15]

Experimental

Preparation of Acyl-aldoximes.—The acetyl-α- and acetyl-β-aldoximes were prepared according to methods previously described.[2]

The carbanilino-α- and carbanilino-β-aldoximes were prepared by treating the corresponding aldoximes in ether solution with phenyl isocyanate according to the methods described by Brady and others.[13] Crystals of the β-derivatives formed almost immediately; these were purified by recrystallization from alcohol and water. Crystals of the α-derivatives formed on standing several hours; these were purified by boiling them in alcohol solution for an hour, followed by recrystallization from alcohol and water as described by Brady and co-workers.[13] The melting points of these derivatives agreed with those reported by the earlier workers.

The carbethoxy-α-aldoximes[14] and benzoyl-α-aldoximes[16] were prepared from α-aldoximes according to methods previously described.

Reactions of Acyl-aldoximes with Pyridine and *n*-Butylamine.—These amines (4–6 cc.) were added, in 1-cc. portions, to 1–2 g. samples of the acyl-aldoximes. The reactions of *n*-butylamine with the acetyl-β- and carbanilino-β-aldoximes were vigorous, generating considerable heat; in the other reactions the acyl-aldoximes dissolved without appreciable rise of temperature. After standing several hours, crushed ice was added to the amine solutions, and the products isolated as described previously for the case of the acetyl-3,4-methylenedioxybenzaldoximes.[7] In the reactions of *n*-butylamine with the carbanilino-α-aldoximes a solid was obtained which was insoluble in alkali; it melted at 130°, and was shown to be identical with N-phenyl-N′-*n*-butylurea[17] synthesized from phenyl isocyanate and *n*-butylamine.

In order to show that α- and β-3,4-methylenedioxybenzaldoximes may be distinguished without isolating the corresponding acetyl derivatives, 1-g. samples of these aldoximes were dissolved in minimum quantities of acetic anhydride (about 1 cc.) at room temperature and the solutions cooled in an ice-bath. The mixtures were then treated with approximately 6 cc. of pyridine or *n*-butylamine; when the latter was added the mixture became very hot. After standing for an hour, ice water was added and the products isolated in the usual manner. The yields of products obtained were as follows: from the β-aldoxime with pyridine, 97% nitrile, and with *n*-butylamine, 84% nitrile; from the α-aldoxime with pyridine, 80% of the corresponding acetyl-α-aldoxime, and with *n*-butylamine, 72% of the original α-aldoxime.

Reactions of Carbanilino-aldoximes with 2 *N* Sodium Hydroxide.—These reactions were carried out and the products isolated as described previously for the reactions of the acetyl-aldoximes with alkali.[2] In the reactions with the carbanilino-α-aldoximes, diphenylurea was obtained as previously reported.[13]

Summary

A method for distinguishing geometrically isomeric aldoximes and their acyl derivatives is described; it is based on the reactions of the latter with pyridine and *n*-butylamine.

Acetyl-β- and carbanilino-β-aldoximes are decomposed by pyridine to form nitrile, while the corresponding α-isomers are stable in pyridine solution.

Acetyl-β- and carbanilino-β-aldoximes react vigorously with *n*-butylamine, the hot mixture giving mainly nitrile, whereas the corresponding α-isomers dissolve in *n*-butylamine without noticeable rise of temperature, giving aldoxime.

α- and β-aldoximes are readily converted into their corresponding acetyl derivatives; consequently, the method may be used to distinguish geometrically isomeric aldoximes.

The carbethoxy and benzoyl derivatives of α-aldoximes are stable in pyridine solution, but are decomposed by *n*-butylamine to regenerate the original aldoxime.

DURHAM, N. C.

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[15] It might be mentioned in this connection that often it is not possible to isolate the β-isomers, especially when the β-aldoximes are treated with the acylating agent in a basic medium; however, the presence of the β-isomers is indicated by the formation of nitrile directly; see ref. 6.

[16] See Brady and McHugh, *J. Chem. Soc.*, 2414 (1925).

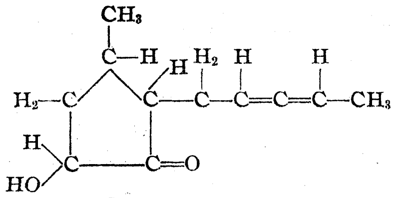
[17] Recently, this compound (m. p. 130°) has been synthesized from *n*-butyl isocyanate and aniline by Boehmer, *Rec. trav. chim.*, **55**, 379 (1936).

[CONTRIBUTION FROM DIVISION OF INSECTICIDE INVESTIGATIONS, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, UNITED STATES DEPARTMENT OF AGRICULTURE]

Constituents of Pyrethrum Flowers. VI. The Structure of Pyrethrolone[1,2]

BY F. B. LAFORGE AND H. L. HALLER

Pyrethrolone, the cyclic ketonic alcoholic component common to the two insecticidal constituents of pyrethrum flowers, has been assigned formula I by Staudinger and Ruzicka.[3]

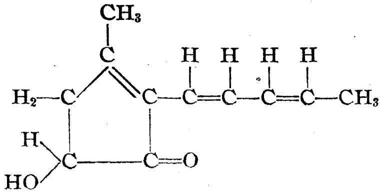


I

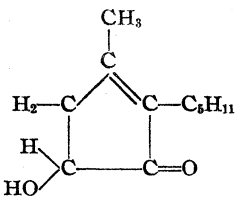
The semicarbazone of pyrethrolone is obtained by saponification of the semicarbazones of either of the pyrethrins or mixtures of their semicarbazones.

In a previous communication[4] it has been shown that the semicarbazone of pyrethrolone should be represented by the empirical formula $C_{12}H_{17}O_2N_3$, and that of tetrahydropyrethrolone, which has a saturated side chain, by $C_{12}H_{21}O_2N_3$. It follows that pyrethrolone corresponds to formula $C_{11}H_{14}O_2$ and tetrahydropyrethrolone to $C_{11}H_{18}O_2$. These formulas, which have been verified by numerous analyses, have two less hydrogen atoms than formula I and its tetrahydro derivative.[5]

This fact calls for a revision of formula I, and it is suggested that pyrethrolone be assigned formula II and tetrahydropyrethrolone formula III.



II



III

In formula II a two-fold revision has been made. An additional double bond is placed in the 2,3-position in the nucleus, and following a later suggestion of Ruzicka and Pfeiffer the cumulated double-bond system has been replaced by a system of conjugated double bonds.[6,7]

Tetrahydropyrethrolone, having a saturated side chain, is better suited for study of the nuclear reactions than is pyrethrolone. It is best prepared by hydrogenation of pyrethrolone semicarbazone and subsequent hydrolysis of the hydrogenated compound.

When tetrahydropyrethrolone, prepared by hydrolysis of its semicarbazone (m. p. 196°), is again treated with semicarbazide, a mixture of semicarbazones that can be separated into two fractions is obtained. The larger part is the original semicarbazone melting at 196°, the other an isomer melting at 168°.[8] This observation has been verified by us. When the semicarbazone of tetrahydropyrethrolone is hydrolyzed with potassium bisulfate solution at 100°, all the tetrahydropyrethrolone is obtained in the form which gives the semicarbazone melting at 168–170°.

The difference between the two tetrahydropyrethrolones derived from these semicarbazones, as suggested by Staudinger and Ruzicka,[8] is due merely to optical inactivation at the carbon atom to which the hydroxyl group is attached, the racemic compound being the one that yields the semicarbazone melting at 170°. This is true because the free ketone is optically inactive and for reasons that will immediately follow.

Preparations of pyrethrolone obtained from the semicarbazones are also without doubt mixtures containing more or less of the inactive form.

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(1) For article V of this series see THIS JOURNAL, **58**, 1061 (1936).

(2) We are indebted to F. Acree, Jr., and P. S. Schaffer for technical assistance throughout this investigation, and to W. G. Rose for the microcombustions.

(3) Staudinger and Ruzicka, *Helv. Chim. Acta*, **7**, 214 (1924).

(4) Haller and LaForge, *J. Org. Chem.*, **1**, 38 (1936).

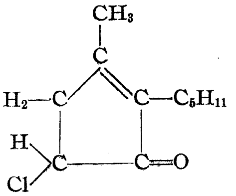
(5) See also analytical figures for pyrethrin II, article II of this series, THIS JOURNAL, **57**, 1893 (1935).

(6) Ruzicka and Pfeiffer, *Helv. Chim. Acta*, **16**, 1208 (1933).

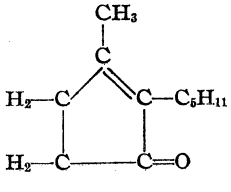
(7) With the suggested change in the nucleus, a reinterpretation of the results of the oxidation and ozonization experiments of Staudinger and Ruzicka from which the arrangement of the double bonds in the side chain of formula 1 was deduced might indicate that the conjugated system so common in natural products is not excluded. We wish to state emphatically, however, that at present no positive evidence for either the conjugated or the cumulated system is available. This phase of the investigation is now in progress.

(8) Staudinger and Ruzicka, *Helv. Chim. Acta*, **7**, 226 (1924).

The hydroxyl group in tetrahydropyrethrolone is readily replaced by chlorine, and the resulting chloro derivative of formula IV yields on reduction an optically inactive ketone of structure V, which gives a semicarbazone that melts at 176°.



IV

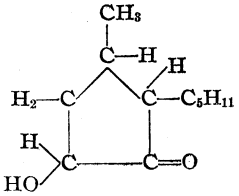


V

Structure V is the one that on the basis of degradation and synthesis has been assigned to dihydrojasmone,[6,9] the semicarbazone of which also melts at 176°. Through the courtesy of Dr. W. Treff, of Heine and Co., Leipzig, Germany, we have obtained a sample of authentic dihydrojasmone semicarbazone. It melted at 176° and a mixture of it with our tetrahydropyrethrone semicarbazone likewise at 176°. The two compounds are therefore identical. The optically inactive tetrahydropyrethrolone, the semicarbazone of which melts at 170°, also yields a chloro compound which on reduction gives the same compound of formula V as that obtained from active tetrahydropyrethrolone. Its semicarbazone also melts at 176°, and a mixture of it with the corresponding derivative obtained from the active substance likewise melts at 176°. The *p*-nitrophenylhydrazone melts at 107°. The two substances are therefore identical, and the proof is established that both active and inactive tetrahydropyrethrolone are to be represented by formula III.

With the assumption that tetrahydropyrethrolone corresponds to formula III, its characteristic reactions are readily explained. In agreement with the recorded observation, it should yield caproic acid on oxidation. The location of the double bond where only carbon-to-carbon linkages are present would render it difficult to hydrogenate, which is also in agreement with experience. Formula III, in fact, not only satisfies all the recorded properties of tetrahydropyrethrolone, but in addition it explains all the recorded divergences from the expected.

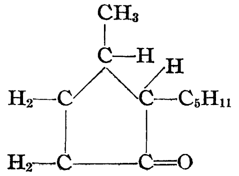
The formula VI, which has been proposed by Staudinger and Ruzicka[3] for tetrahydropyrethrolone, has the same nucleus as formula I, but it has a saturated side chain. From analogy with compounds having the same nucleus, a compound of that structure would be expected to yield 1-amyl-2-methylglutaric acid upon mild oxidation with permanganate. The experiment, however, gave a negative result.[10]



VI

The formation of malonic acid, which has been regarded as a degradation product of the side chain in the oxidation of pyrethrolone (of formula I), may possibly be as an oxidation product of the nucleus (of formula II), and hence could not be regarded as proof of the grouping —$CHCH_2CH$— in the side chain.

Although the ethers and acetates of cyclopentanolones of known structure are stable on hydrogenation, pyrethrolone and its methyl ether and acetate are in part hydrogenated to the completely saturated compound of formula VII.[11,12]



VII

This compound was also prepared synthetically by Staudinger and Ruzicka, and its identity established with the reduction product of pyrethrolone. (The compound of formula V was an intermediate product in this synthesis.)

It is possible that the presence of a double bond, situated as in formulas II and III, might induce a cleavage such as is observed with the pyrethrolone derivatives, with the formation of hexahydropyrethrone of formula VII. The hydrogenation of the pyrethrolone derivatives does not, however, proceed simply or with quantitative yields.

It was in this phase of their investigations that the discontinuity in the reasoning of Staudinger and Ruzicka occurred.

Pyrethrolone and also tetrahydropyrethrolone

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(9) Treff and Werner, *Ber.*, **66**, 1521 (1933); **68**, 640 (1935).

(10) Staudinger and Ruzicka, *Helv. Chim. Acta*, **7**, 228 (1924).

(11) Staudinger and Ruzicka, *ibid.*, **7**, 237 (1924).

(12) This compound has been called "tetrahydropyrethrone" by Staudinger and Ruzicka. In view of the introduction of a double bond in the nucleus of the revised formulas it should be designated as hexahydropyrethrone.

have been found to be very sensitive compounds. Both, although nearly insoluble in water, are probably hygroscopic, and for this reason it is unusually difficult to obtain satisfactory analytical results. It was only when the samples for the combustions were weighed out immediately after distillation that values close to the theoretical for carbon and hydrogen were obtained. Subsequent analyses always showed a decreasing carbon content. When samples were redistilled after standing for a few days, a vigorous evolution of vapor preceded the distillation. This property, not referred to in the literature, may have contributed to the faulty analyses reported. It does not, however, appear to be shared by the enolic forms of pyrethrolone and tetrahydropyrethrolone or by the acetates and ethers.

Experimental

Pyrethrolone.—Staudinger and Ruzicka prepared pyrethrolone by shaking its semicarbazone for a long time in the cold with a concentrated solution of potassium bisulfate in the presence of benzene. The method has been changed slightly, because at a temperature near 0° the salt crystallized out and the benzene solidified. Instead of benzene, peroxide-free ether has been employed as the solvent and the operation carried out during the cool season in a room with open window. Many experiments were performed with quantities of semicarbazone ranging from 5 to 15 g., about 75 g. of potassium bisulfate dissolved in 150 cc. of water, and about 150 cc. of ether. The air in the container was displaced by carbon dioxide. The time required for practically complete decomposition ranged from one to three weeks, depending on the quantity of semicarbazone used. The ether solution was separated, washed, and dried, and the solvent evaporated. The yields of crude product were always somewhat less than quantitative, and a small amount of insoluble solid material always remained. It was necessary to avoid contact of the ether with rubber, as otherwise sulfur was dissolved which was impossible to remove.

The colorless crude product was distilled at about 0.25 mm. and passed over between 130 and 135°. The distillate should be protected as much as possible from contact with air, if satisfactory analytical results are to be obtained. The samples for combustion were therefore weighed out immediately after distillation. Even when all possible care was taken, the figures obtained are not all that could be desired. Results obtained on samples weighed even an hour after distillation showed a decrease in carbon and an increase in hydrogen content, and weighed portions were observed to gain in weight visibly on the balance. When preparations that had been in contact with air a few days were redistilled, a vigorous evolution of vapor preceded the distillation, and the distilled product when again immediately analyzed gave results very close to the calculated. There is also a slight loss in distillation, due perhaps to oxidation or polymerization.

Anal. (freshly distilled material) Calcd. for $C_{11}H_{14}O_2$: C, 74.15; H, 7.87; for $C_{11}H_{16}O_2$: C, 73.33; H, 8.89. Found: C, 73.94, 73.77, 73.36, 73.33; H, 8.34, 8.35, 8.31, 8.13.

Tetrahydropyrethrolone.—The free ketone alcohol was always prepared from the corresponding semicarbazone[4] by hydrolysis with potassium bisulfate under exactly the same conditions as described above. The time required for complete reaction was shorter than for pyrethrolone.

Tetrahydropyrethrolone closely resembles the unhydrogenated compound in its physical properties. The two compounds are both hygroscopic and require the same precautions in handling. It boils at about 120–125° and 0.25 mm.

The following results were obtained with material analyzed immediately after distillation:

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.53; H, 9.98; for $C_{11}H_{20}O_2$: C, 71.74; H, 10.88. Found: C, 72.19, 71.90, 72.00, 71.75; H, 10.05, 10.15, 10.05, 10.05.

The compound gives a pale yellow coloration with tetranitromethane. In ethyl alcohol $[\alpha]^{20}_{D} +11.9°$, $c = 7$; $l = 1$ dm. Staudinger and Ruzicka[8] report a levo rotation ($-11.3°$).

Racemic Tetrahydropyrethrolone and its Semicarbazone.—When the semicarbazone is prepared from distilled tetrahydropyrethrolone, two compounds are obtained. For the most part the mixture consists of the original semicarbazone melting at 196°. The remainder is the semicarbazone of the racemic compound melting at 170°. One gram of distilled tetrahydropyrethrolone was dissolved in 10 cc. of 95% alcohol and 3 cc. of pyridine, and 0.6 g. of semicarbazide hydrochloride in a few drops of water was added to the solution. After standing for two days the 0.6 g. of separated crystalline material was removed by filtration. It melted at 196°. Water was added to the filtrate, and the precipitated material was separated. It melted at 180–185°. It was recrystallized from ethyl acetate and yielded 0.3 g. of the material melting at 196°. The residue obtained on complete evaporation of the solvent was recrystallized from ethyl acetate with addition of benzene. It melted at 170°. The yield was 0.2 g. The total yield of the main product was thus about 66% of the theoretical.

When the semicarbazone of tetrahydropyrethrolone (m. p. 196°) is hydrolyzed with bisulfate solution at 100°, all the resulting tetrahydropyrethrolone is converted into the inactive form, the semicarbazone of which melts at 170°. Two and a half grams of tetrahydropyrethrolone semicarbazone (m. p. 196°) was shaken at 100° with a solution of 15 g. of potassium bisulfate in 30 cc. of water and 15 cc. of toluene. After three hours the toluene solution was diluted with ether, separated from the aqueous solution, washed, dried, and the solvents removed. The residue distilled at about 120° and 0.2 mm. The yield of pure substance was 1.4 g. The compound is optically inactive. A 6.8% solution in ethyl alcohol showed no detectable rotation in a 1-dm. tube. The semicarbazone was prepared and found to melt at 170°.

Tetrahydropyrethrolone Methyl Ether.—Two grams of tetrahydropyrethrolone semicarbazone in 20 cc. of methanol containing 1 cc. of concentrated sulfuric acid was boiled under reflux for two and one-half hours. The solution was poured into 200 cc. of water, and the separated oil was extracted with petroleum ether. Some solid material insoluble in petroleum ether was removed by filtration. Although not further examined, it was probably the semicarbazone of tetrahydropyrethrolone methyl ether. The petroleum ether solution was washed with water and dried. After removal of the solvent the residual oil was distilled and boiled at 82° and 0.35 mm. The yield of distilled product was 0.6 g.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.47; H, 10.20; CH_3O, 15.82. For $C_{12}H_{22}O_2$: C, 72.72; H, 11.11. Found: C, 73.00, 73.16, 73.25; H, 10.01, 10.27, 10.06; CH_3O, 16.1.

3,5-Dinitrobenzoyl Ester of Pyrethrolone.—Four-tenths of a gram of pyrethrolone was dissolved in 8 cc. of benzene and 2 cc. of quinoline, and 0.7 g. of 3,5-dinitrobenzoyl chloride was added in small portions. The solution was heated under reflux on the steam-bath for one hour, and then poured into ice water and extracted with ether. The ether solution was washed with water and carbonate solution, and the residue left on evaporation of the solvent was combined with the small quantity of solid material that had separated during extraction and was recrystallized from methanol. The yield was about 0.5 g. It melted at 145°.

Anal. Calcd. for $C_{18}H_{16}O_7N_2$: C, 58.06; H, 4.28; for $C_{18}H_{18}O_7N_2$: C, 57.76; H, 4.81. Found: C, 57.86, 57.85; H, 4.24, 4.48.

5-Chlorotetrahydropyrethrone (Formula IV) from Active Tetrahydropyrethrolone.—One gram of tetrahydropyrethrolone was cooled to 0°, and 1 cc. of thionyl chloride was added in small portions. Reaction took place readily with gas evolution. After the main reaction had subsided, an additional 0.5 cc. of thionyl chloride was added and the reaction allowed to proceed about fifteen minutes at room temperature. The excess of thionyl chloride was removed by distillation at about 15 mm., and the chloro derivative was then distilled at 0.6 mm. Practically all passed over at 97–100°. The yield was 0.9 g.

Anal. Calcd. for $C_{11}H_{17}OCl$: C, 65.84; H, 8.47. Found: C, 65.19, 65.16; H, 8.52, 8.59.

Tetrahydropyrethrone (Dihydrojasmone), Formula V.—Two grams of zinc dust was added in small portions to a solution of 0.8 g. of 5-chlorotetrahydropyrethrone in 5 cc. of acetic acid. The solution warmed up spontaneously, and the reaction was completed by heating for one hour on the steam-bath. Water was then added and the aqueous suspension decanted. The separated oil was extracted with ether and the ethereal solution freed from acetic acid by washing with water and sodium carbonate solution. The solvent was then removed and the remaining liquid distilled at 15 mm. The temperature was not recorded owing to the small quantity of material handled. The yield of tetrahydropyrethrone was 0.7 g. It has a pleasant odor and $n^{28}\text{D}$ 1.476. It is optically inactive. A 7% solution in alcohol showed no rotation in a 1-dm. tube.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.84. Found: C, 78.92, 78.92; H, 11.16, 10.80.

The semicarbazone was obtained in quantitative yield from 0.1 g. of material and 0.15 g. of semicarbazide hydrochloride in pyridine–alcohol solution. It melted at 176°. The melting point was unchanged after recrystallization from benzene.

5-Chlorotetrahydropyrethrone and Tetrahydropyrethrone (Dihydrojasmone) from Inactive Tetrahydropyrethrolone.—The preparation of the chloro compound and its reduction to dihydrojasmone were repeated to show that no migration of the double bond had occurred in the inactivation of tetrahydropyrethrolone. One and six-tenths grams of the inactive tetrahydropyrethrolone was converted into the chloro derivative by the procedure described above and yielded 1.4 g. of distilled product.

Anal. Calcd. for $C_{11}H_{17}OCl$: Cl, 17.70. Found: Cl, 17.90, 17.93.

One and three-tenths grams of the chloro compound yielded, on reduction with zinc and acetic acid, 1.1 g. of tetrahydropyrethrone, $n^{28}\text{D}$ 1.476. The semicarbazone melted at 176°, and when mixed with an equal quantity of the same compound obtained from active tetrahydropyrethrolone or with authentic dihydrojasmone semicarbazone the melting point was also 176°. The *p*-nitrophenylhydrazone was prepared by dissolving equal quantities of the ketone and *p*-nitrophenylhydrazine hydrochloride in methanolic solution. After recrystallization it melted at 106–107°. Ruzicka and Pfeiffer record the melting point of the *p*-nitrophenylhydrazone of dihydrojasmone as 111.[6] The *p*-nitrophenylhydrazone of the compound of formula VII is reported to melt at 88°.[13]

Summary

The formula I for pyrethrolone proposed by Staudinger and Ruzicka has been revised by placing an additional double bond within the cyclopentane nucleus in the 2,3-position and by changing the cumulated double-bond system in the side chain to a system of conjugated double bonds. The same revision of the nucleus is also made in the formula for tetrahydropyrethrolone. These changes are in agreement with the analytical results found for pyrethrolone and its derivatives.

The new formulas II and III for pyrethrolone and tetrahydropyrethrolone are substantiated by the conversion of the latter compound into a chloro derivative, which on reduction yields dihydrojasmone of the established structure V.

Washington, D. C. Received June 18, 1936

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(13) Staudinger and Ruzicka, *Helv. Chim. Acta*, **7**, 259 (1924).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Open Chain Derivatives of *d*-Mannose

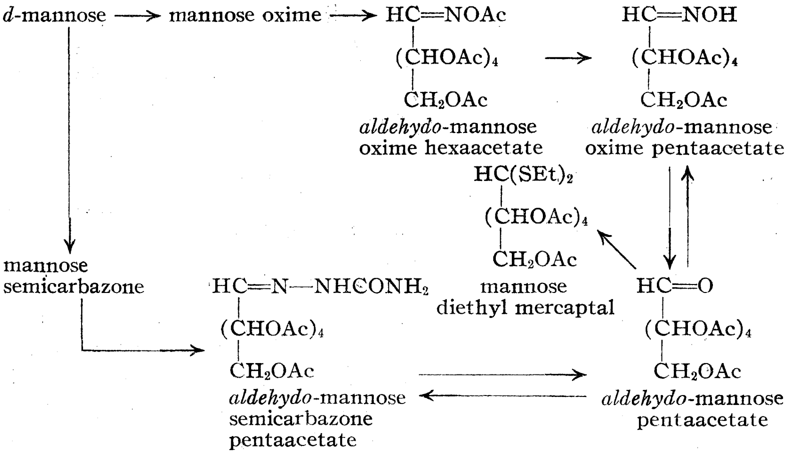
BY M. L. WOLFROM AND L. W. GEORGES

Application of the controlled hydrolysis, with mercuric chloride and cadmium carbonate, to acetylated sugar mercaptals[1] having the *cis*-configuration on carbon atoms two and three, such as mannose, rhamnose and α-glucoheptose, has led to impure sirupy products instead of the desired crystalline *aldehydo*-sugar acetates. The new synthesis of *aldehydo*-sugar acetates reported from this Laboratory[2] offered a different method of approach which has now been applied to *d*-mannose. The desired *aldehydo*-mannose pentaacetate was not obtained in crystalline form but a sirupy product was secured which was less impure than that produced by de-mercaptalation. This sirup was characterized by a number of crystalline derivatives, of an open chain structure, which are of interest and which can be produced by direct acetylation methods.

Deulofeu and co-workers[3] have shown that the low temperature acetylation of mannose oxime gives the open chain or *aldehydo*-mannose oxime hexaacetate in good yield. The assignment of an open chain structure to this compound was based upon its transformation to the acetylated nitrile on heating, a reaction characteristic of the open chain aldose oxime hexaacetates.[4] In the work herein reported, the O-acetyl of the oxime group has been selectively hydrolyzed and the resulting crystalline oxime pentaacetate has been deoximated with nitrous acid to produce the *aldehydo*-mannose pentaacetate as a sirup. This sirup was characterized by two crystalline derivatives, mannose diethyl mercaptal pentaacetate and *aldehydo*-mannose semicarbazone pentaacetate. The formation of these two carbonyl derivatives without loss of acetyl groups indicated that the sirup was essentially the *aldehydo*-pentaacetate. Mild acetylation of mannose semicarbazone formed the same crystalline semicarbazone pentaacetate as was obtained by the reaction between the deoximated product and semicarbazide. Removal of the semicarbazide group from this substance with nitrous acid yielded a sirupy pentaacetate which could be oximated to produce a crystalline *aldehydo*-mannose oxime pentaacetate identical with that obtained from the selective hydrolysis of the oxime hexaacetate of Deulofeu and co-workers. The relationships between these compounds are shown in Fig. 1. It would appear from these results and from those of Deulofeu and co-workers, that *d*-mannose shows a pronounced tendency to react in its open chain form.

Fig. 1

Interrelationships in the *aldehydo*-mannose series



Experimental

Preparation of *Aldehydo-d*-mannose Oxime Hexaacetate.—This substance was prepared by the low temperature acetylation of mannose oxime as described by Deulofeu and co-workers,[3] except that mechanical stirring was employed and the reaction was satisfactorily completed in twelve hours at 2° instead of in eight days at 0°; m. p. 91–92°; $(\alpha)^{25}_D$ $-8.5°$ (c, 4; $CHCl_3$). Deulofeu and co-workers record the constants: m. p. 94°; $(\alpha)^{20}_D$ $-8.3°$ ($CHCl_3$).

***Aldehydo-d*-mannose Oxime Pentaacetate.**—*Aldehydo-d*-mannose oxime hexaacetate (7.5 g.) and 6.5 g. of oxalic acid dihydrate were dissolved in 80 cc. of warm methanol and the solution refluxed for thirty minutes. The solvent

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[1] M. L. Wolfrom, THIS JOURNAL, **51**, 2188 (1929).

[2] M. L. Wolfrom, L. W. Georges and S. Soltzberg, *ibid.*, **56**, 1794 (1934).

[3] V. Deulofeu, P. Cattaneo and G. Mendivelzua, *J. Chem. Soc.*, 147 (1934).

[4] M. L. Wolfrom and A. Thompson, THIS JOURNAL, **53**, 625 (1931).

was removed under reduced pressure and the crystalline residue was washed with several 50-cc. portions of cold water to remove the oxalic acid; yield 4.9 g.; m. p. 119–122°; $(\alpha)_D$ +14° ($CHCl_3$). Pure material was obtained by digestion with ether followed by recrystallization from the minimum amount of hot ethanol by the addition of water; m. p. 122–123°; $(\alpha)^{29}_D$ +15° (*c*, 4; $CHCl_3$).

Anal. Calcd. for $C_6H_8O_6N(COCH_3)_5$: N, 3.45; acetyl, 12.35 cc. of 0.1 *N* NaOH per 100 mg. Found: N, 3.53; acetyl (Freudenberg[5] method), 12.3 cc.

Further acetylation of this substance under mild conditions produced *aldehydo-d*-mannose oxime hexaacetate. The pentaacetate (4.4 g.) was dissolved at 0° in a previously cooled solution of acetic anhydride (13 cc.) and pyridine (26 cc.) and maintained at 0° for one hour. The product was obtained in crystalline form by pouring into 300 cc. of ice and water; yield 3.8 g.; m. p. 89–90°. Pure material was obtained by recrystallization from a small amount of hot ethanol by the addition of water; yield 2.5 g.; m. p. 91–92°; $(\alpha)^{29}_D$ −8.4° (*c*, 4; $CHCl_3$).

De-oximation of *Aldehydo-d*-mannose Oxime Pentaacetate.—*Aldehydo-d*-mannose oxime pentaacetate (1.6 g.) was de-oximated with nitrous acid as described by Wolfrom, Georges and Soltzberg[2] for the corresponding glucose compound. The sirup (1.2 g.) obtained after chloroform removal resisted crystallization and was purified by precipitation from acetone solution by the addition of petroleum ether. The product reduced Fehling's solution and gave a Schiff free aldehyde test.

Anal. Calcd. for $C_6H_7O_6(COCH_3)_5$: acetyl, 12.8 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 12.24 cc.

That the sirup was moderately pure *aldehydo-d*-mannose pentaacetate was proved by the preparation of two crystalline derivatives. Treatment of the sirup with ethyl mercaptan and zinc chloride according to the procedure of Wolfrom and Thompson[6] yielded crystalline mannose diethyl mercaptal pentaacetate; m. p. 51–52° (unchanged on admixture with the product obtained on acetylation of mannose diethyl mercaptal);[7] $(\alpha)^{25}_D$ +32° (*c*, 4; $CHCl_3$). Pirie records the constants: m. p. 51–52°; $(\alpha)^{17}_D$ +31° ($CHCl_3$).

***Aldehydo-d*-mannose Semicarbazone Pentaacetate.**—An amount of 2.4 g. of the sirupy *aldehydo-d*-mannose pentaacetate, obtained by the de-oximation procedure, was dissolved in 35 cc. of hot water, the solution cooled rapidly to room temperature and treated with a solid mixture of semicarbazide hydrochloride (0.95 g.) and potassium acetate (1.5 g.). The semicarbazone separated in crystalline form; yield 1.3 g., m. p. 173–175° (dec.); $(\alpha)^{23}_D$ +9.4° (*c*, 2.5; $CHCl_3$). Pure material was obtained on recrystallization from hot water; m. p. 177–178° (dec.); $(\alpha)^{25}_D$ +9.2° (*c*, 2.5; $CHCl_3$).

Anal. Calcd. for $C_7H_{10}O_6N_3(COCH_3)_5$: N, 9.40; acetyl, 11.2 cc. of 0.1 *N* NaOH per 100 mg. Found: N, 9.12; acetyl, 11.3 cc.

Aldehydo-d-mannose semicarbazone pentaacetate was also obtained in good yield by the direct acetylation of mannose semicarbazone.[8] An amount of 6 g. of mannose semicarbazone was added to a solution of pyridine (36 cc.) and acetic anhydride (18 cc.) and the mixture shaken mechanically at room temperature for four hours. The semicarbazone dissolved and the solution was kept at ice box temperature for twelve hours and was then poured into 800 cc. of ice and water. The crystalline product that separated was removed by filtration and washed with cold water; yield 5 g.; m. p. 176–179° (dec.); $(\alpha)^{23}_D$ +8.9° (*c*, 2; $CHCl_3$). Pure material was obtained on one recrystallization from hot water; m. p. 178–180° (dec.) (m. p. unchanged on admixture with product from the de-oximation); $(\alpha)^{21}_D$ +9.3° (*c*, 2.5; $CHCl_3$).

Splitting of *Aldehydo-d*-mannose Semicarbazone Pentaacetate with Nitrous Acid.—*Aldehydo-d*-mannose semicarbazone pentaacetate (3.2 g.) obtained from the acetylation of mannose semicarbazone was dissolved in 40 cc. of hot ethanol and a warm solution of 10 g. of sodium nitrite in 200 cc. of hot water added. The solution was then placed in a water-bath maintained at 70° and treated with hydrochloric acid and additional sodium nitrite as described by Wolfrom, Georges and Soltzberg[2] for the de-oximation of *aldehydo*-glucose oxime pentaacetate. The sirup so obtained was dissolved in 30 cc. of hot water, cooled to room temperature and treated with a solid mixture of hydroxylamine hydrochloride (0.6 g.) and potassium acetate (1.2 g.). Crystals formed after several hours; m. p. 118–120°. These were recrystallized from hot ethanol by the addition of water; m. p. 121–123° (m. p. unchanged on admixture with the previously described preparations of *aldehydo*-mannose oxime pentaacetate); $(\alpha)^{21}_D$ $+13 \pm 1°$ (*c*, 2.3; $CHCl_3$). The isolation of this product from the oximated sirup indicated that the sirup was essentially *aldehydo-d*-mannose pentaacetate.

Summary

1. *Aldehydo-d*-mannose semicarbazone pentaacetate and *aldehydo-d*-mannose oxime pentaacetate have been synthesized in crystalline condition. Proof is furnished for the structure of these compounds.

2. Mild acetylation of *d*-mannose semicarbazone produces *aldehydo-d*-mannose semicarbazone pentaacetate in good yield.

3. Nitrous acid treatment of either *aldehydo-d*-mannose semicarbazone pentaacetate or *aldehydo-d*-mannose oxime pentaacetate produces *aldehydo-d*-mannose pentaacetate as a sirup characterized by several crystalline derivatives.

COLUMBUS, OHIO RECEIVED JULY 17, 1936

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[5] K. Freudenberg and M. Harder, *Ann.*, **433**, 230 (1923).

[6] M. L. Wolfrom and A. Thompson, THIS JOURNAL, **56**, 882 (1934).

[7] N. W. Pirie, *Biochem. J.*, **30**, 374 (1936).

[8] Maquenne and Goodwin, *Bull. soc. chim.*, [3] **31**, 1075 (1904).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Semicarbazone and Oxime Acetates of Maltose and Cellobiose. *Aldehydo*-Cellobiose Octaacetate

BY M. L. WOLFROM AND S. SOLTZBERG

In previous work reported from this Laboratory we have shown that on acetylation of a sugar oxime or semicarbazone, either acetylated ring structures, or the acetylated open chain structure, or a mixture of both, is obtained. If an open chain structure is produced, methods have been devised for removing the nitrogen residue and obtaining the *aldehydo*-acetate.[1] In the case of the acetylated oximes, the open chain or *aldehydo* forms are readily detected by acetylated nitrile formation on heating and by the selective hydrolysis of the O-acetyl on the oxime group. These criteria are not applicable to the acetylated semicarbazones. With a hexose, a ring structure may be assumed if the product is a tetraacetate. If the substance is a semicarbazone pentaacetate of the ring structure, then the fifth acetyl group is attached to nitrogen and may be distinguished by the difference between the total acetyl and O-acetyl analyses.[2] The total acetyl value is determined by the method of Freudenberg and Harder[3] and the O-acetyl is determined by the Kunz[4] procedure, using phenolsulfonphthalein indicator.

In the work herein reported, the above-described procedures have been extended to maltose and cellobiose. Acetylation of the hitherto unknown crystalline maltose semicarbazone produced a crystalline octaacetate of the ring type. The rotations of these ring forms of acetylated sugar oximes and semicarbazones are very similar to those of the β-forms of the completely acetylated cyclic sugars and we have consequently distinguished them by the prefix β.[5] Acetylation of either the hydrated or anhydrous form of cellobiose semicarbazone likewise yielded the ring octaacetate as the sole crystalline product isolated. Mild acetylation produced the ring heptaacetate.

Cellobiose heptaacetate was oximated and acetylated with the production of the ring or β-cellobiose oxime nonaacetate. We would predict that this should be identical with the product isolated by Zemplén[6] as a by-product in the formation of cellobionic acid nitrile octaacetate.

Zemplén called his product cellobiose *anti*-oxime octaacetate although his published analytical values are in closer agreement with a nonaacetate. His recorded constants are: melting point, 165°; $(\alpha)_D -7°$ (chloroform). Those obtained by us for our compound are: melting point, 195–195.5°; $(\alpha)_D -8.5°$ (chloroform). The β-isomer would be expected to form in Zemplén's experiments by analogy with the behavior of glucose and galactose oximes under the vigorous nitrile forming conditions.[7] The low melting point recorded by Zemplén might be accounted for by the presence of some of the acetylated nitrile, which is frequently very difficult to separate.

When cellobiose oxime was acetylated at low temperatures an amorphous product was obtained which was essentially the *aldehydo*-cellobiose oxime nonaacetate. This fact was established by the formation of cellobionic acid nitrile octaacetate on heating and by its transformation in good yield into a crystalline oxime octaacetate. The latter was deoximated with nitrous acid to yield *aldehydo*-cellobiose octaacetate in the form of an analytically pure, colorless, amorphous powder that resisted crystallization. The substance was nitrogen-free and regenerated the crystalline oxime octaacetate on oximation.

At this point we wish to call attention to the differences in behavior of cellobiose semicarbazone, oxime and heptaacetate as compared to the glucose[1] semicarbazone, oxime and tetraacetate, the latter being analogous to the cellobiose heptaacetate. Thus, cellobiose semicarbazone yielded only the ring form on acetylation, while glucose semicarbazone gave predominantly the open chain form. Cellobiose oxime, on the other hand, produced the open chain acetate, while glucose oxime under the same conditions gave the ring

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[1] M. L. Wolfrom, L. W. Georges and S. Soltzberg, THIS JOURNAL, **56**, 1794 (1934).

[2] M. L. Wolfrom, M. Konigsberg and S. Soltzberg, *ibid.*, **58**, 490 (1936).

[3] K. Freudenberg and M. Harder, *Ann.*, **433**, 230 (1923).

[4] A. Kunz and C. S. Hudson, THIS JOURNAL, **48**, 1982 (1926).

[5] M. L. Wolfrom and A. Thompson, *ibid.*, **53**, 625 (1931).

[6] G. Zemplén, *Ber.*, **59**, 1260 (1926).

[7] A. Wohl, *ibid.*, **26**, 730 (1893); M. L. Wolfrom and A. Thompson, THIS JOURNAL, **53**, 622 (1931); V. Deulofeu, M. L. Wolfrom, Pedro Cattaneo, C. C. Christman and L. W. Georges, *ibid.*, **55**, 3488 (1933).

form. Cellobiose heptaacetate, after oximation and acetylation, yielded the ring form, whereas glucose tetraacetate after the same treatment gave the *aldehydo* form. Thus the introduction of a glucose molecule in the fourth position completely reversed the behavior of the active glucose function with respect to the acetylation of the oximes and semicarbazones under the conditions employed.

Experimental

Maltose Semicarbazone.—Semicarbazide hydrochloride (9 g.) was rubbed to a paste with 6 g. of fused potassium acetate and heated on the water-bath with 75 cc. of absolute ethanol to extract the semicarbazide, the solution being filtered to remove potassium chloride. The warm ethanol extract was added to a warm solution of 25 g. of maltose in 50 cc. of water and the mixture allowed to cool to room temperature. The proportions of ethanol and water should be such that no sirupy phase forms at this point. Crystalline material appeared on standing. After several days, this material was removed by filtration; yield 12.5 g. Pure material was obtained by dissolving in a minimum of hot water and adding ethanol; m. p. 213° (dec.); $[\alpha]^{25}\text{D}$ +80° (*c*, 3.5; H_2O), initial value, changing slowly in the dextro direction. The substance crystallized in the anhydrous condition.

Anal. Calcd. for $C_{13}H_{25}O_{11}N_3$: N, 10.53. Found: N, 10.45.

β-Maltose Semicarbazone Octaacetate.—Powdered maltose semicarbazone (12 g.) and 96 cc. of pyridine were heated in a bath maintained at 60–65° and 48 cc. of acetic anhydride added. The reaction mixture was stirred mechanically for seven hours at this temperature to effect solution of the semicarbazone and was then allowed to stand overnight at room temperature. The solution was then poured into ice and water, a small amount of amorphous material removed by filtration and the filtrate extracted with chloroform. The chloroform extract was washed successively with 5% hydrochloric acid, sodium bicarbonate solution, and water dried, and the solvent removed under reduced pressure. The residue was crystallized from ethanol; yield 8.3 g.; m. p. 206–208° (dec.); $(\alpha)^{25}\text{D}$ +61° ($CHCl_3$). Pure material was obtained on further recrystallization from ethanol; m. p. 209–210° (dec.); $(\alpha)^{26}\text{D}$ +61° (*c*, 3; $CHCl_3$). The analytical data indicated that the compound was a maltose semicarbazone octaacetate with one N-acetyl group.

Anal. Calcd. for $C_{13}H_{17}O_4N_2(OCOCH_3)_7(NCOCH_3)$: total acetyl, 10.9 cc. of 0.1 *N* NaOH per 100 mg.; O-acetyl, 9.5 cc. Found: total acetyl, 11.0 cc.; O-acetyl, 9.5 cc.

β-Cellobiose Semicarbazone Heptaacetate.—Cellobiose semicarbazone dihydrate[8] (6.2 g.) was acetylated at room temperature with pyridine (48 cc.) and acetic anhydride (24 cc.) for eighteen hours with mechanical stirring. The reaction mixture was then poured into 150 cc. of ice and water and on standing at ice box temperature for several hours the liquid set to a semi-solid mass of crystals; yield 5.8 g.; m. p. 205–207°; $(\alpha)^{25}\text{D}$ −20° ($CHCl_3$). A further small amount of material (0.8 g.) of lower purity could be obtained by chloroform extraction of the mother liquor. Pure material was obtained on recrystallization from ethanol; m. p. 207–208°; $(\alpha)^{27}\text{D}$ −21° (*c*, 3; $CHCl_3$).

Anal. Calcd. for $C_{13}H_{18}O_4N_3(OCOCH_3)_7$: total acetyl, 10.1 cc. of 0.1 *N* NaOH per 100 mg.; O-acetyl, 10.1 cc. Found: total acetyl, 10.1 cc.; O-acetyl, 9.8 cc.

β-Cellobiose Semicarbazone Octaacetate.—Further acetylation of β-cellobiose semicarbazone heptaacetate (0.5 g.) with pyridine (3 cc.) and acetic anhydride (1 cc.) for two days at 40° produced β-cellobiose semicarbazone octaacetate; m. p. 238–240° (dec.). This could also be prepared directly from cellobiose semicarbazone dihydrate (6 g.) according to the previously described acetylation procedure except that after the semicarbazone had dissolved in the acetylating mixture, the solution was kept at 40° for two days. No product was obtained on pouring into water but on extraction with chloroform in the usual manner, a crystalline product was obtained on the addition of ether to the concentrated chloroform solution; yield 3.1 g.; m. p. 215–220° (dec.). Pure material was obtained after several recrystallizations from ethanol; m. p. 240–241° (dec.); $(\alpha)^{25}\text{D}$ −26.5° (*c*, 3; $CHCl_3$). Acetylation of anhydrous semicarbazone with the same reagents maintained at 70–75° until solution was complete, produced the same octaacetate.

Anal. Calcd. for $C_{13}H_{17}O_4N_2(OCOCH_3)_7(NCOCH_3)$: N, 5.71; total acetyl, 10.9 cc. of 0.1 *N* NaOH per 100 mg.; O-acetyl, 9.5 cc. Found: N, 5.80; total acetyl, 10.8 cc.; O-acetyl, 9.5 cc.

β-Cellobiose Oxime Nonaacetate.—Cellobiose heptaacetate (10 g.)[9] was refluxed with two equivalents of free hydroxylamine in 35 cc. of ethanol on a water-bath for two hours. The sirup obtained on solvent removal was acetylated for two hours in an ice–salt bath with pyridine (50 cc.) and acetic anhydride (25 cc.). On pouring into water, a crystalline product (8 g.) was obtained which consisted essentially of a mixture of α-cellobiose octaacetate and the oxime nonaacetate. This mixture was heated with sufficient ethyl acetate to make a thin paste, filtered rapidly, and the residue washed with several portions of hot 95% ethanol. The crystals that separated from the filtrate were likewise filtered and washed with alcohol. The filtrate and washings were combined, concentrated to dryness, and the residue crystallized from a small amount of hot ethanol; yield 2.5 g.; m. p. 187–188°; $(\alpha)\text{D}$ +0.5° ($CHCl_3$). Pure material was obtained on repeated crystallization from 95% ethanol; m. p. 195–195.5°; $(\alpha)^{27}\text{D}$ −8.5° (*c*, 2.5; $CHCl_3$).

Anal. Calcd. for $C_{12}H_{14}O_3(OCOCH_3)_8(NCOCH_3)$: total acetyl, 12.25 cc. of 0.1 *N* NaOH per 100 mg.; O-acetyl, 10.9 cc. Found: total acetyl, 12.1 cc.; O-acetyl, 11.0 cc.

Unchanged material was recovered on heating the compound to incipient decomposition and also on refluxing for thirty minutes with a methanol solution of oxalic acid dihydrate. This behavior, together with the analytical data, shows that the compound was the oxime nonaacetate of cellobiose with one acetyl group attached to nitrogen. β-Glucose oxime hexaacetate also resists the hydrolytic ac-

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[8] Maquenne and Goodwin, *Bull. soc. chim.*, [3] **31**, 1075 (1904).

[9] E. Fischer and G. Zemplén, *Ber.*, **43**, 2536 (1910).

tion of a methanol solution of oxalic acid and can be recovered unchanged under the above conditions.

Aldehydo-Cellobiose Oxime Octaacetate.—Cellobiose oxime (3 g.)[10] was acetylated with pyridine (24 cc.) and acetic anhydride (12 cc.) by stirring at 0° for two hours, followed by forty hours of standing at ice box temperature. The sirup ($(\alpha)_D$ +36°, $CHCl_3$) that was precipitated by pouring into ice and water was combined (total, 4.6 g.) with the sirupy material ($(\alpha)_D$ +35°, $CHCl_3$) obtained by chloroform extraction of the mother liquor and precipitated several times from benzene by means of heptane; $(\alpha)_D$ +37°, $CHCl_3$. The material resisted crystallization but produced crystalline cellobionic acid nitrile octaacetate when heated in the solid state to incipient decomposition.

The acetylated product obtained from 12 g. of cellobiose oxime as described above, was refluxed for thirty minutes with a solution of 13 g. of oxalic acid dihydrate in 160 cc. of methanol. The material obtained after solvent removal was dissolved in water, extracted with chloroform, the extract washed with an aqueous solution of sodium bicarbonate, dried, and the solvent removed. The residue was obtained crystalline from ether; yield 10.4 g.; m. p. 150–151°. Pure material was obtained by dissolving in chloroform and adding ether; m. p. 154–155°; $(\alpha)^{28}_D$ +30° (*c*, 3; $CHCl_3$).

Anal. Calcd. for $C_{12}H_{15}O_3N(OCOCH_3)_8$: total acetyl, 11.5 cc. of 0.1 *N* NaOH per 100 mg.; O-acetyl, 11.5 cc. Found: total acetyl, 11.6 cc.; O-acetyl, 11.6 cc.

De-oximation of *Aldehydo*-Cellobiose Oxime Octaacetate.—*Aldehydo*-cellobiose oxime octaacetate (2 g.) was dissolved in 60 cc. of glacial acetic acid and a solution of 20 g. of sodium nitrite in 60 cc. of water was dropped in during one hour with slow stirring. The stirring was continued for an additional hour with the rate greatly increased during the last ten minutes. The reaction mixture was poured into ice and water, extracted with chloroform, the extract washed with an aqueous solution of sodium bicarbonate, dried, and the solvent removed under reduced pressure. The product so obtained was purified three times by precipitation from methanol by the addition of water; $(\alpha)_D$ +17.1° (*c*, 3.6; alcohol-free $CHCl_3$). This procedure was repeated four more times; $(\alpha)_D$ +17.7° (*c*, 3.4; $CHCl_3$). The substance was obtained as a snow-white, amorphous solid that resisted crystallization but was nitrogen-free. It reduced Fehling's solution and reacted with hydroxylamine to produce the original crystalline *aldehydo*-cellobiose oxime octaacetate.

Anal. Calcd. for $C_{12}H_{14}O_{11}(COCH_3)_8$: acetyl, 11.8 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 12.1 cc.

Summary

1. Maltose semicarbazone has been synthesized. This compound on acetylation yields a crystalline octaacetate of ring structure.

2. Mild acetylation of cellobiose semicarbazone produces crystalline cellobiose semicarbazone heptaacetate. Evidence is presented to show that it is the ring form. More vigorous acetylation yields the crystalline octaacetate which also has the ring form.

3. A crystalline cellobiose oxime nonaacetate has been synthesized and evidence is presented to show that it has a ring structure.

4. *Aldehydo*-Cellobiose oxime octaacetate has been synthesized in crystalline form from cellobiose oxime. Evidence is presented to show that it has the true oxime structure.

5. Cellobiose oxime octaacetate has been de-oximated to give an amorphous *aldehydo*-cellobiose octaacetate which re-forms the original oxime on treatment with hydroxylamine.

Columbus, Ohio Received July 17, 1936

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[10] P. A. Levene and M. L. Wolfrom, *J. Biol. Chem.*, **77**, 677 (1928).

[Contribution from the Chemical Laboratory of the Johns Hopkins University]

Pyridinium Vanadate

By S. Katzoff and R. Roseman

In the course of some work on vanadium, crystals were obtained which we have identified as a new compound, of formula $(C_5H_6N)_3V_5O_{14}\cdot H_2O$.

Preparation

1. The compound can be prepared by double decomposition between ammonium metavanadate and pyridine hydrochloride. A 7% water solution of the metavanadate is prepared by saturating at the boiling point (filtering, if necessary), and to the cooled solution is added one-fifth of its volume of a cool 2:1 mixture of pyridine and concentrated hydrochloric acid. Addition of an equal volume of alcohol, and cooling, result in nearly complete precipitation of the crystalline compound.[1] The precipitate is collected on a Büchner funnel and washed with a pyridine–water mixture (1:1), 95% alcohol and, finally, ether.

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[1] The cool solution sometimes remains supersaturated for remarkably long times, but crystallization is readily initiated by the usual methods.

2. The compound can also be prepared directly from vanadium pentoxide and pyridine, with the aid of hydrogen peroxide. To 1 part by weight of vanadium pentoxide powder (prepared by gently warming ammonium metavanadate) is added 3 parts of pyridine, 1 part of water, and then 2 parts of 30% hydrogen peroxide in small portions, not allowing the temperature of the mixture to rise above 50° at any time. Crystals of the compound soon appear,[1] and the conversion is essentially complete after several hours. The function of the hydrogen peroxide is, presumably, to help dissolve the vanadium pentoxide, giving a solution containing pervanadate ions which, either by subsequent decomposition of the peroxide group or simply by maintaining equilibrium with the vanadate ions, leads to the desired compound.

3. The compound is purified by recrystallization, which is easily carried out since there is a large variation of the solubility in water with temperature. The procedure is to dissolve the material in 3 times its weight of hot water (80°) containing a little pyridine, filter through a quantitative paper, and cool.[1] Rapid performance of the operations is desirable, since hydrolysis occurs at the high temperature, with precipitation of vanadic acid. The crystalline product is collected, washed, and dried on a Büchner funnel, as previously described.

Analysis

The compound was analyzed for vanadium and pyridine.

1. Vanadium was determined by direct ignition of a sample (in a platinum crucible) to vanadium pentoxide. Treatment of the residue with a little nitric acid and reignition did not, in general, result in a change in weight.

2. Pyridine was determined by the following method. A sample (0.5 to 1 g.) is dissolved in 25 cc. of water in a 50-cc. Kjeldahl flask, and 3 cc. of 6 *N* sodium hydroxide is added. The solution is then distilled, using a trap, into a slight excess of standard hydrochloric acid (0.25 *N*), the distillation being carried nearly to dryness. The excess hydrochloric acid is titrated with standard sodium hydroxide (0.25 *N*), using methyl orange or brom phenol blue as indicator.[2]

Following the methods outlined above, the ratio of pyridine to vanadium in the compound was found to be 3:5. For the water content, we depend on an accurate determination of the vanadium. Determinations of the V_2O_5 content of our best products gave values between 61.55 and 61.75%. This corresponds satisfactorily to the compound of simple formula $(C_5H_6N)_3V_5O_{14}\cdot H_2O$, the theoretical V_2O_5 content of which is 61.71%.

Properties

The compound has an orange color, which appears of a lighter or a darker shade according as the crystals are small or large. The density is 2.04, as determined with a pycnometer, using pyridine as the immersion liquid. The crystals are monoclinic, generally appearing as parallelepipeds, sometimes with truncated edges or corners. Pyridine, ether, alcohol, benzene, and acetone do not dissolve the compound appreciably. Water dissolves it, giving an orange solution which reacts acid to litmus. Molten phenol was also found to dissolve it.

When exposed to the atmosphere, the compound slowly loses its volatile constituents. For example, a sample kept on a watch glass in the laboratory for one month lost 5% of its weight. Analysis showed that the percentage of vanadium pentoxide had correspondingly risen, proving that no vanadium had been lost. On the other hand, a sample kept in a glass-stoppered container did not change its composition over a period of two weeks.

Some excellent crystals, of a deep orange color, and perfectly transparent, were prepared by using the previously described recrystallization technique without, however, rapid cooling of the filtrate. The crystallography is being studied by Dr. J. D. H. Donnay, of this University, in collaboration with Dr. J. Mélon, of the University of Liége.

We are greatly indebted to Mr. Jerome Strauss, Vice President of the Vanadium Corporation of America, for the generosity with which he supplied us with pure vanadium compounds for our work.

BALTIMORE, MARYLAND RECEIVED JULY 17, 1936

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(2) Care must be taken to choose the end-point color according to the concentration of pyridine hydrochloride in the solution. The *p*H corresponding to this concentration is calculated, and the end-point color is obtained from a previously prepared set of color standards made up in potassium acid phthalate–hydrochloric acid buffers [Clark and Lubs, *J. Biol. Chem.*, **25**, 479 (1916)].

Our method of analysis was checked by showing, first, that the titration method for pyridine gives accurate results over a wide range of concentrations, and, second, that essentially all of the pyridine is recovered in the distillation. The accuracy of the method is about 1%.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Kinetics of the Reaction between Ferric and Stannous Perchlorates in Acid Solution

BY M. H. GORIN

The present investigation was undertaken to study the reduction of ferric salts by stannous salts in solutions in which it is reasonably certain no complex ions exist; perchlorates were therefore used. Sufficient perchloric acid was added to suppress the formation of colloidal ferric hydroxide.

The kinetics of the comparatively rapid reaction between ferric and stannous chlorides has been much investigated.[1] A rather complete discussion of these researches and new experimental material has been given by the author in a thesis.[2] It is sufficient to state here that the rate-determining step is not a third order reaction involving two ferric and one stannous ions, as is generally supposed, but a second order reaction between unpolymerized chloride complexes of ferric iron and stannous tin. Timofeew[1c] first proved that the reaction is second order and the author[2] and Robertson and Law[1d] independently demonstrated the influence of chloride ion.

It was expected that the reaction rate would be very much smaller with perchlorates than with chlorides, since the repulsive forces between the highly charged and positive ferric and stannous ions are very great and those between the lower valent or neutral chloride complexes (as $FeCl_3$ and $SnCl^+$ or $SnCl_3^-$) are small or negligible. Actually the rate was found to be smaller by a factor of 10^5 to 10^6 under comparable conditions. Moreover, no evidence was found that ferric ion itself reacts directly with stannous ion in a range of temperature from 55 to 70° and of hydrogen-ion concentrations from 0.02 to 1 *M*.

The rate-determining step for the reduction of the ferric salt was concluded to be

$$Fe(OH)_2^+ + Sn^{++} \longrightarrow \qquad (1)$$

The actual kinetics are complicated by the fact that the reactions involved in the hydrolysis equilibrium, $H_2O + FeOH^{++} \rightleftarrows Fe(OH)_2^+ + H^+$, are often not rapid compared to reaction 1; and by the fact that in most of the solutions an appreciable proportion of the ferric iron was present in the form of hydrolysis products. It was found that the presence of colloidal ferric hydroxide increased the rate; this complication was avoided by the addition of perchloric acid in amounts sufficient to suppress its formation.

Materials.—A solution of *ferrous perchlorate* was prepared by the addition of equivalent amounts of a barium perchlorate solution to a ferrous sulfate solution; the mixture was held at a temperature of 100° for several hours in the absence of air in order to coagulate the precipitate of barium sulfate. The clear resulting solution was pipetted off after cooling.

A solution of *stannous perchlorate*, free from excess acid, was prepared by a method formerly employed by Noyes and Toabe.[3]

Experimental Method.—The reaction was started in all experiments by adding a small volume of a concentrated solution of stannous perchlorate to a solution containing the other reactants. The progress of the reaction was followed by the method used by all previous investigators: stannous ion was rapidly destroyed by quenching the sample with mercuric chloride solution, and the extent to which the reaction had progressed was determined by an analysis for the ferrous ion produced.

The reaction mixture, exclusive of stannous perchlorate, contained ferric perchlorate and perchloric acid. It was made up by adding the desired amounts of ferrous perchlorate and perchloric acid solution and an excess of hydrogen peroxide to the desired volume of water in a volumetric flask. The reaction mixture was then transferred to the apparatus employed and allowed to remain at the temperature of the run for a period of at least one day in order to ensure complete decomposition of the excess hydrogen peroxide and attainment of equilibrium.

The apparatus shown in Fig. 1 was employed to enable the withdrawal of samples in the complete absence of air and to eliminate the loss of water by evaporation.

The concentration of ferrous ion in the sample was determined by titration with 0.01 *N* potassium dichromate, using diphenylamine[4] as the indicator.

Experimental Results.—If $Fe(OH)_2^+$ is at equilibrium with ferric and hydrogen ions, the rate law corresponding to equation 1 is

$$d(Fe^{++})/dt = 2k_3K_1K_2(Fe^{+++})(Sn^{++})/(H^+)^2 \qquad (2)$$

where

$$K_1 = (Fe(OH)^{++})(H^+)/(Fe^{+++}) \qquad (3)$$

and

$$K_2 = (Fe(OH)_2^+)(H^+)/(Fe(OH)^{++}) \qquad (4)$$

and k_3 is the specific rate of reaction 1.

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[1] (a) Kahlenberg, THIS JOURNAL, **16,** 314 (1894); (b) Noyes, *Z. physik. Chem.*, **16,** 546 (1895); (c) Timofeew, Muchen and Gurewitch, *ibid.*, **115,** 161 (1925); (d) Robertson and Law, *Trans. Faraday Soc.*, **31,** 899 (1935).

[2] Gorin, Ph.D. Thesis, Sept., 1933, University of California Library.

[3] Noyes and Toabe, THIS JOURNAL, **39,** 1539 (1917).

[4] Benedetti-Pichler, *Z. anal. Chem.*, **73,** 200 (1928).

At the moment of starting, the system must be at equilibrium and therefore the initial rate will be given by equation 2. It was found that the experiments fell into two groups: (1) in those with *ferric perchlorate in excess* the results can be accurately extrapolated to obtain the initial rate; (2) in those with *stannous perchlorate in excess* the rate drops off so quickly from the initial value that no accurate extrapolation can be made.

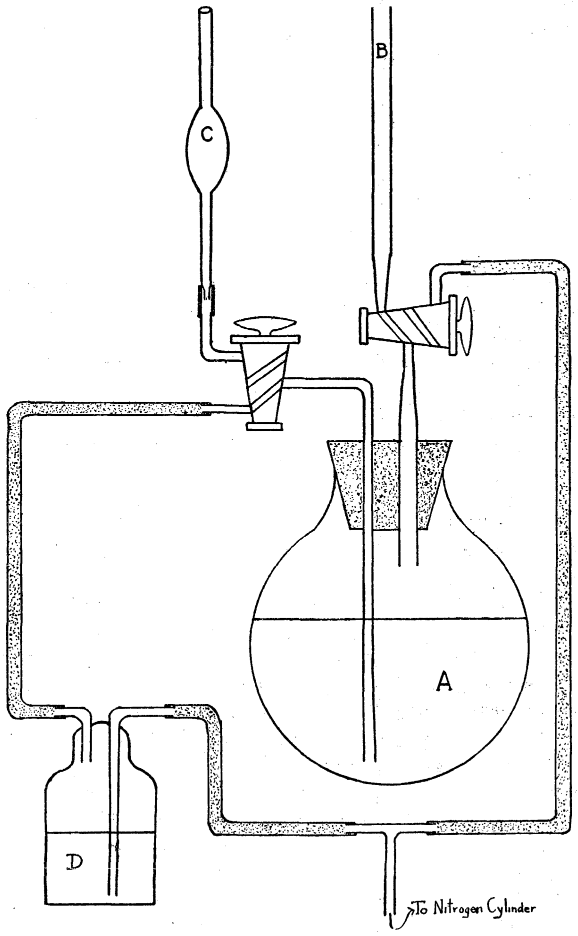

Fig. 1.—Apparatus for rate measurements at 70°: A, reaction vessel in thermostat; B, condenser; C, sampling pipet; D, pressure regulator containing mercury.

Ferric Ion in Excess at 70°.—In Fig. 2, the quantity, $\log (a - x)/(2b - x)$, is plotted against time for the first few experimental points in 6 runs, nos. 1–6. The initial slope, as estimated for each run, is shown by the solid straight lines in Fig. 2. If a, b and c are the initial concentrations of ferric perchlorate, stannous perchlorate and perchloric acid, respectively, x, the concentration of ferrous ion produced at the time, t, and S the slope of the lines drawn in Fig. 2, it follows that

$$(\mathrm{d}x/\mathrm{d}t)_{\text{initial}} = 2.303S(2b)a/(a - 2b)$$

and that

$$2k_3K_1K_2 = \frac{4.606aS[c + (\mathrm{FeOH}^{++})_i + 2(\mathrm{Fe(OH)_2}^{+})_i]^2}{(a - 2b)[a - (\mathrm{FeOH}^{++})_i - (\mathrm{Fe(OH)_2}^{+})_i]} \tag{5}$$

The values of K_1 and K_2 are not well known. Bray and Hershey[5] corrected several equilibria involving ferric ion for hydrolysis by considering the first step only. Although they assumed the second step in the hydrolysis to be negligible, their method is a satisfactory empirical one for correcting ferric ion but not hydrogen-ion concentration. It will be shown later that essentially the same results for ferric ion could have been obtained by including the second step and using a smaller value for K_1. The values given in Table I for K_1 and K_1K_2 were calculated from the values, 0.0250 and 35.2×10^{-4}, respectively, at zero ionic strength by assuming the activity function given by Bray and Hershey.[5] K_1K_2 was obtained from the kinetic data to be described later and K_1 was assumed to have one-quarter of the value obtained by extrapolating the results of Bray and Hershey[5] to 70°.

The values of $2k_3K_1K_2$ calculated from initial rates are given in Table I.

Table I

Evidence for Equation 2 Based on Initial Rates Measured at 70° with Ferric Perchlorate in Excess

Run	$\mu^{1/2}$	γ	a	$2b$	c	S
1	0.64	0.745	0.0544	0.00358	0.1015	0.0318
2	.64	.745	.0544	.00972	.1015	.0246
3	.49	.758	.0272	.00458	.0869	.0186
4	.49	.758	.0272	.01104	.0869	.0119
5	.43	.767	.0137	.00452	.0991	.00600
6	.28	.804	.00656	.00443	.0400	.00680

Run	$K_1 = 0.025$ $(\gamma)^4$	$K_1K_2 \times 10^4 = 35.2$ $(\gamma)^6$	$(\mathrm{FeOH}^{++})_i$	$(\mathrm{Fe(OH)_2}^{+})_i$	$(\mathrm{Fe}^{+++})_i$	$(\mathrm{H}^+)_i$	$2k_3K_1K_2$
1	0.0078	6.0	0.00345	0.00240	0.0485	0.1099	0.0388
2	.0078	6.0	.00345	.00240	.0485	.1097	.0341
3	.0083	6.9	.00210	.00189	.0232	.0927	.0383
4	.0083	6.9	.00210	.00189	.0232	.0927	.0346
5	.0088	7.2	.00102	.00082	.0119	.1017	.0358
6	.0104	9.7	.00090	.00183	.00383	.0446	.0500

It is seen from Table I that equation 2 represents the initial rate of the reaction quite well over an 8-fold variation in ferric ion, a 3-fold variation in stannous ion and 6-fold variation in the square of hydrogen ion. For the expected and observed

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[5] Bray and Hershey, This Journal, **56**, 1889 (1934).

variation of the specific rate, $2k_3K_1K_2$, with ionic strength, see Fig. 7.

In Fig. 3, runs 1–6 are plotted for the entire course of the reaction. Since the main reaction at 70° is

$$3H_2O + 2Fe^{+++} + Sn^{++} \longrightarrow H_2SnO_3 + 2H^+ + 2Fe^{++} \qquad (6)$$

hydrogen ion is produced during the reaction. Therefore the quantity $(c + 2x)/c \log (a - x)/(2b - x)$ is plotted against t rather than the quantity $\log (a - x)/(2b - x)$. The dotted lines in Fig. 3 are the lines that would result if equation 2 were followed over the entire course of the reaction. It is seen that in runs 1 and 3 the dotted line is followed within the experimental error over the entire extent of the reaction. In the other runs the curves slowly deviate from the dotted line and then go through an inflection point and appear to again approach a line whose slope is equal to the slope of the dotted line. The deviation on the positive side of the dotted line at the beginning of the runs is probably due to the fact that the first product is $Sn(OH)_2^{++}$ rather than stannic acid and therefore the calculated hydrogen-ion concentrations in this region are too high; as the run proceeds, $Sn(OH)_2^{++}$ hydrolyzes to stannic acid and toward the end of the reaction the calculated hydrogen-ion concentrations are correct.

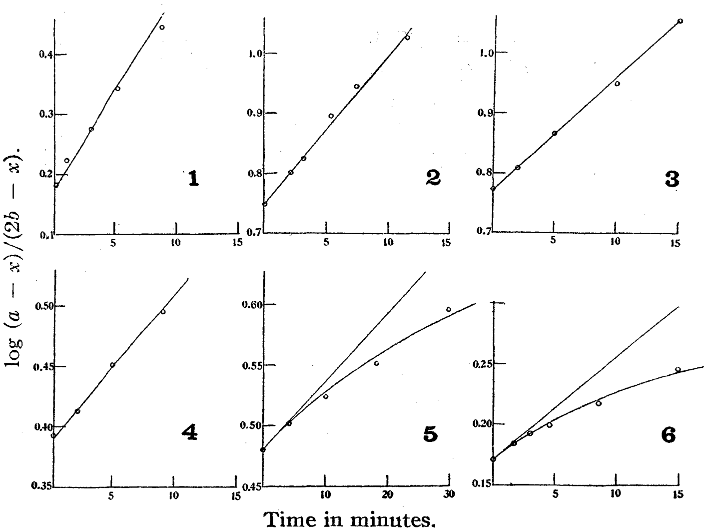

Fig. 2.—Determination of initial rates at 70° in Expts. 1–6: $a - x$ $b - x/2$ are the concentrations in moles per liter of ferric perchlorate and stannous perchlorate at time t.

The appearance of the inflection points in Fig. 3 confirms the theory that the concentration of $Fe(OH)_2^+$ falls below its equilibrium value and then as stannous ion decreases in concentration $Fe(OH)_2^+$ again begins to build up toward equilibrium.

Stannous Ion in Excess at 70°.—In these experiments the rate drops off very quickly from the initial value demanded by equation 2. The results for the entire course of the reaction are plotted in Fig. 4 in the same way as those in Fig. 2; the dotted line represents the initial rate demanded by equation 2. It is seen that the curves very rapidly deviate from the dotted line and appear to approach a straight line. This would correspond to the differential equation

$$\frac{d(Fe^{++})}{dt} = \psi\ (\Sigma Fe^{iii})(Sn^{++}) = \frac{\psi}{2}(a - x)(2b - x) \qquad (7)$$

in the region of the straight line. The quantity, ψ, is of course only a constant within each run and is itself a function of stannous and hydrogen-ion concentrations.

The differential equation

$$\frac{d(Fe^{++})}{dt} = \frac{2k_3K_1K_2(Fe^{+++})(Sn^{++})}{(H^+)^2\,[1 + \chi(Sn^{++})]} \qquad (8)$$

will be applied to the results, where χ of course is a constant. From equations 7, 8, 3 and 4 we obtain the result

$$\chi = \frac{[(2k_3K_1K_2/\psi) - (H^+)[(H^+) + K_1] - K_1K_2]}{(H^+)[(H^+) + K_1](Sn^{++})} \qquad (9)$$

The value of $2k_3K_1K_2$ is taken from the graph in Fig. 7; ψ is calculated from the slopes of the lines in Fig. 4, $\psi = 4.6S/(2b - a)$; χ is calculated for the two points, indicated in each run by the symbols ① and ②. The calculations are presented in Table II.

It is demonstrated in Table II that equation 8 represents the rate quite well for these experiments, which cover a 10-fold variation in (Sn^{++}) and a 20-fold variation in $(H^+)^2$. The variation of χ with ionic strength will be discussed later.

Experimental Results at 55°.—In Fig. 5 the rate measurements at 55° are plotted. In runs 17, 18 and 19 no perchloric acid was added to the reaction mixture and therefore the initial rates could not be used, since small amounts of colloidal ferric hydroxide were present. For this reason the last half of these runs only is presented. In runs 13 and 14 the initial rates were estimated

TABLE II

CALCULATION OF χ AT 70°

Run	$\mu^{1/2}$	S	ψ	$2b - a$	$K_1 \times 10^4$	$K_1K_2 \times 10^4$	$2k_3K_1K_2$
9	0.66	0.00125	0.218	0.0261	78	6.0	0.0376
7	.46	.00262	1.00	.0120	84	7.2	.0386
10	.27	.0109	6.28	.00798	110	10.0	.0436
11	.28	.00635	7.00	.00417	108	9.5	.0432
12	.28	.0161	5.22	.01822	108	9.5	.0432

Run	$(Sn^{++})_1$	$(Sn^{++})_2$	$(H^+)_1$[a]	$(H^+)_2$[a]	$(\chi)_1$	$(\chi)_2$	$(\bar{\chi})$
9	0.0230	0.0191	0.1944	0.2094	149	151	150
7	.0102	.0066	.1131	.1233	173	200	187
10	.0053	.0046	.0457	.0480	242	239	241
11	.0033	.00252	.0492	.0575	235	250	242
12	.0103	.0096	.0430	.0450	210	199	204

[a] Corrected for hydrolysis, $(H^+) = c + 2x + (Fe(OH)^{++}) + 2(Fe(OH)_2^{++})$.

and $2k_3K_1K_2$ calculated by means of equation 2. Equation 2 was also applied to run 17 since (Sn^{++}) is very small. The results are presented in Table III. The values of K_1 and K_1K_2 at 55° were estimated from the temperature coefficients given later.

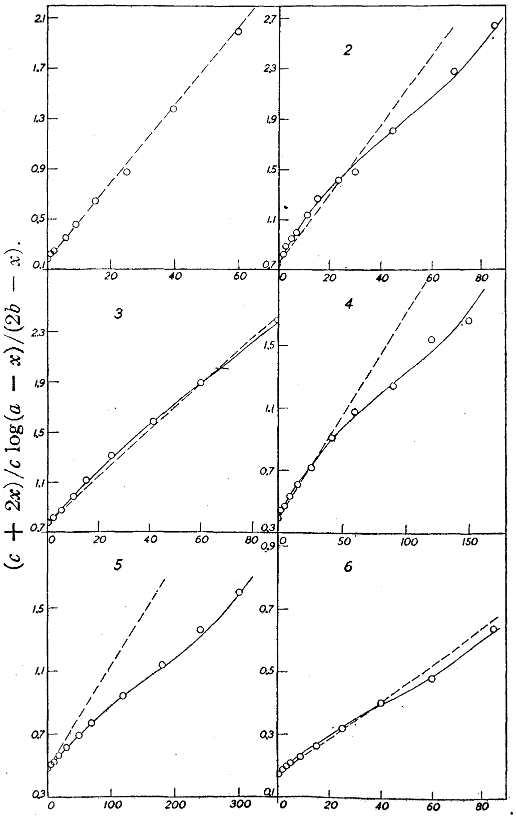

Fig. 3.—Rate measurements in Expts. 1-6, with ferric perchlorate in excess at 70°.

The runs presented in Table III cover a 1500-fold variation in $(H^+)^2$, a 14-fold variation in (Fe^{+++}) and a 6-fold variation in (Sn^{++}), with only a small variation in $2k_3K_1K_2$.

TABLE III

DETERMINATION OF $2k_3K_1K_2$ AT 55°

Run	$\mu^{1/2}$	$\psi \times 10^3$	a	$2b$	c	K_1
14	1.13	1.74	0.0690	0.0292	1.000	0.0039
13	0.54	117.0	.0287	.0287	0.100	.0042
17	0.45	1630.0	.00630	.0051	.0261	.0046

Run	$K_1K_2 \times 10^4$	$(FeOH^{++})_i$	$(Fe(OH)_2^+)_i \times 10^{-6}$	$(Fe^{+++})_i$	$(H^+)_i$	$2k_3K_1K_2$
14	1.05	0.00026	7	0.0687	1.000	0.000175
13	1.20	.00112	340	.0272	0.102	.000129
17	1.31	.00070	700	.0049	.0282	.000168

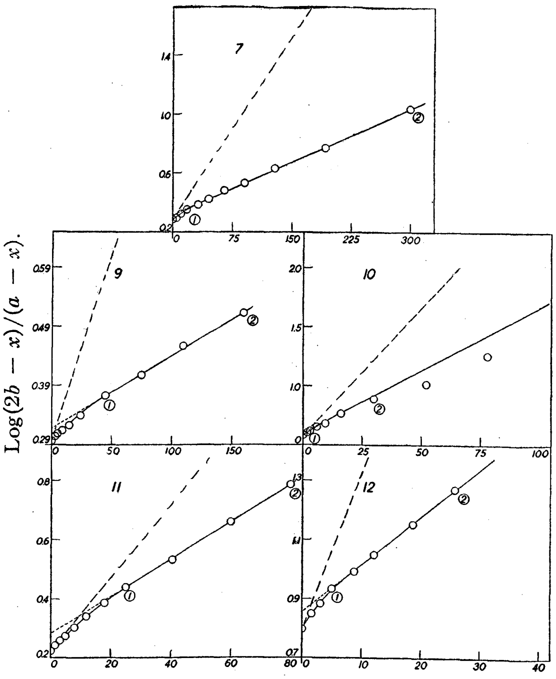

Fig. 4.—Rate measurements with stannous perchlorate in Expts. 7–12 at 70°.

Equation 8 was applied to the latter part of the reaction in the same way as at 70°. The calculations are presented in Table IV; $(\bar{H}^+)$ is the average value of (H^+) in the region through which the points in Fig. 5 fall on a straight line and

TABLE IV

DETERMINATION OF χ AT 55°

Run	$\mu^{1/2}$	K_1	$K_1K_2 \times 10^4$	$2k_3K_1K_2$	$(\bar{H}^+)$	$(\overline{Sn}^{++})$	ψ	χ
18[a]	1.13	0.0039	1.05	0.00180	0.0270	0.0184	0.952	59
14	1.13	.0039	1.05	.00180	1.01	.0121	.00104	61
13	0.54	.0041	1.20	.00150	0.125	.0090	.0504	77
19[a]	0.50	.0041	1.21	.00150	.0258	.0194	.735	93

[a] Runs 18 and 19 are identical except that the reaction mixture in run 18 contained, in addition to 0.0332 M $Fe(ClO_4)_3$ and 0.0323 M $Sn(ClO_4)_2$, 1 M NH_4ClO_4.

$(\overline{\mathrm{Sn}}^{++})$ is defined similarly. The value of $2k_3K_1K_2$ used is taken from Fig. 7. In runs 18 and 19, (H^+) was small and no precipitation of H_2SnO_3 was observed. It was found that one rather than two hydrogen ions were formed per ferric ion produced in these two runs.

Table IV demonstrates that the experimental results at 55° are in good agreement with equation 8 over a 1400-fold change in $(\mathrm{H}^+)^2$.

Interpretation of Results.—The following scheme for the mechanism of the reaction satisfies the experimental results.

Comparatively rapid equilibrium	$\mathrm{Fe^{+++}\cdot 6H_2O} \overset{K_1}{\rightleftharpoons} \mathrm{FeOH^{++}\cdot 5H_2O + H^+} \quad (9)$
Rapid equilibrium	$\mathrm{H_2O} \overset{K_{\mathrm{H_2O}}}{\rightleftharpoons} \mathrm{H^+ + OH^-} \quad (10)$
Slow equilibrium	$\mathrm{OH^- + FeOH^{++}\cdot 5H_2O} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fe(OH)_2{}^+\cdot 4H_2O + H_2O} \quad (11)$
Slow follow reaction	$\mathrm{Sn^{++} + Fe(OH)_2{}^+\cdot 4H_2O} \xrightarrow{k_3} \mathrm{Fe^{++}\cdot 4H_2O + Sn(OH)_2{}^+} \quad (12)$
Rapid follow reaction	$\mathrm{Fe^{+++}\cdot 6H_2O + Sn(OH)_2{}^+ = Fe^{++}\cdot 4H_2O + Sn(OH)_2{}^{++}} \quad (13)$
Main reaction at 55° and low (H^+) is (9) + (10) + (11) + (12) + (13)	$\mathrm{2Fe^{+++}\cdot 6H_2O + Sn^{++} = 2Fe^{++}\cdot 4H_2O + Sn(OH)_2{}^{++} + H_2O + 2H^+} \quad (14)$
Slow follow reaction	$\mathrm{Sn(OH)_2{}^{++} + H_2O = H_2SnO_3 + 2H^+} \quad (15)$
Main reaction at 70° under all conditions and at 55° at high hydrogen-ion concentration, (14) + (15)	$\mathrm{2Fe^{+++}\cdot 6H_2O + Sn^{++} = 2Fe^{++}\cdot 4H_2O + H_2SnO_3 + 4H^+} \quad (16)$

In the most general case the concentration of $\mathrm{Fe(OH)_2{}^+}$ is not negligible and therefore it is not possible to postulate a steady state between reactions 11 and 12. Therefore the following pair of differential equations results

$$\mathrm{d(Fe(OH)_2{}^+)/d}t = k_1(\mathrm{FeOH^{++}})(\mathrm{OH^-}) - (\mathrm{Fe(OH)_2{}^+})\,[k_2 + k_3(\mathrm{Sn^{++}})]$$

$$\mathrm{d(Fe^{++})/d}t = 2k_3(\mathrm{Fe(OH)_2{}^+})(\mathrm{Sn^{++}})$$

or

$$\mathrm{d(Fe(OH)_2{}^+)/d}t = k_1K_1K_{\mathrm{H_2O}}(\mathrm{Fe^{+++}})/(\mathrm{H^+})^2 - (\mathrm{Fe(OH)_2{}^+})\,[k_2 + k_3(\mathrm{Sn^{++}})] \tag{17}$$

$$\mathrm{d(Fe^{++})/d}t = 2k_3(\mathrm{Fe(OH)_2{}^+})(\mathrm{Sn^{++}}) \tag{18}$$

If, however, $\mathrm{Fe(OH)_2{}^+}$ is at equilibrium with $\mathrm{FeOH^{++}}$ and hydrogen ion, as is the case at the start of the reaction, equations 17 and 18 become equation 2

$$\mathrm{d(Fe^{++})/d}t = 2k_3K_1K_2(\mathrm{Fe^{+++}})(\mathrm{Sn^{++}})/(\mathrm{H^+})^2$$

since

$$k_1K_{\mathrm{H_2O}}/k_1 = K_2 = (\mathrm{Fe(OH)_2{}^+})(\mathrm{H^+})/(\mathrm{FeOH^{++}}) \tag{19}$$

In the experiments with stannous ion in excess $\mathrm{Fe(OH)_2{}^+}$ is changing very rapidly while the first 15 or 20% of the reaction occurs. After this initial period, the rate appears to follow the differential equation 8. This indicates that the concentration of $\mathrm{Fe(OH)_2{}^+}$ must be approaching some kind of "steady state." The ordinary steady state postulate, $\mathrm{d(Fe(OH)_2{}^+)/d}t = 0$ for two compensating reactions involving an intermediate, would involve appreciable error in some of the experiments, since it is evident that a considerable portion of the ferric salt is present in the form of $\mathrm{Fe(OH)_2{}^+}$ even at the "steady state stage" of the reaction. It was discovered that another steady state condition could be postulated which involves very much less error. This postulate is that

$$\mathrm{d(Fe^{++})/{-d}(Fe(OH)_2{}^+)} = 0$$

and leads to the equation

$$\frac{-\mathrm{d(Fe(OH)_2{}^+)}}{\mathrm{d}t} = \frac{1}{2}\,\frac{(\mathrm{Fe(OH)_2{}^+})}{(\Sigma\mathrm{Fe^{iii}})}\,\frac{\mathrm{d(Fe^{++})}}{\mathrm{d}t} = \frac{1}{2}\,\alpha\,\frac{\mathrm{d(Fe^{++})}}{\mathrm{d}t} \tag{20}$$

Applying equation 20 to equations 17 and 18, we obtain

$$(\mathrm{Fe(OH)_2{}^+}) = \frac{K_1K_2(\mathrm{Fe^{+++}})}{(\mathrm{H^+})^2[1 + (1 + \alpha)(k_3/k_2)(\mathrm{Sn^{++}})]} \tag{21}$$

and

$$\frac{\mathrm{d(Fe^{++})}}{\mathrm{d}t} = \frac{2k_3K_1K_2(\mathrm{Fe^{+++}})(\mathrm{Sn^{++}})}{(\mathrm{H^+})^2\,[1 + (1 + \alpha)(k_3/k_2)(\mathrm{Sn^{++}})]} \tag{22}$$

Equation 22 is identical with equation 8 and therefore $\chi = (1 + \alpha)\ (k_3/k_2)$. Knowing χ we can easily calculate α from equation 21 and therefore k_3/k_2.

$$\alpha = \frac{(\mathrm{Fe(OH)_2{}^+})}{(\Sigma\mathrm{Fe^{iii}})} = \frac{K_1K_2}{K_1K_2 + (\mathrm{H^+})(\mathrm{H^+} + K_1)[1 + \chi\,\mathrm{Sn^{++}}]} \tag{23}$$

These calculations are given in Table V for the experiments at 70° (see Table II) with stannous in excess.

It is seen that the maximum correction in Table V is about 15%. This is probably smaller than the experimental error (small errors in ψ are greatly magnified in χ). However, it is of inter-

Table V

Calculation of k_3/k_2 at 70°

Run	$(\mu)^{1/2}$	α_1	α_2	χ_1	χ_2	$\frac{(k_3)}{k_2}$	$\frac{(k_3)}{{}_1k_{2\,2}}$	$\frac{(\bar{k}_3)}{k_2}$	$\frac{(\mathrm{FeOH^{++}})}{(\mathrm{Fe(OH)_2^+})}$
9	0.66	0.0035	0.0035	149	151	149	151	150	10.6
7	.46	.0186	.0187	173	200	170	197	184	3.49
10	.27	.145	.144	242	239	211	208	210	1.03
11	.28	.156	.154	234	250	202	216	209	0.94
12	.28	.115	.115	210	199	188	179	184	1.52

est to consider this analysis and to point out its great accuracy as demonstrated by the constancy of α over the whole "steady state region" of each run.

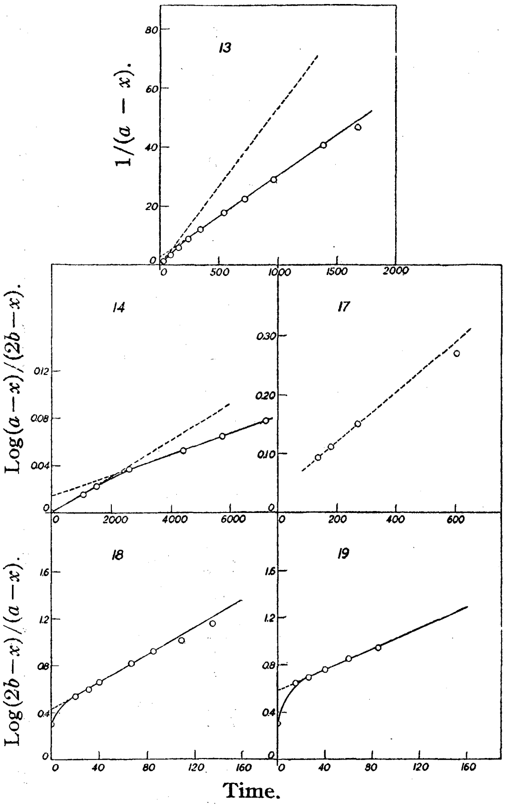

Fig. 5.—Rate measurements at 55°, Expts. 13–19.

Calculation of $\mathbf{K_1K_2}$.—In the initial part of the experiments with stannous perchlorate in excess the concentration of $Fe(OH)_2^+$ is changing much more rapidly than that of ferric ion and therefore the concentration of ferric ion may be assumed to be constant in this region. If this assumption is made equations 17 and 18 may be integrated, and the following result

$$(y - y_0) = \bar{A}t - {}^1/_2x - 2.303(\mathrm{d}t/\mathrm{d}x)^0A^0(2b)\log(2b)(2b - x) \qquad (24)$$

and

$$y = y_0(\mathrm{d}x/\mathrm{d}t)(\mathrm{d}t/\mathrm{d}x)^0\,(2b)/(2b - x) \qquad (25)$$

where $y = (\mathrm{Fe(OH)_2^+})$ and $x = (\mathrm{Fe^{++}})$ at time equals t, y_0 is initial value of y

$$A_0 = \frac{k_1K_{\mathrm{H_2O}}K_1(\mathrm{Fe^{+++}})}{(\mathrm{H^+})^2} = \frac{2k_3K_1K_2}{2(k_3/k_2)}\,\frac{(\mathrm{Fe^{+++}})}{(\mathrm{H^+})^2}$$

at $t = 0$ and $\bar{A} = A^0(a - x)/a$. If x, t and $(\mathrm{d}x/\mathrm{d}t)$ are known, y_0 may be calculated, since $2k_3K_1K_2$, k_3/k_2 and therefore $(\mathrm{d}x/\mathrm{d}t)_0$ are known.

In Fig. 6 x is plotted against t for the first three experimental points in two runs, nos. 7 and 9. A smooth curve was drawn from the origin, using the initial slope calculated from equation 2 (or 5) as a guide. Three points were chosen on the smooth curve, and $(\mathrm{d}x/\mathrm{d}t)$ was determined at each point by estimating the tangent to the curve. The points chosen are marked by the symbol +; the experimental point by the symbol 0 and the estimated tangents by the dotted lines.

It is seen that equations 24 and 25 do not involve K_1 and K_2 directly, but of course these constants are involved in calculating the initial rate, $(\mathrm{d}x/\mathrm{d}t)_0$. However, it is to be noted that the experimental value of $2k_3K_1K_2$ depends upon the choice of K_1 and K_2. Actually, it was found that the value of y_0 from equations 24 and 25 was very slightly dependent upon the choice of K_1 and K_2 and therefore the resulting value of $2k_3K_1K_2$. The calculations presented in Table VI were made using the values of K_1 and K_1K_2 assumed in Table I and of course the resulting value of $2k_3K_1K_2$ from Fig. 7 ($K_1^0 = 0.025$ $K_1^0K_2^0 = 35.2 \times 10^{-4}$).

The constancy of y_0 for the three points in each run in Table VI demonstrates that equations 24 and 25 are good representations of the initial portion of the reaction. Furthermore, the values of y_0 are in good agreement with those calculated and therefore it is demonstrated that the value of K_1K_2 chosen is the experimental value within the experimental error.

Actually of course the value of K_1K_2 assumed in Table I was the experimental value found from equations 24 and 25, but a complete logical presentation of the calculations was avoided in order to save space.

Variation with Ionic Strength and Temperature Coefficients.—By combining the Debye–Hückel theory and the Brönsted theory the following relationships result, as $\mu^{1/2} \longrightarrow 0$

$$\log_{10} K_1 = \log_{10} K_1^0 - 2.0\mu^{1/2} \qquad (26a)$$
$$\log_{10} K_1K_2 = \log_{10} K_1^0K_2^0 - 3.0\mu^{1/2} \qquad (26b)$$
$$\log_{10} 2k_3K_1K_2 = \log_{10} 2k_3^0K_1^0K_2^0 - 1.0\mu^{1/2} \qquad (26c)$$
$$\log_{10} (k_2/k_3) = \log_{10} (k_3^0/k_2^0) + 2.0\mu^{1/2} \qquad (26d)$$

TABLE VI

DETERMINATION OF INITIAL CONCENTRATION OF $Fe(OH)_2^+$ IN TWO RUNS

(a) Calculation of A^0 and $(dx/dt)_0$

Run	$\mu^{1/2}$	a	$2b$	c	$(FeOH^{++})_i$[a]	$(Fe(OH)_2^+)_i$[a]	$(Fe^{+++})_i$	$(H^+)_i$	$A^0 \times 10^4$	$\left(\frac{dx}{dt}\right)_0 10^4$
9	0.66	0.0268	0.0532	0.177	0.00110	0.00046	0.0252	0.179	0.842	7.84
7	.46	.01265	.02486	.1015	.00083	.00072	.0110	.1037	1.20	4.93

[a] For K_1, K_1K_2 and $2k_3K_1K_2$ see Table II.

(b) Presentation of Data

t	x	$\frac{dx}{dt} \times 10^4$	$a - x$	$2b - x$	$\bar{A} \times 10^5$	$y - y_0$	y/y^0	y_0
Run 9								
2	0.00069	2.70	0.0261	0.05251	8.33	0.00029	0.33	0.00044
4	.00114	1.72	.0257	.05206	8.25	.00036	.22	.00046
6	.00149	1.60	.0254	.05171	8.20	.00041	.20	.00051
Run 7								
5	.00132	1.80	.01133	.02354	11.3	.00043	.40	.00072
10	.00211	1.40	.01054	.02275	11.0	.00049	.31	.00071
20	.00343	1.20	.00922	.02148	10.3	.00055	.29	.00078

However, all of the experimental results are in a region of ionic strength where equations 26 cannot be expected to apply. Instead the method of Randall[6] was used. Applying this method, it follows

$$-{}^1/_4 \log K_1 = -{}^1/_4 \log K_1^0 + f(\gamma) \quad (27a)$$
$$-{}^1/_6 \log K_1K_2 = -{}^1/_6 \log K_1^0K_2^0 + f(\gamma) \quad (27b)$$
$$-{}^1/_2 \log 2k_3K_1K_2 = -{}^1/_2 \log 2k_3^0K_1^0K_2^0 + f(\gamma) \quad (27c)$$
$${}^1/_4 \log (k_3/k_2) = {}^1/_4 \log (k_1^0/k_2^0) + f(\gamma) \quad (27d)$$

where $f(\gamma)$ may be represented by some one of the family of log γ curves for single electrolytes. For K_1 and K_1K_2 the same $f(\gamma)$ was used as that given by Bray and Hershey[5] in Table I, page 1890.

In Fig. 7 the quantities $^1/_2$ log $2k_3K_1K_2$ at 70°, and $^1/_2$ log $2k_3K_1K_2 + 0.7$ at 55°, are plotted against $\mu^{1/2}$. The curve that seemed to fit best is one somewhere between the curve chosen by Bray and Hershey[5] for ferric equilibria and the curve for hydrochloric acid. It can be said that all the points except the one at the lowest ionic strength fit the curve within the experimental error. The 20% deviation of this point from the curve might be attributed to small amounts of colloidal ferric hydroxide.

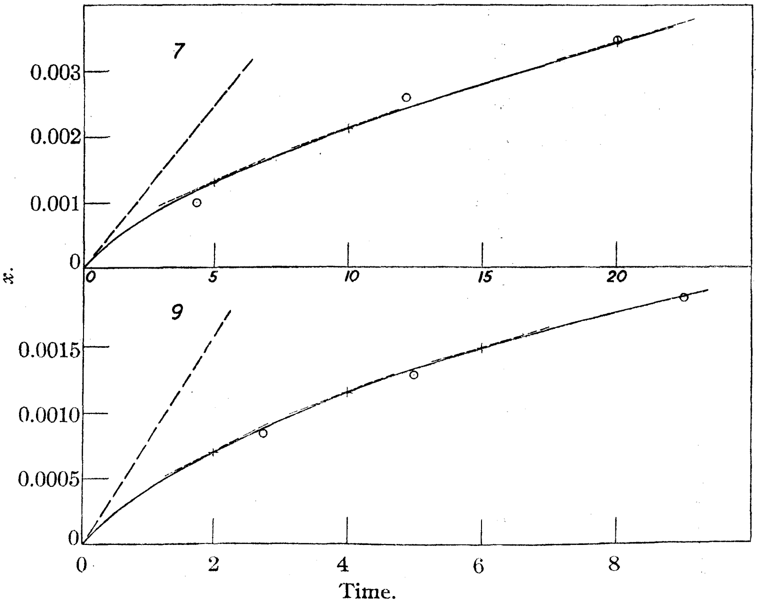

Fig. 6.—Determination of equilibrium concentration of $Fe(OH)_2^+$ in two experiments, nos. 7 and 9.

In Fig. 8, $-{}^1/_4$ log k_3/k_2 at 70° and $-{}^1/_4$ log $k_3/k_2 - 0.087$ at 55°, are plotted against $\mu^{1/2}$. The curve is the same one used in Fig. 7 and is purposely drawn through the points at the higher ionic strengths. The failure of the three points at the lowest ionic strength to reach the curve can be attributed to inaccuracies in the ionic strength functions used, since small errors in K_1K_2, K_1, and especially in $2k_3K_1K_2$, will cause larger errors in k_3/k_2.

Using the extrapolations in Figs. 7 and 8 the following values are obtained for $2k_3^0K_1^0K_2^0$ and k_3^0/k_2^0 at 70 and 55°.

$2k_3^0K_1^0K_2^0$ at 70° is 0.0660 and at 55° is 0.00262, therefore ΔH = 48,600 calories; k_3^0/k_2^0 at 70° = 58 and at 55° = 25.7, ΔH = 12,300 calories.

The quantities in bold figures in Table VII can

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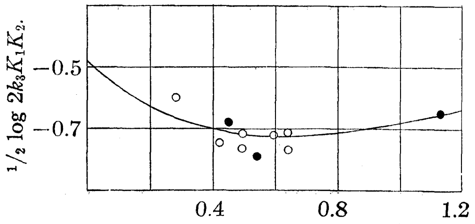
(6) See Refs. 5 and 6(a), Randall and Vietti, THIS JOURNAL, **50**, 926 (1928); (b) Randall, *J. Chem. Educ.*, **8**, 1062 (1931); (c) unpublished results.

be calculated without knowing ΔH for K_1K_2 and K_1; those in italics depend upon the choice of ΔH for K_1K_2 and K_1, 2 × 12,650 and 12,650, respectively.



Square root of the ionic strength.

Fig. 7.—Variation of $2k_3K_1K_2$ with ionic strength: ○, at 70°; ●, at 55°, $^1/_2 \log (2k_3K_1K_2) + 0.7$.

The values assumed for ΔH_{K_1} and $\Delta H_{K_1K_2}$ depend upon the following: Bray and Hershey[5] would have obtained essentially the same result if they had used a smaller value of K_1 and taken the second step of the hydrolysis into consideration. There are two reasons for this: the first is that the equilibria they were considering did not involve hydrogen ion, and the second that K_1 decreases more rapidly than K_2 with ionic strength. The kinetic value which was obtained at 70° for K_1K_2 was extrapolated to 25° by using Bray and Hershey's value[5] for ΔH_{K_1}, 12,650, and assuming that $\Delta H_{K_1K_2} = 2\Delta H_{K_1}$. It was found that the value obtained for K_1K_2 at 25°, 13.0×10^{-6}, taken together with a value for K_1, one-quarter of that used by Bray and Hershey,[5] will give approximately the same results as those obtained by Bray and Hershey.[5]

TABLE VII

TEMPERATURE COEFFICIENTS

	70°	55°	ΔH
$2k_3K_1K_2$	660×10^{-4}	26.2×10^{-4}	48,600
k_3/k_2	58	25.7	12,300
$K_1k_1K_{H_2O}$	568×10^{-6}	50.9×10^{-6}	36,300
K_{H_2O}	2×10^{-11}	8.12×10^{-12}	13,200
K_1k_1	284×10^{5}	63×10^{5}	23,100
K_1K_2	35.2×10^{-4}	$\mathit{6.5 \times 10^{-4}}$	*(25,400)*
k_3	9.4	*2.01*	*23,200*
k_2	0.162	*0.0783*	*10,900*
K_1	*(0.025)*	*0.0106*	*(12,650)*
k_1	$\mathit{11.4 \times 10^{8}}$	$\mathit{5.9 \times 10^{8}}$	*10,400*

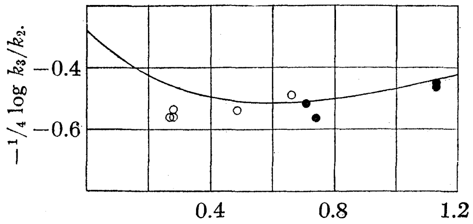
Discussion of Results.—It is considered by the author that the following have been definitely established in perchlorate solutions: (1) the rate determining step for the reduction of the ferric salt is

$$Fe(OH)_2{}^+ \cdot 4H_2O + Sn^{++} \longrightarrow$$

and (2) the mechanism for the reactions involved in the equilibrium

$$FeOH^{++} + H_2O \rightleftarrows Fe(OH)_2{}^+ + H^+$$

is the one given by equation 11. All alternative formulations to the two above that were tried failed to explain one or more portions of the experimental data.



Square root of the ionic strength.

Fig. 8.—Variation of k_3/k_2 with ionic strength at 70°: ○, at 70°; ●, at 55°, $-^1/_4 \log (k_3/k_2) - 0.087$.

The most plausible explanation of the failure of ferric and stannous ions to react directly is that ions of like and multiple charges cannot approach each other closely enough to cause reaction unless their relative kinetic energy is very high. This minimum kinetic energy is estimated to be, at the very least, 15,000 calories. If it is assumed that the ordinary chemical heat of activation for ferric plus stannous is the same as for $Fe(OH)_2{}^+$ plus stannous, then the ratio of the rates at 70° will be less than

$$e^{-15,000/(343 \times 1.986)} = 3 \times 10^{-10}$$

The products of the rate determining step, equation 1, were assumed in equation 12 to be 2-valent iron and 3-valent tin, rather than 1-valent iron and 4-valent tin. There is no evidence for the existence of univalent iron and Ball[7] and co-workers have recently published evidence for the existence of trivalent tin as an intermediate.

The mechanism of the reactions involved in the hydrolysis of $FeOH^{++} \cdot 5H_2O$ was demonstrated to be

$$FeOH^{++} \cdot 5H_2O + OH^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} Fe(OH)_2{}^+ \cdot 4H_2O + H_2O$$

the replacement of water by hydroxide ion and the replacement of hydroxide ion by water. This replacement mechanism is analogous to the theory of Olson[8] for organic substitution reactions. It differs from the one generally assumed for the hydrolysis of hydrated metallic ions

$$FeOH^{++} \cdot 5H_2O \longrightarrow Fe(OH)_2{}^+ \cdot 4H_2O + H^+$$

a simple splitting off and addition of a proton.

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[7] Ball, Wulfkuehler and Wingard, THIS JOURNAL, **57**, 1729 (1935).

[8] Olson, *J. Chem. Phys.*, **1**, 418 (1933).

In conclusion I wish to express my gratitude to Professor William C. Bray for his advice and suggestions during the progress of the work.

Summary

Rate measurements are presented for the reaction between ferric and stannous perchlorates in solutions containing perchloric acid at 70 and 55°. The rate is much slower than when chloride ion is present.

There is no evidence for a direct reaction between ferric ion and stannous ion. The failure of the two ions to react at an appreciable rate is attributed to the high repulsive forces between these polyvalent, positive ions.

The experimental results are in agreement with the theory that the rate determining step for the reduction of the ferric salt is

$$Fe(OH)_2^+ + Sn^{++} \xrightarrow{k_3} \qquad (1)$$

When the hydrolysis equilibria

$$Fe^{+++} + H_2O \overset{K_1}{\rightleftarrows} FeOH^{++} + H^+ \qquad (3)$$

and

$$FeOH^{++} + H_2O \overset{K_2}{\rightleftarrows} Fe(OH)_2^+ + H^+ \qquad (4)$$

are maintained the rate law is

$$d(Fe^{++})/dt = 2k_3K_1K_2(Fe^{+++})(Sn^{++})/(H^+)^2 \qquad (2)$$

This law represents the initial rate in all experiments and applies throughout when the concentration of ferric ion is high compared to that of stannous ion. The specific rate, $2k_3K_1K_2$, is 660 $\times 10^{-4}$ at 70° and 26.2 $\times 10^{-4}$ at 55°.

A study of the deviations from equation 2 led to the conclusions that reaction 4 is not rapid compared to Reaction 1 and that the mechanism of reaction 4 is

$$\text{Rapid equil. } H_2O \overset{K_{H_2O}}{\rightleftarrows} H^+ + OH^-$$

$$\text{Slow equil. } OH^- + Fe(OH)_2^{++}\cdot 5H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} Fe(OH)_2^{+}\cdot 4H_2O + H_2O$$

The study resulted in the determination of the product, K_1K_2, at 70° and the ratio, k_3/k_2 at 70° and 55°. Combination with the value of the specific rate, $2k_3K_1K_2$, gave the following values at 70°: $K_1K_2 = 35.2 \times 10^{-4}$, $k_3 = 9.4$ and $k_2 = 0.162$.

While neither of the hydrolysis quotients, K_1 nor K_2, has been determined directly, values of each have been chosen which are consistent with the above results and with available data for the hydrolysis of ferric ion. The resulting values of the various equilibrium quotients and specific rates at 70 and 55° are listed in Table VII. Concentrations are expressed in moles per liter and time intervals in minutes.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Activation of Specific Bonds in Complex Molecules at Catalytic Surfaces. II. The Carbon–Hydrogen and Carbon–Carbon Bonds in Ethane and Ethane-*d*

BY KIYOSHI MORIKAWA,[1] W. S. BENEDICT AND HUGH S. TAYLOR

The activation of the carbon–hydrogen and carbon–carbon bonds in ethane at nickel catalyst surfaces can be studied with the aid of deuterium since two reactions may be examined: (a) the exchange reaction which may be generalized as $C_2H_xD_y + D_2 = C_2H_{x-1}D_{y+1} + HD$ in which $x + y = 6$ and y may have any integral values from 0 to 5; and (b) the methane producing reaction $C_2H_6 + H_2 = 2CH_4$. The former reaction involves the C–H bond, the latter the C–C bond. Deuterium permits these reactions to be studied when they are occurring simultaneously on a given catalyst under given conditions of temperature and pressure. During the course of this work, also, investigation was made of the kinetics of methane formation from ethane and hydrogen, the data providing interesting aspects of the mechanism of activation of the ethane at nickel surfaces.

Experimental Details

Materials.—Electrolytic hydrogen and deuterium from the electrolysis of ordinary and heavy water ($d^{25}_{25} = 1.1079$) were employed. Ethane was produced catalytically from ethylene and hydrogen over a nickel catalyst at room temperature. It was purified by combustion of the excess hydrogen over copper–copper oxide, followed by fractional distillation to remove nitrogen and methane present.

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The comparison of exchange reaction and methane formation was conducted by a dynamic method in which the gas mixtures $C_2H_6 + D_2(H_2)$ were slowly passed backward and forward over a nickel catalyst supported on kieselguhr. Vapor baths were employed for temperature control. The catalyst was similar to that described in Part I of this series,[2] and was protected against mercury vapor by two traps at −78°. The kinetic studies were made in a static system.

Analytical Procedure.—The progress of the exchange reaction was again followed by infra-red absorption measurements of the C–H and C–D bonds as already described.[2,3] The formation of methane was followed by combustion of the hydrogen over copper–copper oxide at 300°. From the data thus obtained, the volume of hydrogen consumed in the reaction could be checked against the increase in hydrocarbon volume. This double check was occasionally further confirmed by fractional extraction of methane from ethane at liquid air temperature. The accuracy attainable may be illustrated by expt. 27. In this experiment 19.6 cc. of C_2H_6 and 20.4 cc. of H_2 were treated for one hour in contact with 2.0 g. of nickel catalyst at 184° to give a final volume of 39.7 and 26.2 cc. of residual hydrocarbon. Calculating from the hydrogen decrease 13.8 cc. of CH_4 was formed. From the hydrocarbon increase 13.2 cc. was formed. Fractionation of the residual hydrocarbon gave >12.1 cc. of methane and <14.1 cc. of ethane, the latter certainly still containing some dissolved methane. It was found that methane dissolved readily in and was persistently retained by the condensed higher hydrocarbon. The larger the methane content the easier and more accurate was the fractionation.

Experimental Results

Comparison of Exchange Reaction and Methane Formation.—The data of Tables I and II represent the measurements made by the dynamic method to effect this comparison, the same nickel catalyst, 2.5 g., being used for both sets of data.

TABLE I

THE REACTION $C_2H_6 + H_2 = 2CH_4$

Expt.	C_2H_6, cc.	H_2, cc.	Temp., °C.	Time, hrs.	Conversion % C_2H_6 reacted
4	20.9	21.0	110	1	0
11	25.9	28.5	157	3	11.9
9	24.8	26.4	172	1	19.3
10	22.9	25.4	184	1	92
5	21.8	22.5	184	1	73.2
2	22.4	22.5	302	1	100

These results show that the exchange reaction becomes, under the given conditions, quite marked already at 110° whereas methane formation only becomes appreciable around 150° and is fast at 180°. There is therefore about 60° difference in temperature, on this catalyst, between comparable activations of the C–H and C–C bonds in ethane. The data of Table II also suggested the following method of preparation of C_2D_6.

TABLE II

THE EXCHANGE REACTION $C_2H_xD_y + D_2 = C_2H_{x-1}D_{y+1} + HD$

Expt.	C_2H_6, cc.	D_2, cc.	Temp., °C.	Time, hrs.	C–D Bond % equilibrium
12	22.1	44.4	25	22	0
13	21.4	43.1	110	2.5	33
8	25.6	52.3	138	2.5	100
7	22.7	41.5	302		0[a]

[a] This experiment was conducted in presence of Cu–CuO at 302° to show that the hydrogen removal during analysis did not effect exchange.

Preparation of Ethane-*d*$_6$.—Two grams of nickel catalyst was reduced at 450° for five and a half hours and then evacuated for two hours. At 0°, 22.2 cc. of C_2H_4 and 50.4 cc. of D_2 were introduced to the catalyst and when hydrogenation was complete the temperature was raised to 138° and there maintained for two and a half hours. The hydrogen–deuterium was then removed by combustion at 275° and next the partially deuterized ethane was subjected to the same procedure, each time with twice its volume of pure deuterium, for seven successive treatments. If the equilibrium constant is approximately 1 and the equilibrium is established in each treatment the final ethane should have been ~99% C–D. This was actually found to be the case by infra-red measurements. The recovered C_2D_6 had a volume of 22 cc. and the methane formed throughout the experiment was 0.27 cc. The C_2D_6 had a negligible vapor pressure at liquid air temperatures. We shall report elsewhere some of the physical properties of this product.

The Kinetics of the Reaction $C_2H_6 + H_2 = 2CH_4$.—The data of Table III record the results of static experiments on 1 g. of nickel catalyst at 172 and 184° in a reaction space of 125 cc. with 3 cc. dead space for the dry ice traps. The experiments were so conducted that, at each stage, the hydrogen, removed by combustion for analytical purposes, was replaced by an equal volume of hydrogen and the next stage followed. The data are all recorded as pressures of gas in mm. at a constant volume of 88 cc. corrected to 25°.

Comparison of expts. 2a and 3 indicates that the activity of the catalyst is constant and that the trend upward in conversion per hour as the re-

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(2) Morikawa, Benedict and Taylor, THIS JOURNAL, 58, 1445 (1936).

(3) Benedict, Morikawa, Barnes and Taylor, *J. Chem. Phys.*, forthcoming publication.

TABLE III

THE REACTION $1C_2H_6 + 1H_2 = 2CH_4$

Expt.	Temp., °C.	Initial pressure, mm. Total	C_2H_6	H_2	CH_4	Time interval, hrs.	Final pressure, mm. Total	H.C.	+ΔH.C.	$-\Delta H_2$	$-\Delta P_{C_2H_6}$, % per hr.
1a	172	349.6	174.4	175.2	0	0–1.5	345.7	182.0	7.6	11.5	2.9
b	172	364.3	166.8	182.4	15.2	1.5–3	364.1	189.0	7.0	7.3	2.7
c	172	355.5	159.8	166.5	29.2	3–6.2	355.1	202.1	13.1	13.5	2.4
d	172	355.1	136.7	152.9	75.4	6.2–16.2	355.7	250.4	48.3	47.6	2.8
e	172	353.8	98.4	103.4	152.0	16.2–18.2	352.5	263.3	12.9	14.2	3.7
f	172	354.5	84.8	91.1	179.2	18.2–20.7	353.9	281.6	18.3	18.8	4.2
2a	184	352.3	175.5	176.8	0	0–1	351.5	193.5	18.0	18.8	10.3
b	184	351.8	157.5	158.3	36.0	1–3	350.7	232.0	38.5	39.6	11.0
c	184	353.3	119.0	121.3	113.0	3–4	352.2	257.4	25.4	26.5	14.5
3	184	351.8	175.8	176.0	0	0–1	350.7	193.6	17.8	18.9	10.1

TABLE IV

THE REACTIONS $xC_2H_6 + yH_2$ AT 184°

Expt.	Ratio $C_2H_6:H_2$	Initial pressure, mm. Total	C_2H_6	H_2	CH_4	Time, hrs.	Final pressure, mm. Total	H.C.	+ΔH.C.	$-\Delta H_2$	$-\Delta P_{C_2H_6}$, % per hr.
1	2:1	267.3	176.2	91.2	0	1.1	301.2	298.6	122.4	88.6	63.2
2a	2:1	264.9	175.4	89.6	0	0.33	236.4	209.0	33.6	62.2	63.7
b	2:1	235.8	141.8	26.8	67.2	.67	264.2	...	..	..	..
3a	1:2	264.0	87.9	176.1	0	2.0	245.9	102.2	14.3	32.4	8.1
b	1:2	248.3	73.6	146.1	28.6	1.0	247.6	103.8	1.6	2.3	1.8
c	1:2	250.1	72.0	146.3	31.8	3.0	248.1	106.0	2.2	4.2	0.8
4	1:2	269.8	84.5	185.3	0	15.5	268.1	90.0	5.5	7.2	.4
5	3:2	289.0	174.7	114.3	0	0.5	289.5	182.8	8.1	7.6	9.2
6	3:2	290.6	175.8	114.8	0	.5	289.4	182.7	6.9	8.1	7.9
7	2:1	263.2	176.1	87.1	0	.33	262.8	184.1	8.0	8.4	15.2

action proceeds is real and is to be ascribed to the reasonable assumption that hydrogen is strongly adsorbed but the hydrocarbons only weakly. As the hydrogen is consumed more of the surface becomes accessible to activated adsorption of the hydrocarbons. This conclusion is supported by the following data with varying ratios of hydrogen to ethane. The concordance between the data of the two columns +ΔH.C. and $-\Delta H_2$ save in expt. 1a indicates also the absence of any side reactions, which is not true with other ratios of reactants (*vide infra*). The apparent activation energy of the reactants calculated from the data at the two temperatures gives $E_{\text{app.}} \sim 43$ kcal.

In Table IV are recorded experiments with $1C_2H_6 + 0.5\ H_2$, $1C_2H_6 + 2H_2$ and $1C_2H_6 + 0.69H_2$.

All the experiments recorded in this Table IV were done successively on one catalyst. The comparison of expts. 1 and 2 with a gas ratio of $2C_2H_6{:}1H_2$ with expts. 2 and 3 of Table III where the ratio is 1:1 indicates that increase of hydrogen ratio severely reduces the reaction rate. Calculations from the data 2a and 3a of Table III and 1 and 2 of Table IV and from the data of expts. 5, 6, 7 of this latter table would indicate an effect of hydrogen proportional to $\sim P_{H_2}{}^{-2.5}$. We shall discuss this later. Comparison of expts. 1 and 2 of Table IV with the subsequent experiments of this table at other ratios indicates that during expts. 1 and 2 the nickel catalyst suffered a considerable degree of poisoning leading to abnormally low conversions in expts. 3–7. A critical analysis of the data of the table reveals that the poisoning is due to carbon deposition. In addition to the reaction forming methane (1) $C_2H_6 + H_2 = 2CH_4$ there are occurring simultaneously reactions which may be represented by the over-all equations (2) $2C_2H_6 = C + 3CH_4$ and (3) $C + 2H_2 = CH_4$. These conclusions may be reached especially from a comparison of the columns recording initial and final pressures, *i. e.*, ΔP_{total} and those recording increase of hydrocarbon +ΔH.C. and decrease of hydrogen pressure $-\Delta H_2$. Thus, in expt. 1a of Table IV, the recovered gas exceeds the amount introduced by 33.9 mm. and the increase in hydrocarbon is 122.4 mm. The increase of hydrocarbon due to reaction (1) with hydrogen is not less than 88.6 mm., which leaves 122.4 − 88.6 =

TABLE V

DECOMPOSITION OF ETHANE ON NICKEL AT 218°

Expt.	Initial $P_{C_2H_6}$, mm.	Time, hrs.	Final pressure, mm. Total	+ΔP	H.C.	+ΔH.C.	+H_2	CH_4	C_2H_6	CO_2 from combustion of C_2H_6 fraction
1a	169.4	10.3	186.2	16.8	184.9	15.5	1.3	50.7	136.2	260.5
b	159.7	57	184.6	24.9	183.4	23.7	1.3	76.4	108.5	205.3

33.8 mm. increase coming from reaction (2). This corresponds to a decomposition according to (2) of 67.6 mm. ethane, and therefore to carbon deposition on the surface equivalent to ~33.8 mm. In expt. 2a the recovered gas is less than the initial by 28.5 mm. Of the hydrogen consumed some 57 mm. must have reacted in the main with the previously deposited carbon to give 28.5 mm. methane. This leaves only 5.2 mm. hydrogen to react with an equivalent of ethane to give a further 10.4 mm. methane. This would give a total increase of hydrocarbon of 28.5 + 5.2 = 33.7 mm. to be compared with the observed hydrocarbon increase of 33.6 mm. Expt. 2b appears to repeat 1 since the carbon laid on the surface in expt. 1a was more than 90% consumed by hydrogen in 2a. Similar variations in the nature of the important reaction with change in the carbon–hydrogen ratio of the reaction mixture and change in carbon content of the surface may be traced through the results of expts. 2b–7. It emerges that, in a catalyst heavily charged with carbon, reaction (3) between carbon and hydrogen occurs preferentially to reaction (1). A certain amount of the carbon, however, appears to be laid down in such a form that subsequent reaction does not readily occur. Also, the activity of the catalyst falls steadily due to the deposition of the carbon.

The experiments presented in Table V are concerned with the decomposition of ethane alone on the same nickel catalyst at 218°. The catalyst after evacuation was washed with ethane at 218° for one and a half hours and then evacuated for one hour further. The three final columns of the table give the data obtained by a fractional separation of the hydrocarbon product and a combustion of the ethane fraction to carbon dioxide as a check on its composition.

The fact that the methane formed is, in each case, equal to three times the increase in pressure due to reaction or equal to three times the increase in hydrocarbon plus twice that of the hydrogen, is indicative of the over-all reaction (2) $2C_2H_6 = C + 3CH_4$. The methane yields from the fractionation of the product further confirm this view. The carbon deposited on the catalyst by reason of this reaction can be removed in part by reaction with hydrogen as indicated in the two experiments of Table VI.

TABLE VI

INTERACTION OF HYDROGEN WITH CARBON DEPOSITED ON NICKEL AT 218°

Expt.	P_{H_2}, mm.	Time, hrs.	Recovered gas, mm.	−ΔP	+ΔH.C.	−ΔH_2	CH_4 by fractionation
1a	416.1	4.5	356.0	60.1	57.1	117.2	56.7
b	421.0	14.0	414.4	6.6	6.0	12.6	..

Since −ΔH_2 is twice (−ΔP) or twice (+ΔH.C.) it follows that the hydrocarbon formed is all methane. This was confirmed in the first case by fractionation. The total methane produced amounts to 63.1 mm. equivalent to 42 mm. of C_2H_6. Some carbon is left on the catalyst and a subsequent measurement of reaction rate with $1C_2H_6{:}1H_2$ gave very low activity, *i. e.*, 0.9% per hour at 184°.

The Activation Energy of the Reactions of Ethane with Hydrogen and Deuterium to Form Methane and Methane-*d*.—To check the apparently high activation energy deduced from the data of Table III and to obtain comparison between the rates of reaction of hydrogen and deuterium with ethane the data of Table VII were obtained on a new catalyst containing 2 g. of nickel. Again the static method was employed and the experiments with deuterium were interposed between two experiments with hydrogen under comparable conditions.

TABLE VII

REACTION OF ETHANE WITH HYDROGEN AND WITH DEUTERIUM TO FORM METHANE

Expt.	Initial volumes, cc. C_2H_6	H_2	D_2	Temp., °C.	Time, hrs.	Conversion % C_2H_6
28	20.0	20.0		184	1.0	53.7
29	20.1	20.1		172	2.5	28.3
30	20.3		19.4	172	2.5	16.7
31	20.3	19.7		172	2.5	23.9
32	20.3	20.4		157	10.0	21.2
33	20.3		20.9	157	10.0	10.3
34	20.3	21.4		157	10.3	17.5

A slow deterioration of the catalyst with successive experiments does not obscure the obvious result that reaction with deuterium is slower than that with hydrogen. Nor is it serious enough to prevent the conclusion that the activation energy has the high value previously indicated. The data at 157 and 172° in this table indicate an observed activation energy of ∼42 kcal. The relative rates of the hydrogen and deuterium reactions at the two temperatures 157 and 172° can be accounted for on the basis of a difference in activation energies of ∼450 cal.

General Discussion

From these studies of reactivity of ethane–hydrogen mixtures on nickel in the temperature range 157–300°, we conclude that, in the presence of excess hydrogen, the ethane undergoes a dissociative adsorption to methyls which are converted quantitatively with adsorbed hydrogen to methane. With deficiency of hydrogen the activated adsorption of ethane continues beyond the stage of formation of adsorbed methyls at the surface and the dissociative adsorption proceeds via CH_2 and CH to C with simultaneous formation of adsorbed atomic hydrogen. Reaction of this latter with adjacent methyls produces methane which then evaporates. In this temperature range the dissociative process to C appears to be practically complete, carbon and methane being the products formed in overwhelmingly preponderant amount. A small amount of hydrogen escapes from the surface as such. Some of the carbon formed goes over into a form in which it is no longer capable of undergoing the reverse reactions of the dissociative processes discussed and acts as a permanent poison to the catalyst. The bulk of the carbon formed in this temperature range is however recoverable by reaction with hydrogen as methane. All these observations are in best agreement with the calculated equilibrium data in such systems. In the system $2C + 3H_2 = C_2H_6$ this is quite remarkably true since we compute that at 227° partial pressures $P_{C_2H_6} = 0.46$, $P_{H_2} = 0.54$ atm. are in equilibrium with carbon with a total pressure of 1 atm. In contrast to this in the system $C + 2H_2 = CH_4$ at atmospheric pressure the equilibrium partial pressure at 255° is $P_{H_2} = 0.03$ atm. The necessity for excess hydrogen in the ethane system is thus evident, while with the methane system minimal pressures of hydrogen prevent carbon formation. In the system $C_2H_6 = C + 3CH_4$ the equilibrium partial pressure at 184° is $P_{C_2H_6} = 0.6 \times 10^{-4}$ atm., and in the system $C_2H_6 + H_2 = 2CH_4$ at the same temperature $P_{C_2H_6} = 2 \times 10^{-4}$ atm.

The occurrence of the exchange reaction to yield deutero-ethanes in a temperature range where dissociative adsorption to yield methyls is unimportant indicates that the dissociative adsorption of ethane to yield ethyl and hydrogen atom is a process of lower activation energy than that of adsorption to yield methyls. The reverse of the ethane–ethyl–hydrogen dissociative process is the final stage in the formation of ethane from ethylene and hydrogen on such catalysts in the low temperature range. In our previous study of the methanes we found an activation energy of 19 kcal. for the dissociative adsorption to methyl and hydrogen. We expect that the corresponding process for ethane might be less than this value.

The high apparent activation energy of the reaction of ethane with hydrogen to yield methane, ∼43 kcal., is worthy of note especially since the temperature range in which the reaction occurs is not considerably higher than that in which the exchange reaction occurs. We compare this result with the case of methane and deuterium in which $E \sim 28$ kcal. In both cases the retarding influence of hydrogen contributes to the high value. From the earlier work we assess its contribution at ∼9 kcal. The simplest explanation of the high activation energy in the present work appears to be that it is associated with a somewhat higher energy of activated adsorption involving dissociation of the C–C bond. Sterically we would expect this to be higher than that involving the C–H bond. Further, of the surface free from hydrogen, available to ethane adsorption, a fraction will be occupied by ethane adsorbed by a mechanism involving the C–H dissociation. Such adsorption will cause an increase in the observed activation energy of the ethane–hydrogen reaction as does hydrogen. If we ascribe the difference between the two observed activation energies in the ethane and methane reactions, $43 - 28 = 15$ kcal., to such an effect, we arrive at the reasonable values for the activation energies of dissociative adsorption of ethane, for the C–C bond ∼ 19 kcal., and for the C–H bond ∼ 15 kcal. Qualitatively such results are entirely consonant with all our data.

One final point for discussion involves the abnormal inhibitory action of hydrogen ($\propto P_{H_2}^{-2.5}$) which we deduce from the data of Tables III and IV. Such a high power of the hydrogen pressure cannot be explained on the basis of pressure influence on surface occupied by hydrogen molecules. It may, however, be explained as due to the increasing deposition of carbon with decrease in hydrogen concentration and the preferential occurrence of the reaction between hydrogen and the deposited carbon rather than that between ethane and hydrogen. As we have already observed, our experimental data abundantly confirm this preferential reaction and thus account for the abnormal effect of hydrogen concentration. One alternative possibility is that activation involving the C–C bond requires at least two adjacent elementary spaces of catalyst and that this condition at high hydrogen coverage of the surface might be inversely proportional to a higher power of the hydrogen concentration. Further studies in the general field of hydrocarbon–hydrogen reactions are planned to test these points of view.

Summary

1. The exchange reaction between ethane and deuterium on a nickel catalyst takes place in a lower temperature range, 100–130°, than that required for the interaction to yield methane, 160–300°.

2. The formation of methane by this reaction has been studied kinetically. The surface reaction is inhibited by hydrogen.

3. At low hydrogen concentrations side reactions occur representable by the equations $2C_2H_6 = C + 3CH_4$ and $C + 2H_2 = CH_4$ and these may become the predominant reactions.

4. The activation energy of the reaction on nickel between ethane and hydrogen to form methane is $\sim$43 kcal. The reaction with deuterium is somewhat slower with an activation energy $\sim$0.5 kcal. higher.

5. An interpretation of these data in terms of a dissociative activated adsorption of ethane is given, leading to the conclusion that the activation energy of dissociative adsorption at the C–C bond is greater than that of the C–H bond.

6. A method of preparation of ethane-d_6 has been described.

PRINCETON, N. J. RECEIVED JULY 3, 1936

[CONTRIBUTION NO. 142 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

Studies in the Urea Series. XIII.[1] Alkyl-nitroureas and Alkyl-nitrobiurets

BY TENNEY L. DAVIS AND NICHOLAS D. CONSTAN

Experiments reported in the tenth paper of this series led to the conclusion that "only those alkylguanidines which contain an unsubstituted amino group form nitro-compounds by direct nitration, the nitro group entering the non-alkylated amino group." A similar generalization is evidently not valid for the alkylureas, for Degner and von Pechmann[2] have reported that N-nitro-N-methylurea is produced by the nitration of methylurea with ethyl nitrate and concentrated sulfuric acid. Thiele and Lachmann[3] on the other hand reported somewhat earlier that ethylurea yields N-nitro-N′-ethylurea by a similar procedure. We have wished to verify this difference between methyl- and ethylurea and to determine in general the behavior of the alkylureas on nitration—and have carried the study farther to the nitration of two ω-substituted biurets and to the preparation from one of the resulting nitro compounds of certain ω,ω,ω'-trisubstituted biurets.

The nitrate of methylurea on treatment with concd. sulfuric acid yields N-nitro-N-methylurea in which the nitro and methyl groups are both attached to the same nitrogen atom, as is demonstrated by the fact that it yields methylnitramine and urea when treated with ammonia. The nitrates of ethyl-, *n*-propyl- and *n*-butylurea on treatment with concd. sulfuric acid yield alkylnitroureas in which the nitro group and the alkyl group are attached to different nitrogen atoms. Unlike methylurea they behave in the same manner as the corresponding alkylguanidines. The structure of the N-nitro-N′-alkylureas is demonstrated by the facts that with ammonia water they yield the alkylureas and with aniline the N-phenyl-N′-alkylureas. As would be expected they dearrange somewhat less readily than nitro-

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[1] Earlier papers of this series: I, Davis and Underwood, THIS JOURNAL, **44**, 2595 (1922); II, VI, VII, VIII, Davis and Blanchard, *ibid.*, **45**, 1816 (1923); **51**, 1790, 1801, 1806 (1929); III, Davis, *Proc. Nat. Acad. Sci.*, **11**, 68 (1925); IV, Davis and Abrams, *Proc. Am. Acad. Arts, Sci.*, **61**, 437 (1926); V, Davis and Luce, THIS JOURNAL, **49**, 2303 (1927); IX, X, Davis and Elderfield, *ibid.*, **54**, 1499 (1932); **55**, 731 (1933); XI, Davis and Farnum, *ibid.*, **56**, 883 (1934); XII, Davis and Ebersole, *ibid.*, **36**, 885 (1934).

[2] Degner and von Pechmann, *Ber.*, **30**, 652 (1897).

[3] Thiele and Lachmann, *Ann.*, **288**, 285 (1895).

urea itself. With cupric salts and pyridine they form colored complex compounds which are soluble in chloroform and may be extracted from aqueous solution by means of that solvent.

The nitrates of N,N-dimethyl-, N,N-diethyl- and N,N-di-*n*-butylurea on treatment with concd. sulfuric acid yield the corresponding dialkylnitramines. No nitrourea derivatives could be found. In one experiment in which N,N-diethylurea nitrate was treated with acetic anhydride, diethylnitramine was produced and a portion of the diethylurea was recovered. The N,N-dialkylureas differ then in their behavior on nitration from N,N-dimethylguanidine, which yields N,N-dimethyl-N′-nitroguanidine.

N,N′-dimethyl- and N,N′-diethylurea could not be nitrated.

ω-Methyl- and ω,ω-dimethylbiuret on nitration with mixed acid yield, respectively, ω-methyl-ω′-nitrobiuret and ω,ω-dimethyl-ω′-nitrobiuret, in which the nitro group has entered the otherwise unsubstituted amino group at the remote end of the molecule. The position of the nitro group is proved by the fact that the nitro compounds react with ammonia to reproduce the original un-nitrated alkylbiurets. A consideration of the facts already known about the urea dearrangement[4] leads to the conclusions (1) that ω-methyl-ω-nitrobiuret would dearrange to form methylnitramine and dicyanic acid and with ammonia water would yield unsubstituted biuret, (2) that ω-methyl-α-nitrobiuret would dearrange to form nitroamide, cyanic acid and methyl isocyanate, and with ammonia water would yield urea and methylurea and (3) that ω-methyl-ω′-nitrobiuret would dearrange to form nitroamide and methyldicyanic acid, and with ammonia water would yield ω-methylbiuret.

$$CH_3NHCONHCONHNO_2 \longrightarrow NH_2NO_2 + CH_3NHCONCO$$

$$CH_3NHCONCO + NH_3 \longrightarrow CH_3NHCONHCONH_2$$

ω,ω-Dimethyl-ω′-nitrobiuret similarly would yield dimethyl-dicyanic acid by dearrangement, and ω,ω-dimethylbiuret by reaction with ammonia. The probable presence of dimethyl-dicyanic acid is further confirmed by the reaction of ω,ω-dimethyl-ω′-nitrobiuret with primary amines.

$$(CH_3)_2NCONCO + RNH_2 \longrightarrow (CH_3)_2NCONHCONHR$$

In this way we have prepared ω,ω,ω′-trimethylbiuret, ω,ω-dimethyl-ω′-*n*-amylbiuret, and ω,ω-dimethyl-ω′-phenylbiuret. None of these tri-substituted biurets gave the biuret test with cupric salts and sodium hydroxide.

Experiments

N-Nitro-N-methylurea.—Twenty-two grams of dry methylurea nitrate, m. p. 125–126°, was added gradually and with stirring to 35 cc. of concd. c. p. sulfuric acid (sp. gr. 1.84) while the temperature was maintained below −15°. The homogeneous mixture was drowned in 120 cc. of ice-water, and the precipitate, washed, dried in a desiccator, and recrystallized from petroleum ether, yielded 8 g. (41.7%) of N-nitro-N-methylurea, m. p. 156–158° with decomposition. The material yielded methylnitramine and urea by interaction with warm ammonia water. Its properties were the same as those reported by Degner and von Pechmann[2] for the N-nitro-N-methylurea prepared by the nitration of methylurea with ethyl nitrate in concd. sulfuric acid solution, and were different from those of the N-nitro-N′-methylurea, m. p. 105–106°, which the same workers prepared by the action of diazomethane on nitrourea.

N-Nitro-N′-ethylurea.—Forty grams of ethylurea nitrate, treated in a similar manner with 60 cc. of concd. sulfuric acid and drowned in 200 cc. of ice-water, yielded 17 g. (49.3%) of N-nitro-N′-ethylurea, pearl-white flakes from petroleum ether, not hygroscopic, m. p. 133–134°. Thiele and Lachmann[3] reported m. p. about 130–131°. The material yielded ethylurea by interaction with warm ammonia water.

N-Nitro-N′-*n*-propylurea.—Fifteen grams of *n*-propylurea nitrate, treated in a similar manner with 23 cc. of concd. sulfuric acid and drowned in 100 cc. of ice-water, yielded 8 g. (60%) of N-nitro-N′-*n*-propylurea, crystals from petroleum ether, m. p. 96°.

Anal. Calcd. for $C_4H_9O_3N_3$: N, 28.5. Found: N, 28.7, 28.6.

The structure of the N-nitro-N′-*n*-propylurea was proved by the fact that it reacted with aniline in warm water to yield N-phenyl-N′-*n*-propylurea, m. p. 116–117°, identified by mixed melting point with a sample prepared by the combination of phenyl iosocyanate with *n*-propylamine in benzene solution. Oliveri-Mandalà and Noto[5] reported the melting point of N-phenyl-N′-*n*-propylurea as 114–116°.

***n*-Butylurea Nitrate.**—Twenty-five grams of *n*-butylurea was made into a paste with 25 cc. of water, 20 cc. of nitric acid (sp. gr. 1.42) was added, and the solution was cooled in a freezing mixture of ice and salt. The crystals which separated, after drying in a vacuum desiccator, melted at 62–65°. They were found to be appreciably soluble in benzene; recrystallized from that solvent they yielded the pure substance, m. p. 70–71°, 33 g. (85.5%).

Anal. Calcd. for $C_5H_{13}O_4N_3$: N, 23.5. Found: N, 23.2, 23.3.

N-Nitro-N′-*n*-butylurea.—Thirty grams of *n*-butylurea nitrate, treated with 45 cc. of concd. sulfuric acid and drowned in 150 cc. of ice-water, yielded 18 g. (66.5%) of N-nitro-N′-*n*-butylurea, m. p. 80–81°, pearl-white fluffy leaflets from petroleum ether.

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[4] Especially the seventh and eighth papers of this series.

[5] Oliveri-Mandalà and Noto, *Gazz. chim. ital.*, **43**, I, 517 (1913).

Anal. Calcd. for $C_5H_{11}O_3N_3$: N, 26.1. Found: N, 26.0, 25.9.

The behavior of N-nitro-N′-*n*-butylurea with ammonia and with aniline is typical of the behavior of the N-nitro-N′-alkylureas in general. It reacts less vigorously with these reagents than does nitrourea. The effect of the alkyl group is to reduce the ease of the dearrangement.

Two grams of N-nitro-N′-*n*-butylurea treated with 60 cc. of strong ammonia water gave no evidence of any reaction, and the viscous liquid which remained after spontaneous evaporation was strongly acid to litmus and gave a blue color with a solution of diphenylamine in concd. sulfuric acid. In another experiment, the materials were warmed; a vigorous evolution of nitrous oxide took place, and the evaporation of the liquid on the water-bath gave a residue of *n*-butylurea which, even without purification, failed to give a test for the nitro group with the diphenylamine reagent.

Three grams of N-nitro-N′-*n*-butylurea was treated with a slight excess of aniline dissolved in water. There was no evidence of reaction at room temperature. On spontaneous evaporation of the liquid, aniline separated first and afterward unchanged N-nitro-N′-*n*-butylurea. When a similar mixture was warmed gently it became milky from innumerable small bubbles of nitrous oxide. On continued boiling of the mixture, gassing ceased, and acicular crystals began to separate from the boiling liquid. These on recrystallization from benzene yielded pure N-phenyl-N′-*n*-butylurea, m. p. 129–130°, identified by analysis and by mixed melting point with a sample prepared by the combination of phenyl isocyanate with *n*-butylamine in benzene solution.

Anal. Calcd. for $C_{11}H_{16}ON_2$: N, 14.6. Found: N, 14.8, 14.3.

***n*-Amylurea nitrate**, m. p. 75°, was prepared in the same way as the nitrate of *n*-butylurea.

Anal. Calcd. for $C_6H_{15}O_4N_3$: N, 21.8. Found: N, 21.9, 22.0.

N-Nitro-N′-*n*-amylurea.—Twelve grams of *n*-amylurea nitrate, treated with 16 cc. of concd. sulfuric acid and drowned in 80 cc. of ice-water, yielded an oil which on chilling solidified to crystals. These, dried and recrystallized from ether, gave 6 g. (67%) of N-nitro-N′-*n*-amylurea, m. p. 62°.

Anal. Calcd. for $C_6H_{13}O_3N_3$: N, 24.6. Found: N, 24.6, 24.7.

By reaction with aniline in warm water N-nitro-N′-*n*-amylurea yielded N-phenyl-N′-*n*-amylurea, m. p. 92°, identified by analysis and by mixed melting point with a sample prepared by the combination of phenyl isocyanate with *n*-amylamine in benzene solution.

Anal. Calcd. for $C_{12}H_{18}ON_2$: N, 13.6. Found: N, 13.5.

N,N-Dimethylurea nitrate was prepared by the same method as the nitrate of butylurea, 86.8% yield, crystals from benzene, m. p. 103–104°.

Anal. Calcd. for $C_3H_9O_4N_3$: N, 27.8. Found: N, 28.0, 28.2.

Ten grams of N,N-dimethylurea nitrate was treated with 15 cc. of concd. sulfuric acid and drowned in 75 cc. of of ice-water, as described, but no precipitate appeared. The liquid was extracted repeatedly with small portions of ether, and the ether extract, evaporated and cooled to a low temperature, gave stout needle crystals of dimethylnitramine, m. p. 79°. Franchimont[6] obtained the same material by the action of strong nitric acid on the nitrate of N,N-dimethylurea.

N,N-Diethylurea nitrate was prepared by the same method as the other nitrates, 77% yield, crystals from benzene, m. p. 118°.

Anal. Calcd. for $C_5H_{13}O_4N_3$: N, 23.5. Found: N, 23.7, 23.5.

Twelve grams of N,N-diethylurea nitrate was treated with 16 cc. of concd. sulfuric acid and drowned in 80 cc. of ice-water, the liquid was extracted with ether, and the ethereal extract on distillation in vacuum yielded a small amount of diethylnitramine boiling as reported at 93° at 16 mm. pressure.[7] In another experiment the sulfuric acid solution of N,N-diethylurea nitrate was diluted with ether before it was poured into water, but no nitrodiethylurea was obtained. In another, acetic anhydride was used instead of sulfuric acid; some diethylnitramine was produced and a portion of the N,N-diethylurea nitrate was recovered unchanged.

N,N-Di-*n*-propylurea nitrate was procured in excellent yield by the same method as the other nitrates, m. p. 165°.

Anal. Calcd. for $C_7H_{17}O_4N_3$: N, 20.3. Found: N, 20.5, 20.4.

On treatment with sulfuric acid, water and ether in the same manner as the other nitrates, it yielded a small quantity of di-*n*-propylnitramine boiling as reported at 76–79° at 10 mm. pressure.[8]

Action of Sulfuric Acid on the Nitrates of N,N′-Dialkylureas.—Ten grams of finely powdered dry N,N′-dimethylurea nitrate was added gradually to 15 cc. of concd. sulfuric acid while the mixture was kept at a temperature below −15°. When the liquid was poured into 75 cc. of ice-water, no precipitate appeared. Ether and benzene extracts of the acid solution gave no residues when they were evaporated. The solution was treated with barium carbonate in excess, filtered, and evaporated to dryness at a temperature below 55°. Ether, petroleum ether, and benzene extracts of the residue gave no products which showed a positive test with the diphenylamine reagent.

An experiment with the nitrate of N,N′-diethylurea gave a similar result.

In another experiment with N,N′-dimethylurea nitrate, the sulfuric acid solution was diluted with ether instead of with water. The ether removed most of the sulfuric acid. In order to determine whether any cyanic acid from the dearrangement of the N,N′-dimethylurea was present, the residue from the ether was treated with benzylamine in the expectation that the cyanic acid, if present, would combine with that material to form benzyl- or dibenzylurea, but only benzylamine sulfate, nitrate and N,N′-dimethylurea were identified in the mixture.

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[6] Franchimont, *Rec. trav. chim.*, **2**, 122 (1883).

[7] Franchimont and Umgrove, *ibid.*, **16**, 396 (1897).

[8] Thomas, *ibid.*, **9**, 79 (1890).

ω-Methyl-ω′-nitrobiuret.—Four grams of finely powdered dry ω-methylbiuret[9] was added gradually and with stirring to a mixture, below −15°, of 12 cc. of concd. sulfuric acid (1.84) and 3 cc. of nitric acid (1.42). On drowning the clear liquid in 25 cc. of ice-water, the ω-methyl-ω′-nitrobiuret precipitated as an almost impalpable powder. Washed with ice-water and dried in vacuum, this yielded without recrystallization 2.9 g. (52%) of product which did not melt but decomposed at 99–100°.

Anal. Calcd. for $C_3H_6O_4N_4$: N, 34.5. Found: N, 34.5, 34.6.

ω-Methyl-ω′-nitrobiuret did not yield a chloroform soluble copper pyridine complex. Warmed with ammonia water, it yielded ω-methylbiuret, identified by mixed melting point with a known sample.

ω,ω-Dimethyl-ω′-nitrobiuret.—Ten grams of ω,ω-dimethylbiuret, nitrated with a mixture of 18.5 cc. of concd. sulfuric acid (1.84) and 4.5 cc. of nitric acid (1.42) and drowned in 100 cc. of ice-water, gave 9.8 g. (73%) of ω,ω-dimethyl-ω′-nitrobiuret, m. p. 114–115°, with decomposition.

Anal. Calcd. for $C_4H_8O_4N_4$: N, 31.8. Found: N, 31.7, 31.4.

ω,ω-Dimethyl-ω′-nitrobiuret, warmed with ammonia water, yielded ω,ω-dimethylbiuret, identified by mixed melting point with a known sample. It did not form a chloroform soluble copper pyridine complex.

ω,ω-Dimethyl-ω′-phenylbiuret.—Two grams of ω,ω-dimethyl-ω′-nitrobiuret was treated with a slight excess of aniline in aqueous solution. Gassing set in at once. The material was warmed until gassing ceased and evaporated to dryness on the water-bath. The product was purified by recrystallization from methyl alcohol and by sublimation in vacuum. At ordinary pressure it sublimed without melting at about 225°.

Anal. Calcd. for $C_{10}H_{13}O_2N_3$: N, 20.3. Found: N, 20.6.

ω,ω,ω′-Trimethylbiuret, prepared in similar manner from ω,ω-dimethyl-ω′-nitrobiuret and methylamine, melted at 154°, small crystals from chloroform.

Anal. Calcd. for $C_5H_{11}O_2N_3$: N, 29.0. Found: N, 29.2, 29.3.

ω,ω-Dimethyl-ω′-*n*-amylbiuret, prepared in similar manner from ω,ω-dimethyl-ω′-nitrobiuret and *n*-amylamine, melted at 149°, small crystals from chloroform.

Anal. Calcd. for $C_9H_{19}O_2N_3$: N, 20.9. Found: N, 21.1.

Very few substituted biurets containing substituents in both the ω- and the ω′-positions are described in the literature. Experimentation along this line is being continued.

Summary

The nitration of alkylureas has been studied by the method of treating the urea nitrates with concentrated sulfuric acid.

Ethyl-, *n*-propyl- and *n*-butylurea, like the corresponding guanidines, nitrate in the nonalkylated amino group.

Methylurea, unlike methylguanidine, nitrates on the nitrogen atom which is attached to the methyl.

Dialkylureas in which the two alkyl groups are attached to the same nitrogen atom yield dialkylnitramines.

Dialkylureas in which the two alkyl groups are attached to different nitrogen atoms could not be nitrated.

ω-Methyl- and ω,ω-dimethylbiuret with mixed acid take on a nitro group in the non-alkylated amino group at the remote end of the molecule.

Three ω,ω,ω′-trisubstituted biurets are described.

CAMBRIDGE, MASS.

RECEIVED JULY 1, 1936

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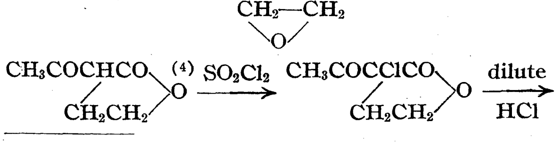
[9] Prepared according to the method of Davis and Blanchard, seventh paper of this series.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Studies of Crystalline Vitamin B_1. XIV. Sulfite Cleavage. IV. The Thiazole Half

BY EDWIN R. BUCHMAN

The vitamin B_1 molecule is split by sulfite[1] yielding 4-methyl 5-(β-hydroxyethyl) thiazole[2] as basic cleavage product. The synthesis of this substance from brominated acetopropyl alcohol and thioformamide was announced[3] over a year ago. Subsequently H. T. Clarke and S. Gurin prepared[2] the compound in connection with their establishment of the presence of the thiazole nucleus in the vitamin. Recently the following improved method has been developed.



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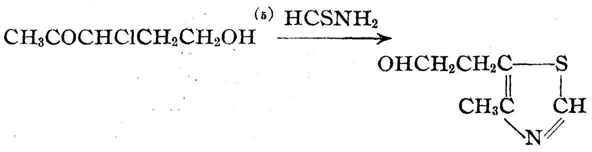
[1] R. R. Williams, R. E. Waterman, J. C. Keresztesy and E. R. Buchman, THIS JOURNAL, **57**, 536 (1935).

[2] H. T. Clarke and S. Gurin, *ibid.*, **57**, 1876 (1935).

[3] E. R. Buchman and R. R. Williams, Paper read before the Organic Division of the American Chemical Society at the New York meeting, April, 1935.

[4] I. L. Knunyantz, G. V. Chelintzev and E. D. Osetrova, *Compt. rend. acad. sci.* (U. R. S. S.), [N. S.], **1**, 312 (1934); *C. A.*, **28**, 4382 (1934).



The yield of thiazole varies from 8 to 12 g. per 100 g. of ethyl acetoacetate used as starting material.

The similarity between the vitamin and the methiodide of the basic cleavage product has been pointed out.[6] Although the resemblance does not extend to the sulfite cleavage,[1] it was found that the characteristic color test which the vitamin gives with diazotized sulfanilic acid is a property of quaternary salts of the hydroxy thiazole.

Experimental

Brominated Acetopropyl Alcohol and Thioformamide.[7]—Thirty-one grams of γ-acetopropyl alcohol[4] was dissolved in 150 cc. of water and stirred while 48 g. of bromine was added slowly at room temperature over a period of two hours. The aqueous layer was decanted from a small amount of oil, extracted with ether and the ethereal solution dried over sodium sulfate. After removal of the solvent *in vacuo*, the crude bromo compound (unstable even at room temperature), weighing 30 g., was added directly to 13 g. of crude thioformamide[8] dissolved in 10 cc. of ethanol. A spontaneous reaction took place during which the temperature was kept below 60° by external cooling. The reaction mixture, after standing overnight at room temperature, was heated for one hour on the steam-bath, taken up in water and washed with ether. Excess alkali was added and the liberated thiazole extracted with ether, dried over sodium sulfate and fractionated. The yield was 7.1 g.; b. p. 110–112° (3 mm.).

Anal.[9] Calcd. for C_6H_9NSO: C, 50.30; H, 6.34. Found: C, 49.96; H, 6.29.

The presence in the product of a small amount of the isomer, 4-(γ-hydroxypropyl) thiazole, may be inferred from the unsharp melting points of crude derivatives. These, on recrystallization, were found to be identical with corresponding material[6a] from the vitamin: picrolonate, m. p. 184° d.; picrate, from ethanol, m. p. 163°; *p*-nitrobenzoate, from methanol, m. p. and mixed m. p. 124°.[10]

α-Chloro-α-acetobutyrolactone.—Sixty-four grams of α-acetobutyrolactone[4] was placed in a flask equipped with a mechanical stirrer and 68 g. of sulfuryl chloride added over a period of one and one-half hours. The reaction was accompanied by spontaneous warming and a steady evolution of hydrogen chloride and sulfur dioxide. The product was washed with water, taken up in ether and dried over calcium chloride. Fractionation yielded 67.5 g. (83% of the theoretical); b. p. 84–86° at 3 mm.; d^{24}_{4} 1.325.

Anal. Calcd. for $C_6H_7O_3Cl$: C, 44.30; H, 4.35. Found: C, 44.19; H, 4.39.

γ-Chloro-γ-acetopropyl Alcohol.—Eighty-one grams of the chloro lactone, 80 cc. of water and 15 cc. of concentrated hydrochloric acid were mixed and heated under reflux at 100° for seventy-five minutes. During this time carbon dioxide was evolved and complete solution took place. The reaction mixture was extracted several times with small portions of ether and the ethereal solution dried over sodium sulfate and distilled. The portion boiling at 85–110° at 3 mm. was collected; yield 50 g. or 73%; d^{25}_{4} 1.221.

Anal. Calcd. for $C_5H_9O_2Cl$: Cl, 25.97. Found: Cl, 27.26.

The stability of the chloro alcohol is in marked contrast to the behavior of the corresponding bromo compound.

4-Methyl 5-(β-Hydroxyethyl) Thiazole.—Nine and one-half grams of chloroacetopropyl alcohol, 6.7 g. of crude thioformamide and 3 cc. of ethanol were mixed and allowed to stand in a stoppered vessel for three days at room temperature. During this time an additional 3.0 g. of thioformamide was added. The product was isolated as described above. On distillation at 2 mm. there was obtained a 4.9-g. fraction (corresponding to a 50% yield) boiling at 93–95°; d^{24}_{4} 1.196.

Anal. Calcd. for C_6H_9NSO: C, 50.30; H, 6.34; N, 9.79. Found: C, 50.27; H, 6.31; N, 9.52.

The sharp melting points of even crude derivatives attest the high purity of the product.

The thiazole was also prepared by brominating the acetobutyrolactone in aqueous suspension, hydrolyzing the bromo lactone with 10% hydrobromic acid and condensing the resulting γ-bromo-γ-acetopropyl alcohol with thioformamide as before. The yields however are only about one-half of those obtained through the chloro lactone.

The thiazole methiodide,[6a] m. p. 89°, when treated with sulfite[1] did not cleave appreciably but with alkali and diazotized sulfanilic acid[11] gave the red color characteristic of the vitamin under these conditions. The azo test is not given by the hydroxythiazole itself nor is it a general reaction of quaternary thiazolium salts. Acetopropyl alcohol gave a strong positive test.

4-Methyl 5-(β-Chloroethyl) Thiazole.[6a]—Two grams of the hydroxythiazole was heated with 25 cc. of concentrated hydrochloric acid for three hours in a sealed tube at 145°. After evaporation of excess acid, the free base was liberated with alkali and isolated by distillation; yield 1.5 g. The compound has a characteristic odor and is stable[12] at room temperature: b. p. 74–75° (3 mm.) d^{25}_{4} 1.233. *Anal.* Calcd. for C_6H_8NSCl: C, 44.56; H, 4.99; N, 8.67. Found: C, 44.40; H, 5.06; N, 8.60. Picrate[2] m. p. 139–140°; chloroplatinate m. p. 215–218° d.; methiodide m. p. 165°.

The author wishes to acknowledge the kind cooperation of Drs. R. R. Williams and E. E. Reid.

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(5) Acetopropyl alcohol and its simple derivatives exist largely in the cyclic oxide form.

(6) (a) E. R. Buchman, R. R. Williams and J. C. Keresztesy, THIS JOURNAL, **57**, 1849 (1935); see also (b) R. R. Williams and A. E. Ruehle, *ibid.*, **57**, 1856 (1935), and ref. 2.

(7) This experiment was carried out at Teachers College, Columbia University, Department of Physiological Chemistry.

(8) S. Gabriel, *Ber.*, **49**, 1115 (1916).

(9) Microanalyses by Dr.-Ing. A. Schoeller, Berlin.

(10) The previously recorded[6a] m. p. (131°) is in error.

(11) Spot plate technique of T. B. Johnson and S. H. Clapp, *J. Biol. Chem.*, **5**, 163 (1908).

(12) Compare F. E. Hooper and T. B. Johnson, THIS JOURNAL, **56**, 470 (1934).

Summary

There has been described a practical method of synthesis of the thiazole half of vitamin B_1.

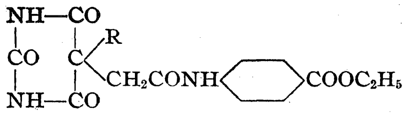
BALTIMORE, MARYLAND RECEIVED JULY 20, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Alkylacetanilidobarbituric Acids. II. *p*-Carbethoxy Derivatives

BY JOHN A. TIMM AND JOHN B. HOWARD[1]

In many instances the simultaneous administration of either mixtures or addition products of hypnotic and antipyretic substances produces an analgesic effect.[2] Further, compounds have been synthesized in which groups tending to exhibit hypnotic properties and others, antipyretic properties are present within the same molecules. Hepner and Frenkenberg[2] have prepared 5,5-dialkyl derivatives of 1-phenyl-3-methylbarbituric acid. Dox and Yoder[3] have synthesized derivatives of two dialkylbarbituric acids (5-ethyl-5-propyl- and 5-isoamyl-5-propylbarbituric acids) with diethylamine, ethylaniline, acetanilide, and phenacetin, respectively, attached to the γ-carbon atom of the propyl group. Timm[4] prepared a series of 5-alkyl-5-acetanilidobarbituric acids. This work has now been extended to include a series of 5-alkyl-5-*p*-carbethoxyacetanilidobarbituric acids of the type



These compounds may be considered as derivatives of ethyl *p*-aminobenzoate, the local anesthetic.

Experimental Part

Barbituric Acids Containing the *p*-Carbethoxyacetanilido Group.—The method used in the synthesis of these compounds was identical with that used for the corresponding acetanilido derivatives[4] except that ethyl *p*-chloroacetaminobenzoate[5] was substituted for chloroacetanilide. The products were recrystallized from 90% ethyl alcohol except in the cases of the allyl and the isopropyl derivatives in which cases absolute alcohol was used to avoid the formation of hydrates. All melt with decomposition at temperatures above 225°.

TABLE I

Barbituric acid, 5-*p*-carbethoxyacetanilido-	Yield, %	N Analysis, %		
		Calcd.	Found	
5-Ethyl-	40	11.63	11.54	11.60
5-Isopropyl-	9	11.20	11.22	11.24
5-*n*-Butyl-	13	10.79	10.78	10.81
5-Isobutyl-	25	10.79	10.73	10.77
5-Isoamyl-	43	10.42	10.41	10.43
5-Allyl-	20	11.25	11.18	11.22

Summary

The following 5-*p*-carbethoxyacetanilidobarbituric acids have been prepared: 5-ethyl-, 5-isopropyl-, 5-*n*-butyl-, 5-isobutyl-, 5-isoamyl- and 5-allyl-.

NEW HAVEN, CONN. RECEIVED JULY 2, 1936

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(1) From the essay presented by John B. Howard to the Faculty of the Sheffield Scientific School of Yale University in partial fulfilment of the requirements for the degree of Bachelor of Science with Honors, June, 1936.

(2) For a review of the literature in this field see Hepner and Frenkenberg, *Ber.*, **65B**, 123 (1932).

(3) Dox and Yoder, THIS JOURNAL, **45**, 1757 (1923).

(4) Timm, *ibid.*, **57**, 1943 (1935).

(5) This compound has been prepared in this Laboratory by Ruth Watts. Its preparation and properties will be reported shortly.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Reaction of Butylacetylene with Hydrogen Bromide[1]

BY CHARLES A. YOUNG, R. R. VOGT AND J. A. NIEUWLAND

Although it is a problem of much interest, relatively little attention has been directed toward the addition of hydrogen bromide to acetylene compounds. Bauer[2] obtained vinyl bromide and ethylene dibromide from acetylene and hydrogen bromide in the presence of gaseous oxidizing agents. Using catalysts such as mercuric bromide on asbestos, Wibaut[3] obtained from acetylene and hydrogen bromide a mixture of ethylidene dibromide and ethylene dibromide, the latter compound being formed in the larger amount. Réboul[4] found that aqueous hydrogen bromide and methylacetylene reacted to form 2,2-dibromopropane and a small amount of 2-bromopropene.

During the course of the investigation in this Laboratory, there appeared two papers which furnished further data on the addition of hydrogen bromide to acetylene compounds. Harris and Smith[5] found that in the presence of perbenzoic acid hydrogen bromide added to 10-undecynoic acid to yield the 11-bromo acid, while in the absence of peroxides the 10-bromo acid was formed. Only one molecule of hydrogen bromide was added. On adding hydrogen bromide to methylacetylene Kharasch, McNab and McNab[6] obtained 1,2-dibromopropane in the presence of ascaridole, and 2,2-dibromopropane in the absence of peroxides. No monobromopropenes were obtained. The results of these two papers agree with certain portions of the present communication.

The existence of peroxides in many acetylene derivatives has been demonstrated by Young, Vogt and Nieuwland.[7] In view of the importance in the field of olefins of the peroxide effect discovered by Kharasch and Mayo,[8] it has been deemed advisable to study carefully the influence of peroxides on the addition of hydrogen bromide to some convenient member of the acetylene series. For this purpose butylacetylene has been chosen.

When hydrogen bromide is passed into butylacetylene containing an appreciable amount of peroxides, there is formed a mixture of 1-bromo-1-hexene and 1,2-dibromohexane in quantities depending on the conditions of the experiment. At 0° the hydrogen bromide is absorbed very rapidly and at the end of an hour only a small amount of unreacted butylacetylene remains. The product of the reaction is 1-bromo-1-hexene, together with a small amount of 1,2-dibromohexane. If the reaction is carried out for a longer period of time, greater amounts of 1,2-dibromohexane are formed. There is no formation of 2-bromo-1-hexene in the presence of peroxides.

The reaction of hydrogen bromide with butylacetylene in the absence of peroxides occurs at a very much slower rate. In order to accelerate the addition the reaction was carried out at 15°. In one experiment using hydroquinone as the inhibitor and toluene as a solvent, less than one-half of the butylacetylene reacted in six hours, and the products of the reaction consisted of about one-sixth 2-bromo-1-hexene and about five-sixths 1-bromo-1-hexene. Since the hydrogen bromide was not completely free from oxygen, the 1-bromo-1-hexene was probably produced by the formation of a trace of peroxide in the reaction mixture.

It has been found that ferrous salts rapidly destroy the peroxides which are formed in butylacetylene. Consequently, in attempting to add hydrogen bromide to butylacetylene in the absence of peroxides, both hydroquinone and ferrous bromide were finally used as inhibitors. No solvent was used, and the reaction was carried out at 15°. At the end of twelve hours about one-half of the butylacetylene had not yet reacted, and the remainder of the butylacetylene had been converted to 2-bromo-1-hexene and 2,2-dibromohexane, together with a small quantity of 1-bromo-1-hexene.

The addition of hydrogen bromide to butylacetylene in the presence and in the absence of peroxides has therefore been shown to be similar

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[1] Fourteenth paper of a recent series on the reactions of alkylacetylenes; previous paper, *J. Org. Chem.*, **1**, 163 (1936). Original manuscript received January 20, 1936.

[2] Bauer, U. S. Patent 1,414,852; *C. A.*, **16**, 2150 (1922); U. S. Patent 1,540,748; *C. A.*, **19**, 2210 (1925).

[3] Wibaut, *Rec. trav. chim.*, **50**, 313 (1931).

[4] Réboul, *Ann. chim. phys.*, [5] **14**, 465 (1878).

[5] Harris and Smith, *J. Chem. Soc.*, 1572 (1935).

[6] Kharasch, McNab and McNab, THIS JOURNAL, **57**, 2463 (1935).

[7] Young, Vogt and Nieuwland, *ibid.*, **56**, 1822 (1934); *ibid.*, **58**, 55 (1936); *J. Chem. Soc.*, 115 (1935).

[8] Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933).

to the additions of hydrogen bromide which numerous workers have obtained with olefins having a terminal double bond. However, the results with butylacetylene are particularly interesting because the peroxide effect is shown in the addition of both one and two molecules of hydrogen bromide.

In order to obtain further information concerning the manner in which the dibromohexanes were formed, hydrogen bromide was added to 1-bromo-1-hexene and to 2-bromo-1-hexene, both in the presence and in the absence of peroxides. With 1-bromo-1-hexene containing a small amount of peroxide, hydrogen bromide reacted rapidly at 10°, giving at the end of one and one-half hours a 75% yield of 1,2-dibromohexane. No 1,1-dibromohexane was formed. Using hydroquinone and ferrous bromide as inhibitors, hydrogen bromide was passed for one hundred and twenty hours into 1-bromo-1-hexene at room temperature. The only reaction product was a small quantity of 1,2-dibromohexane. It is evident that the "normal" addition to form 1,1-dibromohexane occurs very slowly, if at all, under the conditions used.

In the presence of peroxides hydrogen bromide reacted readily with 2-bromo-1-hexene at 25°, most of the olefin being converted to 1,2-dibromohexane in four hours. No 2,2-dibromohexane was formed. On the other hand, the addition of hydrogen bromide to 2-bromo-1-hexene in the absence of peroxides, using hydroquinone and ferrous bromide as inhibitors, was considerably slower. At a temperature of 23° about two-thirds of the olefin had reacted at the end of nine hours. The product was mainly 2,2-dibromohexane, but a small amount of 1,2-dibromohexane was also formed.

Experimental

Butylacetylene.—The butylacetylene, b. p. 70.5–70.7°, corr., (747 mm.), was prepared from sodium acetylide and butyl bromide in liquid ammonia by a modification of the method described by Lebeau and Picon.[9]

Detection of Peroxides.—In all cases where peroxides were used, they were formed by the unsaturated compounds themselves. The peroxides were estimated colorimetrically, using as the reagent an acidified solution of ferrous ammonium sulfate and ammonium thiocyanate in absolute methyl alcohol. Details of this method are to be published elsewhere.

Addition to Butylacetylene in the Presence of Peroxides.—Two typical experiments will be reported. The reactions were carried out in all experiments in a 500-cc. three-necked flask equipped with an efficient mechanical stirrer, an inlet tube and a reflux condenser. In all cases the products of the reactions were washed with aqueous sodium carbonate and then with water. The products were dried with anhydrous sodium sulfate or with calcium chloride.

In one experiment 1.5 moles of dry hydrogen bromide was passed rapidly into 82 g. (1 mole) of butylacetylene containing a fairly good quantity of peroxides (about 0.8 mole %). The reaction flask was cooled with an ice-bath. At the end of one hour the reaction was stopped. Upon distillation of the reaction mixture through an efficient column there were obtained 5 g. of unreacted butylacetylene, 120 g. of 1-bromo-1-hexene and 3 g. of 1,2-dibromohexane.

In another experiment 2 moles of hydrogen bromide was passed for three hours into 82 g. of butylacetylene containing a fair amount (about 0.6 mole %) of peroxides. The reaction flask was cooled with an ice-bath. From the reaction mixture there were obtained 85 g. of 1-bromo-1-hexene and 91 g. of 1,2-dibromohexane.

Addition to Butylacetylene in the Absence of Peroxides.—Two moles of hydrogen bromide was added to a solution of 102 g. of peroxide-free butylacetylene in 138 g. of toluene to which had been added 0.5 g. of hydroquinone. The toluene facilitated somewhat the absorption of the hydrogen bromide. The reaction flask was maintained at 17°. At the end of six hours the reaction was stopped, and the product washed and dried in the usual manner. Upon distillation of the product there were obtained 67 g. of unreacted butylacetylene, 8 g. of 2-bromo-1-hexene and 38 g. of 1-bromo-1-hexene.

Using 0.25 g. of hydroquinone and 0.5 g. of ferrous bromide as inhibitors, 4 moles of hydrogen bromide was passed into 156 g. of peroxide-free butylacetylene without any solvent. The temperature was kept at 15°, and the reaction continued for twelve hours. There were obtained on distilling the reaction product 42 g. of butylacetylene, 135 g. of 2-bromo-1-hexene, 6 g. of 1-bromo-1-hexene and 39 g. of 2,2-dibromohexane.

Addition to 1-Bromo-1-hexene.—One-half mole of hydrogen bromide was passed during a period of one and one-half hours into 54 g. ($^1/_3$ mole) of 1-bromo-1-hexene containing a trace of peroxides. The reaction temperature was 10°. On distilling the reaction product there were obtained 11 g. of unreacted 1-bromo-1-hexene and 60 g. of 1,2-dibromohexane.

A solution of 138 g. of peroxide-free 1-bromo-1-hexene, 78 g. of benzene, 0.5 g. of hydroquinone and 1 g. of ferrous bromide was kept saturated with hydrogen bromide for one hundred twenty hours at room temperature. Three moles of hydrogen bromide was used. After removing the benzene from the reaction product, there were obtained 120 g. of unreacted 1-bromo-1-hexene and 5 g. of 1,2-dibromohexane. The distillation curve gave no indication of 1,1-dibromohexane.

Addition to 2-Bromo-1-hexene.—In the presence of a small quantity of peroxide 0.4 mole of hydrogen bromide was passed into a solution of 32.6 g. (0.2 mole) of 2-bromo-1-hexene in 39 g. of benzene. The solution was kept at 25°. The reaction was continued for four hours. The

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[9] Lebeau and Picon, *Compt. rend.*, **156**, 1077 (1913); Picon, *ibid.*, **158**, 1346 (1914); *ibid.*, **169**, 32 (1919).

reaction product consisted of 3.5 g. of 2-bromo-1-hexene and 41 g. of 1,2-dibromohexane.

One-half mole of hydrogen bromide was passed for nine hours into a solution of 32.6 g. of peroxide-free 2-bromo-1-hexene in 39 g. of benzene; 0.2 g. each of hydroquinone and ferrous bromide were used to inhibit peroxide formation. The temperature of the reaction was 23°. The reaction product contained 10 g. of unreacted 2-bromo-1-hexene, 24 g. of 2,2-dibromohexane and 4 g. of 1,2-dibromohexane.

Identification of Products.—The properties of 2-bromo-1-hexene, b. p. 132.5–133.5° (740 mm.), n^{19}_{D} 1.4555, d_{20} 1.1960, agree closely with those reported by Bourguel:[10] b. p. 134° (760 mm.), n^{19}_{D} 1.455, d_{19} 1.203.

The 1-bromo-1-hexene had the properties: b. p. 139–141° (751 mm.), n^{20}_{D} 1.4596, d_{21} 1.1998. Bachman[11] reported for this compound: b. p. 138–140° (747 mm.), n^{20}_{D} 1.4584, d^{20}_{20} 1.1910. The slight discrepancy in these physical constants may be caused by a difference in the ratio of *cis-trans* isomers obtained in the two cases. The 1-bromo-1-hexene was analyzed for bromine by the method of Chablay, as modified by Vaughn and Nieuwland:[12] calcd. for $C_6H_{11}Br$, 49.0; found, Br, 49.1.

The properties of the 1,2-dibromohexane, b. p. 89–90° (18 mm.), n^{20}_{D} 1.5023, d_{21} 1.5767, agree well with those reported by Schmitt and Boord:[13] b. p. 89–90° (18 mm.), n^{20}_{D} 1.5024, d_{20} 1.5774.

The 2,2-dibromohexane has not been reported previously. The following physical constants were obtained: b. p. 83.5–84.0° (24 mm.), n^{22}_{D} 1.4930, calcd. MR_D 45.45, found MR_D 45.57, d_{22} 1.5463. *Anal.*:[12] calcd. for $C_6H_{12}Br_2$: Br, 65.5; found: Br, 65.4. The identity of the 2,2-dibromohexane was established by hydrolyzing it to 2-hexanone. This was accomplished by refluxing with silver sulfate in 10% sulfuric acid. The 2-hexanone boiled at 126.1° (747 mm.), reported b. p. 126.0–126.5° (760 mm.),[14] and the semicarbazone melted at 118°, reported m. p. 118°.[15]

Summary

1. The addition of hydrogen bromide to butylacetylene in the presence of peroxides derived from butylacetylene yielded 1-bromo-1-hexene and 1,2-dibromohexane.

2. In the absence of peroxides hydrogen bromide yielded mainly 2-bromo-1-hexene and 2,2-dibromohexane.

3. The addition of hydrogen bromide was much more rapid in the presence of peroxides than in their absence.

4. The addition of hydrogen bromide to 1-bromo-1-hexene in the presence of peroxides formed only 1,2-dibromohexane, while in the absence of peroxides scarcely any reaction occurred under the conditions used. No 1,1-dibromohexane was formed in either case.

5. In the presence of peroxides 2-bromo-1-hexene yielded with hydrogen bromide only 1,2-dibromohexane; under peroxide-free conditions the chief product was 2,2-dibromohexane, the other product being 1,2-dibromohexane.

Notre Dame, Indiana Received March 28, 1936

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(10) Bourguel, *Compt. rend.*, **177**, 688 (1923).

(11) Bachman, This Journal, **55**, 4282 (1933).

(12) Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).

(13) Schmitt and Boord, This Journal, **54**, 760 (1932).

(14) Clarke, *ibid.*, **34**, 681 (1912).

(15) Michael, *ibid.*, **41**, 416 (1919).

[Contribution from the Furman Chemical Laboratory, Vanderbilt University]

Extensions of the Leuckart Synthesis of Amines

By A. W. Ingersoll, J. H. Brown, C. K. Kim, W. D. Beauchamp and Garland Jennings

The conversion of certain ketones (and aldehydes) to the corresponding amines by heating with excess ammonium formate was described by Leuckart[1] as early as 1885. The mechanism of the reaction has been discussed by Wallach,[2c] but is not definitely known. The equation

$$\begin{aligned} &R—CO—R' + 2HCO_2NH_4 \longrightarrow \\ &\qquad R—CH(NHCHO)R' + 2H_2O + NH_3 + CO_2 \end{aligned}$$

appears to summarize the primary reaction, although formamide is doubtless an intermediate and may be used instead of ammonium formate. The amine is formed by subsequent hydrolysis of the formyl derivative.

Although Leuckart's method has been applied by Wallach[2] to a number of alicyclic and terpenoid ketones, and appears to be rather general, it has found little use by others. Possibly the obvious advantages of economy and simplicity have appeared to be outweighed by the unsatisfactory procedures that have so far been suggested. Leuckart himself, and also Wallach, ordinarily heated the reagents in a sealed tube at 210–240°. In some instances, however, Wallach[2b,2c] and others[3] have shown that the primary reaction

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(1) Leuckart, *et al.*, *Ber.*, **18**, 2341 (1885); **19**, 2128 (1886); **20**, 104 (1887); **22**, 1409, 1851 (1889).

(2) Wallach, *et al.*, (a) *ibid.*, **24**, 3992 (1891); *Ann.*, **269**, 347 (1892); **276**, 306 (1893); (b) *ibid.*, **300**, 283 (1898); (c) *ibid.*, **343**, 54 (1905).

(3) (a) Freylon, *Ann. Chim.*, [8] **15**, 141 (1908); (b) Read and Robertson, *J. Chem. Soc.*, 2217 (1926); (c) Read and Johnston, *ibid.*, 231 (1934).

occurs, though rather slowly, upon refluxing the reagents at atmospheric pressure. In a recent example Read and Johnston[3c] have reported only a 20–25% conversion of carvomenthone to carvomenthylamines after forty-eight hours of refluxing at 130°. Thus neither the sealed tube process nor the refluxing process is attractive and the method is also known to yield the corresponding secondary and tertiary amines as by-products.

Since other work in this Laboratory required large quantities of a variety of asymmetric amines, which are conveniently derived from ketones, it was sought to improve Leuckart's method with a view to adapt it to large scale laboratory use and, if possible, to extend its scope. As the result of several years of experience a simple procedure has been worked out which, when applied to some twenty ketones of various types, has given the corresponding primary amines in yields usually ranging from 60 to 85% of the theoretical and in amounts as large as several hundred grams per run. It has been found that the proportion of secondary and tertiary amine produced is so small as to cause no difficulties. In most cases a uniform procedure can be followed, with slight modifications for special cases. A number of amines have been prepared by this method for which no other method of synthesis appears feasible.

In preliminary experiments with the refluxing procedure it soon appeared that formamide rather than ammonium formate must be made the effective reagent. Thus when the process was tried with acetophenone and initially solid ammonium formate, as suggested by Freylon,[3a] it was found that the mixture boiled freely at 150–160° but remained in two layers; no appreciable reaction occurred in ten hours. On the other hand, when water was allowed to distil during the process or when formamide was used initially, the mixture soon became homogeneous and the reaction occurred in a few hours at 150 to 190°. The improved procedure involves, therefore, essentially a slow distillation, with occasional return of any ketone that may distil; both processes may be combined by the use of an automatic separator. The general procedure is described in the Experimental part.

Scope of the Method.—The improved method has been studied thus far principally in instances in which the main concern was the suitability of the amine for other work. In its usual form the method appears best adapted to the conversion of stable, water-insoluble ketones boiling at about 120° or higher. These include the higher aliphatic ketones, acetophenone and its numerous analogs, and certain terpenoid ketones. For such ketones the yields are consistently good and the method is definitely superior in economy and convenience to the familiar methods involving the formation and reduction of ketoximes.

Of even greater interest is the fact that the method can be used successfully in instances in which the reduction of an oxime is inadmissible. Thus it was found that when *p*-chloroacetophenoneoxime was reduced in the usual way with sodium and alcohol or with sodium amalgam and acetic acid, about half of the resulting mixture of amines was α-phenylethylamine, formed by the removal of nuclear halogen. On the other hand, the improved Leuckart method gave a high yield of pure α-*p*-chlorophenylethylamine. In the same way *p*-bromoacetophenone and even *m*-nitroacetophenone were readily converted to the corresponding amines.

When applied to benzalacetone or to carvone the method yielded chiefly a neutral resin and only small amounts of the corresponding amines. From present experience the method is believed to be unsuitable for application to α,β-unsaturated ketones, but otherwise appears widely applicable.

Most of the amines that were prepared have not been described previously. For these the principal constants, derivatives and analyses are given in the accompanying table. It is hoped to describe the new amines more fully in later papers. There are also included in the table yield data on these amines and on a few other representative amines. In most cases the stated yields are the average of two or more runs and make no allowance for recovered ketone.

Experimental

General Procedure.—A satisfactory ammonium formate–formamide reagent, sufficient for one mole of ketone, is made most economically as follows. In a 1-liter round-bottomed flask is placed 215 g. (4 mole-equivalents of ammonia) of commercial ammonium carbonate–carbamate. The flask is fitted with a cork bearing a thermometer that extends nearly to the bottom, a small separatory funnel, and a wide bent tube attached for distillation to a short, wide condenser. There is then added cautiously 215–230 g. (4.1 moles) of commercial 85–90% formic acid. When the reaction moderates the mixture is heated cautiously and then slowly distilled until the temperature is about 165°. The same amount of reagent can

TABLE I

Ketones	Amines	Yield, %	B. p., °C.[j]	Sp. gr.	n^{25}_{D}	Benzoyl deriv., °C.[j]	Hydrochloride		
							M. p., °C.[j]	Analysis, % Cl ion Calcd.	Found
Acetophenone	*dl*-α-Phenylethyl-[c]	72	184–185	...	...	...	...	...	...
p-Methylacetophenone	*dl*-α-*p*-Tolylethyl-[d]	72	204–205	...	...	...	...	...	...
m-Methylacetophenone[a]	*dl*-α-*m*-Tolylethyl-[f]	70	204–205	0.9344^{20}_{20}	1.4924	113–114	164–165	20.60	20.79
p-Chloroacetophenone	*dl*-α-*p*-Chlorophenylethyl-[f]	82	105/10 mm.	1.1178^{20}_{20}	1.5420	144–145	192–193	18.46	18.47
p-Bromoacetophenone	*dl*-α-*p*-Bromophenylethyl-[f]	79	116/10 mm.	1.3910^{20}_{20}	1.5641	150–151	213–214	14.99	15.02
p-Methoxyacetophenone	*dl*-α-*p*-Methoxyphenylethyl-[f]	68	126/20 mm.	1.0174^{25}_{4}	1.5280	117–118	160–161	18.90	18.79
p-Phenylacetophenone	*dl*-α-*p*-Xenylethyl-[e]	77	[i]	...	...	178–179	220–221		
p-Phenoxyacetophenone[b]	*dl*-α-*p*-Phenoxyphenylethyl-[f]	69	[i]	...	...	113–114	180–181	14.21	14.09
β-Acetonaphthone	*dl*-Methyl-β-naphthylcarbin-[f]	84	[i]	...	...	151–152	198–199	17.09	17.19
m-Nitroacetophenone	*dl*-α-*m*-Nitrophenylethyl-[f]	56	[i]	...	...	156–157	223–224	18.81	18.76
dl-Fenchone	*dl*-Fenchyl-[f]	85	190–191	0.8971^{20}_{20}	1.4711	131–133	>250	18.70	18.72
d-Camphor	*d*-Bornyl- + neobornyl-[g]	62	...	...	...	...	...	...	...
Pinacolone	*dl*-Methyl-*t*-butylcarbin-[h]	52	102–103	...	...	98–99	>250	...	...

[a] Prepared from *m*-tolylmagnesium bromide and acetonitrile. The yield was poor. *Cf.* Jaspers, *Bull. soc. chim. belg.*, **34**, 182 (1925). [b] From diphenyl ether and acetic anhydride in 90–94% yields by the procedure of Noller and Adams, THIS JOURNAL, **46**, 1892 (1924). B. p. 182° (8 mm.), m. p. 50°; oxime m. p. 136°; semicarbazone m. p. 164°; 2,4-dinitrophenylhydrazone m. p. 213°, *cf.* Kipper, *Ber.*, **38**, 2491 (1905). [c] Kraft, *ibid.*, **23**, 2783 (1890). [d] Stenberg, *Z. physik. Chem.*, **70**, 534 (1910). [e] Ingersoll and White, THIS JOURNAL, **54**, 274 (1932). [f] Not previously described. [g] The mixture contains about 70% of neobornylamine. *Cf.* Forster, *J. Chem. Soc.*, **73**, 386 (1898). [h] Markownikoff, *Ber.*, **32**, 1448 (1889). [i] Distilled with partial decomposition at 10 mm. Purified by crystallization of the hydrochloride or *p*-toluene sulfonate. [j] Temperature taken with short range thermometer without further correction.

be obtained by distilling 250 g. of commercial solid ammonium formate instead of the reagents mentioned, but this offers no advantage.

To the reagent described above the ketone is added and the heating continued with a small flame. The reaction occurs fairly rapidly in the range 160–185° and may be accompanied by mild foaming. Water, ammonia, carbon dioxide and more or less ketone distil. The distillate is conveniently collected in a separatory funnel. The mixture gradually becomes homogeneous as the proportion of formamide increases. The distilled ketone, if any, is separated from time to time and returned to the reaction mixture. Alternatively, when rather volatile ketones are used, the reaction may be run in a flask fitted with a simple automatic separator so arranged as to return the (upper) ketone layer and discharge the aqueous layer.

When distillation of water practically ceases and the temperature reaches 175–185°, the temperature is maintained in this range for three to ten hours longer. In most cases three to four hours is sufficient; a longer time was found necessary only for "hindered" ketones such as camphor and fenchone. The end of the reaction is fairly clearly marked when the deposition of ammonium carbonate in the condenser nearly ceases. The rate of reaction increases somewhat with temperature, but above about 185° a faint odor of cyanide becomes apparent and the mixture tends to change from straw-color to dark brown The heating may be interrupted and resumed at any time.

When the reaction is complete the mixture is cooled and stirred thoroughly with twice its volume of water. The aqueous layer is separated and may be used for the recovery of formamide by distilling to 165°. Recovered formamide should be used only with the same ketone. The formyl derivative of the amine, mixed with unused ketone, may or may not solidify. It can be purified by vacuum distillation or crystallization, but this is not necessary. The crude, water-insoluble material is refluxed with about 100 cc. of concentrated hydrochloric acid for each mole of ketone used. Water may be added, if necessary, to keep the amine hydrochloride in solution. Hydrolysis is usually complete in thirty to fifty minutes, as shown by the solution of all but a small amount of inert material, consisting of unchanged ketone and condensation products. This is extracted with small portions of benzene and discarded or saved for recovery of the ketone. The latter may sometimes be recovered conveniently by steam distillation of the acid mixture. When the ketone is resinified by the action of hot acid, it may best be steam-distilled previously to hydrolysis. The corresponding formyl derivative of the amine is usually much less volatile, but may also distil with steam.

The amine is obtained from the aqueous acid solution by a method appropriate to its physical properties. When sufficiently volatile it is best purified by liberation with alkali and distillation with steam. The small amounts of secondary and tertiary amines present are thereby almost completely left behind. The distilled amine is extracted with benzene, dried, and redistilled as usual. When the amine is not very volatile it may often be obtained directly from the acid solution by fractional crystallization of the hydrochloride or may be purified in other ways.

Notes and Modifications.—The above procedure was not satisfactory with camphor because the sublimate rapidly clogged the apparatus. This difficulty was readily overcome by adding to the camphor about one-half its weight of nitrobenzene. The latter is unaffected by heating with formamide and serves to liquefy the camphor in both the reaction mixture and the distillate. The nitrobenzene and unchanged camphor are removed by steam distillation following the hydrolysis of the amine.

A similar procedure was fairly successful when applied to pinacolone. The nitrobenzene in this case appeared to diminish the distillation of the rather volatile ketone (b. p. 106°) and also served to extract it from the aqueous portion of the distillate. However, the general procedure described above is not regarded as suitable for the more volatile and water-soluble ketones. With such ketones it would appear better to start with substantially pure formamide and carry out the reaction entirely by refluxing. The small amount of water formed in the reaction causes no difficulty. In comparative experiments upon acetophenone and fenchone the yield was 4–6% better with pure formamide (4 moles) than with the usual reagent. With cheap ketones, however, the use of formamide is not justified, because of the extra cost.

In a series of experiments with acetophenone the percentage yields of amine were 53, 62, 72 and 72, respectively, when the molar ratios of reagent to ketone were 3.0, 3.5, 4.0 and 5.0. In experiments with 2:1 and 4:1 ratios of pure formamide the yields were 23 and 78%, respectively.

Runs were made with from 0.1 mole to 4.0 moles of ketone without important variations in yield. There is no apparent reason why the scale may not be as large as desired.

Summary

1. The Leuckart synthesis of amines from ketones has been improved and adapted to large scale use. A general procedure is described.

2. Eight new amines have been prepared and described.

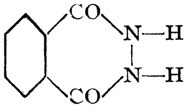
NASHVILLE, TENNESSEE RECEIVED JUNE 29, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

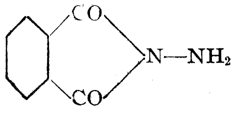
The Methyl and Phenyl Derivatives of the Nitrophthalhydrazides

BY C. N. ZELLNER AND GREGG DOUGHERTY

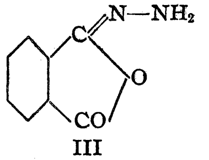
The brilliant chemiluminescence of some of the phthalhydrazide derivatives has created an interest in the chemistry and structure of these compounds. Of the three structures which have been proposed for phthalhydrazide



I



II



III

I and II have received the most serious consideration. The work of Radulescu and Georgescu,[1] Moyer,[2] and Rowe and Peters[3] on the various methylated and acetylated phthalhydrazides has indicated that structure I or a tautomeric modification of it is preferable to structure II. These workers confined their efforts to phthalhydrazide which was not substituted in the benzene ring.

It is obvious that, if the hydrazide structure I is correct, the presence of a substituent in the aromatic nucleus would make possible the existence of various isomeric non-nuclear alkyl or aryl derivatives not capable of existence on the basis of the aminophthalimide formula II. Also the study of a nuclear substituted hydrazide should give some indication of the normal tautomeric condition of the molecule. In order to test these points the present work with the nitrophthalhydrazides was undertaken.

The reaction of 3-nitrophthalic anhydride with methylhydrazine acetate gave two isomeric monoethyl derivatives which were produced in almost equal proportions, one melting at 305°, and the other at 273°. Both were readily acetylated, the two monomethyl monoacetyl derivatives melting at 211 and 144°, respectively. (All melting points have been corrected.) The existence of two *n*-methyl compounds is easily accounted for on the basis of the hydrazide structure

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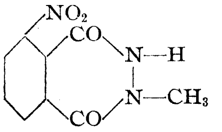
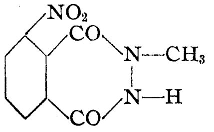
[1] Radulescu and Georgescu, *Bull. soc. chim.*, **37**, 881 (1925).

[2] Moyer, private communication.

[3] Rowe and Peters, *J. Chem. Soc.*, 1331 (1933).

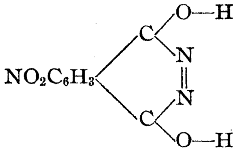


and

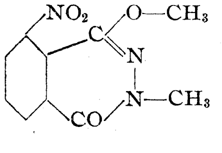


It is not yet possible to say which of the structures should be assigned to which isomer. On the basis of Mihailescu's aminophthalimide structure II,[4] this type of isomerism would not be possible.

The same two *n*-methyl-3-nitrophthalhydrazides were obtained by treating 3-nitrophthalhydrazide with dimethyl sulfate in alkaline solution. This is an indication that the double enolic form, *i. e.*,



does not occur to any extent at least in alkaline solution, otherwise an *o*-methyl derivative would have been obtained. With excess dimethyl sulfate two dimethylnitrophthalhydrazides were obtained, melting at 207 and 138–139°, respectively. The derivative of m. p. 207° was also prepared by reaction of the higher melting *n*-methyl-3-nitrophthalhydrazide with dimethyl sulfate in alkaline solution, whereas the lower melting dimethyl derivative was obtained from the lower melting mono-methyl compound. Again, the existence of the isomeric dimethyl derivatives is evidence against Mihailescu's formula. The fact that the two were obtained by the methods outlined indicates strongly that they are *n*-methyl *o*-methyl derivatives



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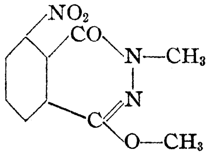
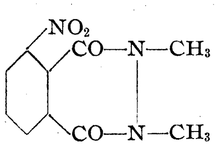
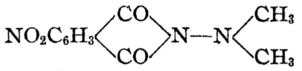


This was further substantiated by the preparation of a third dimethyl derivative from 3-nitrophthalic anhydride and symmetrical dimethyl hydrazine. In this case there is little doubt but that both methyl groups are attached to nitrogen:

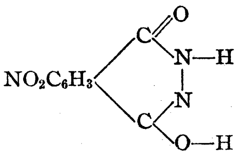


A fourth dimethyl derivative was obtained from the anhydride and unsymmetrical dimethyl hydrazine to which the aminophthalimide structure,

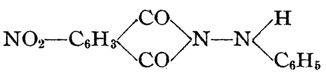


must be assigned. The remaining structurally possible dimethyl derivative in which both methyl groups are attached to oxygen is apparently not formed by any of the ordinary methods of methylation.

Since in the alkylation of 3-nitrophthalhydrazide in alkaline solution, the first methyl group goes to the nitrogen and the second to oxygen, it appears that the lactam–lactim form of the compound, is present and most reactive under the conditions. This conclusion, also arrived at by Rowe and Peters,[3] is important when considering the mechanism of the oxy-luminescence of phthalhydrazide derivatives, always carried out in alkaline solution.



Using 4-nitrophthalic anhydride and the hydrazide, a set of monomethyl and dimethyl derivatives was prepared similar to those obtained from the 3-nitro compounds. These are described in the experimental part. The reaction between phenylhydrazine and the 3 and 4-nitrophthalic anhydrides was studied. In this case only one of the two possible *n*-phenylhydrazides was formed in sufficient quantity to permit isolation and purification. A second compound was formed of the anilinophthalimide type, so that methylhydrazine and phenylhydrazine do not behave in quite the same way in this reaction. The anilinophthalimide type is insoluble in alkalies which differentiates it sharply from the *n*-phenyl derivatives of the nitrophthalhydrazides.



Experimental

α-3-Nitro-N-methyl Phthalhydrazide.—9.6 g. (0.05 mole) of 3-nitrophthalic anhydride was dissolved in 50 cc. of acetic acid. To the hot solution, a 20-cc. aqueous solution of 7.2 g. (0.05 mole) of mono-methylhydrazine sulfate and 6.8 g. of sodium acetate crystals, was added. The reaction mixture was heated to boiling, using an air condenser, until all the acetic acid was driven off. The residue was washed in portions of warm water and the two isomers were fractionally recrystallized from alcohol, until constant melting points were obtained. The more insoluble isomer melted at 305° (cor.).

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[4] Mihailescu and Protopopescu, *Chem. Zentr.*, **101**, II, 3021 (1930); *Bulet. Soc. Chim. Romania*, **12**, 95 (1930).

Anal. Calcd. for $C_9H_7O_4N_3$: C, 48.86; H, 3.19. Found: C, 48.62; H, 3.09.

Boiled in acetic anhydride, it yielded a mono-acetyl derivative which when recrystallized from alcohol melted at 211° (cor.).

Anal. Calcd. for $C_{11}H_9O_5N_3$: C, 50.18; H, 3.45. Found: C, 50.52; H, 3.72.

β-3-Nitro-N-methyl Phthalhydrazide.—The more soluble β-compound melted at 273° (cor.).

Anal. Calcd. for $C_9H_7O_4N_3$: C, 48.86; C, 48.86; H, 3.19. Found: C, 48.56; H, 3.19. Its acetyl derivative melted at 144° (cor.).

Anal. Calcd. for $C_{11}H_9O_5N_3$: C, 50.18; H, 3.45. Found: C, 50.17; H, 3.71.

3-Nitro-N,N'-dimethyl Phthalhydrazide.—In like manner, from 3-nitro phthalic anhydride and symmetrical dimethylhydrazine hydrochloride and sodium acetate; m. p. 203° (cor.).

Anal. Calcd. for $C_{10}H_9O_4N_3$: C, 51.05; H, 3.86. Found: C, 50.89; H, 4.06.

3-Nitro-N-dimethylamino Phthalimide.—From 3-nitrophthalic anhydride and *unsym.*-dimethylhydrazine hydrochloride and sodium acetate; m. p. 200–201° (cor.).

Anal. Calcd. for $C_{10}H_9O_4N_3$: C, 51.05; H, 3.86. Found: C, 50.93; H, 4.08.

3-Nitro-N-methyl *o*-Methyl Phthalhydrazides.—Prepared by the action of excess dimethyl sulfate, in a dilute alkaline solution, on 3-nitrophthalhydrazide. The two isomers are separated by fractional crystallization from alcohol; the α-derivative melted at 207° (cor.).

Anal. Calcd. for $C_{11}H_9O_5N_3$: C, 51.05; H, 3.86. Found: C, 51.31; H, 3.97. The β-derivative melted at 138–139° (cor.).

Anal. Calcd. for $C_{11}H_9O_5N_3$: C, 51.05; H, 3.86. Found: C, 51.20; H, 3.69.

The former was also obtained from α-3-nitro-N-methylphthalhydrazide with dimethyl sulfate, in alkaline solution, and the latter from the β-derivative.

In like manner from 4-nitrophthalic anhydride and the corresponding hydrazines the following were obtained: **α-4-Nitro-N-methyl Phthalhydrazide and β-4-Nitro N-methyl Phthalhydrazide** separated by fractional crystallization from alcohol. The α-compound melted at 310–311° (cor.).

Anal. Calcd. for $C_9H_7O_4N_3$: C, 48.86; H, 3.19. Found: C, 48.89; H, 3.11.

Its acetyl derivative melted at 213–214° (cor.).

Anal. Calcd. for $C_{11}H_9O_5N_3$: C, 50.18; H, 3.45. Found: C, 50.23; H, 3.50.

The β-compound melted at 271–272° (cor.). Upon acetylation it yields an acetyl derivative melting at 170–171° (cor.).

Anal. Calcd. for $C_{11}H_9O_5N_3$: C, 50.18; H, 3.45. Found: C, 49.93; H, 3.36.

4-Nitro-N,N'-dimethyl Phthalhydrazide.—M. p. 203.5° (cor.).

Anal. Calcd. for $C_{10}H_9O_4N_3$: C, 51.05; H, 3.86. Found: C, 51.03; H, 3.86.

4-Nitro-N-dimethylamino Phthalimide.—M. p. 202° (cor.). A mixed melting point determination with the preceding compound showed a large depression.

4-Nitro-anilino Phthalimide.—Prepared by refluxing 4-nitrophthalic anhydride and phenylhydrazine in HOAc for two and a half hours. On cooling, the crystals were filtered and treated with sodium carbonate solution. The insoluble product, recrystallized from alcohol several times, melted at 182° (cor.).

Anal. Calcd. for $C_{14}H_9O_4N_3$: C, 59.31; H, 3.21. Found: C, 59.54; H, 3.26.

4-Nitro-N-phenyl Phthalhydrazide.—Was obtained on acidifying the above sodium carbonate solution. After three recrystallizations from alcohol, it melted at 253° (cor.).

Anal. Calcd. for $C_{14}H_9O_4N_3$: C, 59.31; H, 3.21. Found: C, 59.24; H, 3.33; C, 59.38; H, 3.33.

Its acetyl derivative melted at 186° (cor.).

Anal. Calcd. for $C_{16}H_{11}O_5N_3$: C, 59.08; H, 3.38. Found: C, 58.81; H, 3.31.

3-Nitroanilino Phthalimide.—From 3-nitrophthalic anhydride and phenylhydrazine, after washing in dilute sodium hydroxide solution, and recrystallization from alcohol: m. p. 198–199° (cor.).

Anal. Calcd. for $C_{14}H_9O_4N_3$: C, 59.31; H, 3.21. Found: C, 59.39; H, 3.18.

Summary

Evidence has been obtained in favor of the hydrazide structure as opposed to the amino–imide structure for substituted phthalhydrazides. It has been shown that in the methylation of the nitrophthalhydrazides in alkaline solution, the compounds behave as if they possessed the lactam–lactim structure.

The preparation of various methylated and phenylated nitrophthalhydrazides has been described and some of their properties noted.

PRINCETON, N. J. RECEIVED JULY 15, 1936

NOTES

New Types of Racemization Reactions

By Ernst Bergmann and Alfred Bondi

To the number of racemization reactions which obviously are of fundamental importance for our knowledge of the stability of spacial configurations, three new types have recently been added: (a) the racemization of methylalkyliodomethanes by interaction with iodide ions,[1] (b) the racemization of 2-bromohexane during its conversion into the Grignard compound,[2] and (c) the racemization occurring during the interaction between active ethyl propylmethylacetate and phenylmagnesium bromide.[3] Only the first of these three types has so far a theoretical and experimental treatment.

For case (b) one would perhaps be inclined to assume that racemization is due to electrolytic dissociation of the Grignard compound. But this assumption seems inadmissible, since negative carbonium ions seem to be sufficiently stable,[4] while positive ions of carbon are unstable.[5] Therefore one has probably to conclude that the racemization belongs to type (a): the bromide is racemized by bromide ions, which are formed by the ordinary equilibrium reaction $2RMgBr \rightleftharpoons R_2Mg + MgBr_2$. The case, therefore, is analogous to the racemization of phenylmethylchloromethane by interaction with magnesium or sodium metal.[1,6]

For case (c) the following suggestion has been advanced by Bergmann and Hartrott.[3] The ester does not undergo racemization—it is unstable only in alkaline solution[7]—but the carbinol is subjected to an equilibrium $(Me)(Pr\text{-}\alpha)CH\text{-}C(OH)Ph_2 \rightleftharpoons H_2O + (Me)(Pr\text{-}\alpha)C{=}CPh_2$, whereby the asymmetry is destroyed. It is well known that diphenylalkylcarbinols are easily dehydrated. If this explanation is correct, ethyl propylmethylacetate should give optically active carbinols with simple aliphatic alkylmagnesium halides, since compounds like (2-pentyl)-diethylcarbinol, $(Me)(Pr\text{-}\alpha)CHC(OH)Et_2$, do not lose water so easily. The conclusion has been confirmed by experiment. Into a solution of ethylmagnesium bromide (from 2.5 g. of magnesium and 11 g. of ethyl bromide), active methyl propylmethylacetate (4 g., rotation in acetone, $l = 1$, $c = 2.70$, α_D $-0.19°$; hence $[\alpha]_D$ $-7.04°$) was introduced. The rather violent reaction was completed by boiling for thirty minutes, then the mixture was decomposed with ice and ammonium chloride and the ethereal layer dried with anhydrous sodium sulfate and evaporated. The (2-pentyl)-diethylcarbinol boiled at 92–93° (32 mm.); yield 2.9 g. Calcd. for $C_{10}H_{22}O$: C, 75.9; H, 14.0. Found: C, 75.8, 75.4; H, 14.4, 14.1. Rotation in acetone: $l = 1$, $c = 2.80$, α^{22}_D $-0.365°$; hence $[\alpha]^{22}_D$ $-13.04°$.

The Daniel Sieff Research Institute
Rehovoth, Palestine
Received April 9, 1936

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(1) Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, **20B**, 161 (1933); *Trans. Faraday Soc.*, **32**, 843 (1936).

(2) Porter, This Journal, **57**, 1436 (1935).

(3) Bergmann and Hartrott, *J. Chem. Soc.*, 1218 (1935).

(4) Wallis and Adams, This Journal, **54**, 4753 (1932); **55**, 3838 (1933).

(5) Bergmann and Polanyi, *Naturwissenschaften*, **21**, 378 (1933).

(6) Ott, *Ber.*, **61**, 2124 (1926).

(7) Menon and Peacock, *J. Ind. Chem. Soc.*, **12**, 268 (1935).

The Preparation of Pure Apocodeine and its Hydrochloride

By Karl Folkers

Early preparations of apocodeine were complex mixtures.[1] Knorr obtained "pseudoapocodeine"[2] by melting codeine with oxalic acid, and later he showed[3] that his apocodeine was identical with the monomethylation product of apomorphine; although this latter product had been reported earlier by Pschorr,[4] but with widely different physical properties. Later methods[5] of making apocodeine from codeine with zinc and sodium chlorides still introduced apomorphine impurities, which necessitated the use of a troublesome perchlorate, chromate or phosphate salt for purification.

Nevertheless, a certain confusion exists in the

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(1) Small, "Chemistry of the Opium Alkaloids," Supp. No. 103, Public Health Reports, 1932, pp. 183, 362.

(2) Knorr and Roth, *Ber.*, **40**, 3355 (1907). The name pseudoapocodeine was introduced by Knorr as he believed pseudocodeine to be an intermediate in the transformation of the morphine nucleus to the aporphine nucleus. Apocodeine is the generally accepted name, and it suggests the same relationship to codeine that apomorphine has to morphine.

(3) Knorr and Raabe, *ibid.*, **41**, 3050 (1908).

(4) Pschorr, Jaeckel and Fecht, *ibid.*, **35**, 4377 (1902).

(5) German Patent 489,185, *Frdl.*, **16**, 2485.

literature[6] concerning the chemical properties of pure apocodeine.

The herein described method is an improvement of the Knorr reaction, and a confirmation of Knorr's properties of apocodeine with ethanol of crystallization. The pure anhydrous base and hydrochloride have not been described previously.

Apocodeine.—Twenty grams of anhydrous codeine and 60 g. of anhydrous oxalic acid,[7] were heated for one and one-half hours at 150–155° bath temperature with very slow stirring. The melt was cooled and diluted with 250 ml. of water. After complete solution, it was further diluted to 600 ml. in a separatory funnel, shaken with 300 ml. of ether, and the bases precipitated with addition of concentrated ammonia solution. Too slow operation caused troublesome crystallization of ammonium oxalate. The ether layer was separated, filtered and distilled *in vacuo*. A residue of 5.8 g. remained, which was dissolved in 15 ml. of absolute ethanol. Nearly pure apocodeine with a molecule of ethanol crystallized on standing at 10°; yield 2.7–2.8 g. (12.8%). One crystallization gave pure white products of m. p. 104.5–106.5° with gas evolution $[\alpha]^{23}\text{D}$ −90.0, *C*, 0.533, abs. ethanol, $l = 1$. Further crystallization did not change the melting point or optical rotation.

Anal. Calcd. for $C_{18}H_{19}O_2N{\cdot}C_2H_5OH$: C, 73.35; H, 7.70; C_2H_5OH, 14.06. Found: C, 72.99, 73.01; H, 7.57, 7.76; C_2H_5OH, 13.76.

The base was best purified by recrystallization from absolute ethanol. The use of the hydriodide as Knorr suggested resulted in partial oxidation. The crystals showed no ready tendency to oxidize, unless they were finely pulverized. The ethanol was lost very slowly at 25° (2 mm.), but readily at 78° (2 mm.). The anhydrous base showed m. p. 122.5–124.5°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.82; H, 6.81. Found: C, 76.63, 76.80; H, 7.02, 7.06.

As Knorr described, there were ether and water insoluble bases present. It was found, however, that nearly all the apocodeine was extracted by the ether. In one experiment very little more was obtained by redissolving the insoluble bases with acid, reprecipitating, extracting etc. A third repetition of this process yielded no more apocodeine. Thus it was not necessary to bring all the precipitated bases into ether solution as Knorr described. In fact, the moderate insolubility of pseudocodeine[8] and the amorphous products in ether make the first extraction one of considerable purification.

Apocodeine Hydrochloride.—To a solution of the base in absolute ethanol was added the calculated amount of dry hydrogen chloride in absolute ethanol and, while hot, absolute ether was added until crystallization started. The yield of pure white salt was quantitative; m. p. softening started at 140°, dec. at 260–263°; $[\alpha]^{22}\text{D}$ −41.3 to 43.3°; *c*, 0.508; H_2O, $l = 1$. Recrystallization from 95% ethanol and ether did not alter the physical constants. The salt was practically anhydrous.

Anal. Calcd. for $C_{18}H_{19}O_2N{\cdot}HCl$: C, 68.00; H, 6.35. Found: C, 68.26, 67.92; H, 6.35, 6.22.

RESEARCH AND DEVELOPMENT
MERCK & CO., INC.
RAHWAY, N. J.

RECEIVED JULY 3, 1936

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[6] For example, see Krayer, *Arch. exptl. Path. Pharm.*, **111**, 60 (1920). Schwartze, *Arch. intern. pharmacodynamie*, **41**, 461 (1931).

[7] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 415.

[8] Lutz and Small, THIS JOURNAL, **54**, 4723 (1932).

The Thermal Decomposition of Acetone

BY JOHN R. HUFFMAN[1]

The present experiments were undertaken to discover whether the unimolecular rate constant for the thermal decomposition of acetone fell off at low pressures and in such a case to apply the theories of Rice and Ramsperger and of Kassel.[2] Recently Winkler and Hinshelwood[3] working at 875°K. and pressures down to 2.5 mm. reported that this decrease of rate constant started at 100 mm.

Acetone was decomposed in a 200-cc. silica bulb in a furnace automatically controlled to

TABLE I

Run	P_0, mm.	$k \times 10^4$	Run	P_0, mm.	$k \times 10^4$
59	128.6	10.86	46	56.2	9.70
65	127.2	11.39	63	55.9	9.85
64	124.3	11.17	42	53.5	9.41
69	120.4	10.72	22	47.8	9.38
71	115.5	11.42	37	45.9	8.80
58	112.6	11.33	35	41.6	8.68
73	107.0	10.96	24	34.9	9.05
72	101.2	10.32	75	35.2	8.50
57	100.2	10.69	76	35.1	8.66
61	100.2	11.31	36	27.8	8.12
66	99.0	11.27	32	27.8	7.98
70	98.6	11.35	45	25.6	8.18
60	86.7	10.78	31	22.9	7.65
68	83.4	10.42	23	21.5	8.07
74	80.4	10.60	52	21.85	8.36
50	78.8	10.93	34	18.54	7.43
40	78.3	10.75	29	17.86	7.68
51	78.2	10.48	27	17.08	7.43
55	74.3	10.79	44	16.60	7.48
62	79.1	10.32	43	16.53	7.37
56	76.3	10.13	25	15.53	6.83
49	72.5	10.53	33	12.80	6.86
39	72.9	10.60	30	9.71	5.92
41	66.0	9.79	28	7.51	5.51
48	62.1	10.08	26	7.49	5.40
38	60.7	9.54	54	5.65	5.06
47	57.7	9.90	53	4.68	4.50
67	58.5	9.88			

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[1] Sterling Research Fellow in Chemistry, Yale University, 1933–1934.

[2] For a detailed discussion and references see Kassel, "Kinetics of Homogeneous Gas Reactions," A. C. S. Monograph No. 57, Chemical Catalog Company, New York, 1932.

[3] Winkler and Hinshelwood, *Proc. Roy. Soc.* (London), **A149**, 340 (1935).

±0.2°. Pressures were read either on a mercury or a bromonaphthalene–mercury manometer. Experimental errors were smoothed out by a process of graphical differentiation and re-integration.[4] To correct for dead space (1.7%) the rate constants were calculated by the method suggested by Allen.[5] These constants fell off during a run due to the second step in the decomposition and consequently were extrapolated to zero time. The results, corrected slightly to 826°K., are presented in Table I.

A second series of runs was made to determine the temperature effect of the high pressure reaction. This is expressed by the equation

$$\ln k_\infty = 34.52 - 68120/RT$$

and is shown in Table II.

TABLE II

T, °K.	817	826	836	845.5	854
$k_\infty \times 10^4$	5.85	9.3	15.41	24.18	34.88

A plot of *k versus* P_0 (k_∞ = 0.001125 at 826°K.) establishes 100 mm. as the pressure where the reaction commences to fall off, checking the results of previous workers. A plot of $1/k$ versus $1/P_0$ indicates a break at 40 mm. pressure suggesting a second mode of activation.

Application of Hinshelwood's simple theory gives 22 active degrees of freedom. Using O. K. Rice's classical theory, 8 degrees of freedom and a molecular diameter of 28.3×10^{-8} cm. appear to be the best values to use. Kassel's quantum theory gives curves that fit the experimental results the best. The most reasonable values in this case appear to be 8 degrees of freedom, 22 quanta, and a diameter of 45×10^{-8} cm. This gives a frequency in the infra-red and a vibrational specific heat contribution of 12 cal./g. The results of Winkler and Hinshelwood at 875°K. are satisfied by 8 degrees of freedom, 22 quanta and 35×10^{-8} cm. Table III gives a comparison of the experimental and calculated results.

TABLE III

P_0, mm.	826°K. k/k_∞ exptl.	826°K. k/k_∞ calcd.	875°K.[a] k/k_∞ exptl.	875°K.[a] k/k_∞ calcd.
200		0.916		0.855
100	1.000	.864	1.000	.780
50	0.865	.791	0.708	.685
20	.675	.664	.540	.540
10	.537	.555	.437	.427
5	.426	.439	.344	.320

[a] From the work of Winkler and Hinshelwood.

It was impossible to obtain a fit of theory to experiment throughout the whole pressure range. The calculated results fit within the experimental error from about 50 mm. pressure down. The rate constant falls off with decreasing pressure rather abruptly in comparison with other unimolecular reactions in such a manner as to indicate a free radical chain mechanism as proposed by F. O. Rice and Herzfeld.[6] This is further substantiated by the recent publication of A. O. Allen.[7]

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[4] Nybölle, *Nordisk Statistisk Tidskrift*, **8**, 103 (1929), Stockholm Aftonbladets Tr.

[5] Allen, THIS JOURNAL, **56**, 2053 (1934).

[6] F. O. Rice and Herzfeld, *ibid.*, **56**, 284 (1934).

[7] Allen, *ibid.*, **58**, 1052 (1936).

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONN.

RECEIVED MARCH 11, 1936

Semiquinones of Neutral Red and Safranines

BY LEONOR MICHAELIS

Many derivatives of phenazine have been shown to form semiquinones on partial reduction, all of green color in compounds containing only benzene and no naphthalene rings. The separation of the two steps of reduction is more distinct as the acidity of the solvent increases. The degree of acidity at which a distinct separation of the steps becomes easily recognizable varies from dye to dye. So far, no semiquinone has been observed in a number of those phenazine or phenazonium compounds containing amino groups as side chains. However, even in these compounds a semiquinone will be demonstrated by the following experiment, in which the conditions of reduction are slightly changed. One simply has to work in extremely acid solution. The experiment can be performed with neutral red, phenosafranine or the commercial "safranine."

Dissolve a small amount of the dye in concentrated hydrochloric acid. The color will be, according to the dye, blue to green. Dilute with water just enough to make it blue, with a shade of violet. Add some particles of solid chromous chloride and stir. The color will change first to an intense green, then to the almost colorless condition of the leuco dye. On reoxidizing, say by adding a crystal of potassium persulfate, the twofold change of color will be reversed. Zinc dust may also be used as reductant.

Since the color of the oxidized form of the dye in utmost acid solution (especially in concentrated sulfuric acid) itself is green, the acidity has to be lowered just to such an extent as to make it blue-violet before adding the reductant. Otherwise there is no visible change on reducing the dye to the semiquinone state.

FROM THE LABORATORIES OF
THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N. Y.

RECEIVED JUNE 18, 1936

Polymolecular Films

BY WILLIAM D. HARKINS AND ROBERT J. MYERS

Surface films which spread over water are supposed to be monomolecular. However, Harkins and Morgan[1] were able to produce solid, partly crystalline films with a mean thickness much greater than this. Thus to a spreading substance whose organic molecules contain a polar group (stearic acid, etc.) they added a thickening or non-polar substance (phenanthrene). In the present work polymolecular liquid films were produced by thickening the films with a liquid paraffin oil (nujol) of low volatility.

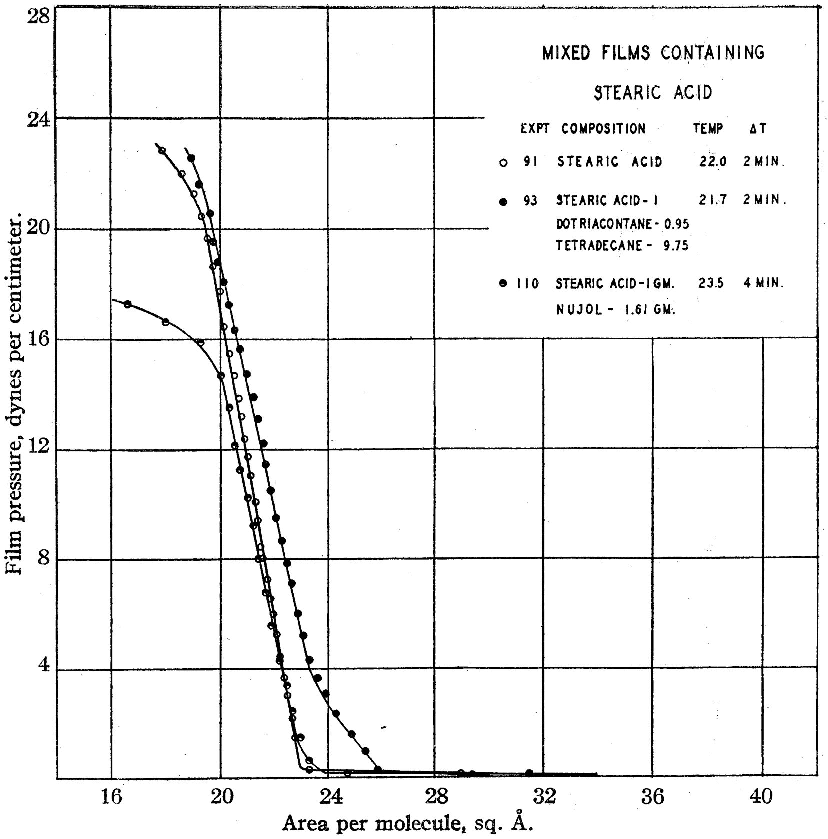

Fig. 1.—Poly- and mono-molecular films with stearic acid.

1. Condensed Films.—Films of pure stearic acid form condensed films on 0.01 N hydrochloric acid at room temperature except at pressures below about 0.2 dyne per cm. The addition of 1.61 g. of nujol to 1 g. of stearic acid in the film forming substances does not seem to increase the area of the condensed film (Fig. 1, expts. 91 and 110), but only weakens it at high pressures.

The areas given in the figures of this paper represent the area per molecule of the more polar constituent (stearic acid, etc.).

2. Expanded Films of Oleic Acid.—The effects are, however, markedly different in cases in which the acid when alone forms an "expanded" film, as in the case of oleic acid (Fig. 2). Here the mixed film contains 1.66 parts by weight of the paraffin oil to 1 part of oleic acid. The effect of the paraffin oil is very great, since it raises the surface pressure greatly at large areas, and decreases it very markedly at low areas. At 36.4 sq. Å. per molecule of oleic acid the pressures are the same for the pure acid and the mixture.

3. Expanded Films of Myristic Acid.—At 22.8° films of pure myristic acid exhibit a kink in the curve at an area of 25.45 sq. Å. and a pressure of 17.25 dynes per cm. The addition of 1.67 parts

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[1] Harkins and Morgan, *Proc. Nat. Acad. Sci.*, **11**, 631 (1925).

by weight of nujol to 1 part of myristic acid removes the kink and increases the film pressure at any given area. The increase is particularly great at the lower pressures (larger areas). With a greater proportion of nujol (9.08 parts) the phenomenon encountered with oleic acid is found, that is, the paraffin oil increases the pressure at large molecular areas and decreases it at the lower areas. The decrease in surface pressure at the lower areas becomes much more marked as the amount of paraffin oil is increased (expt. 104, Fig. 3).

4. Films of Pentadecylic Acid (Fig. 4).—The addition of 1.5 g. of the paraffin oil to 1 g. of pentadecylic acid increases the film pressure very greatly, both above and below the kink in the curve. However, at about 20 sq. Å. per molecule the two sets of curves cross. The curve for experiment 97 indicates that the tetradecane has evaporated.

5. Surface Potentials of Polymolecular Films.—Figure 5 exhibits interesting relations and shows that there is a kink in the potential area curves of both the pure acid and the mixture.

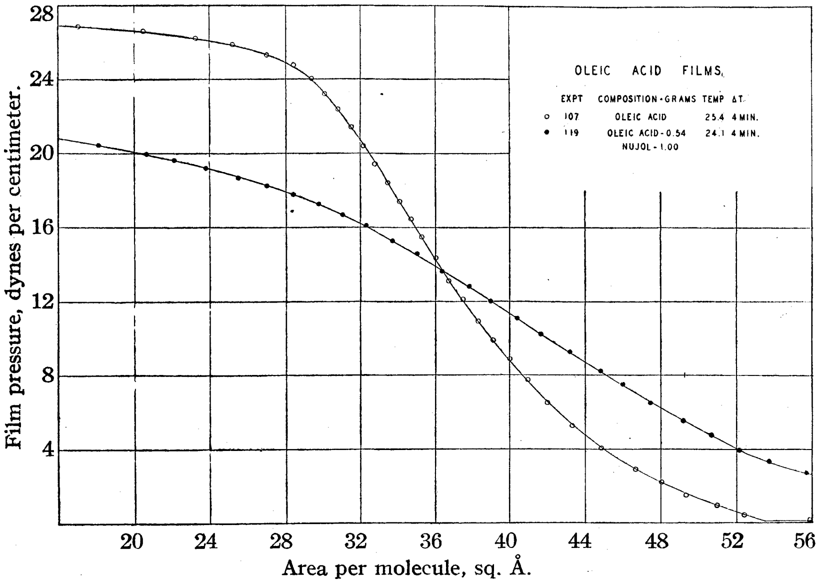

Fig. 2.—Poly- and mono-molecular films with oleic acid.

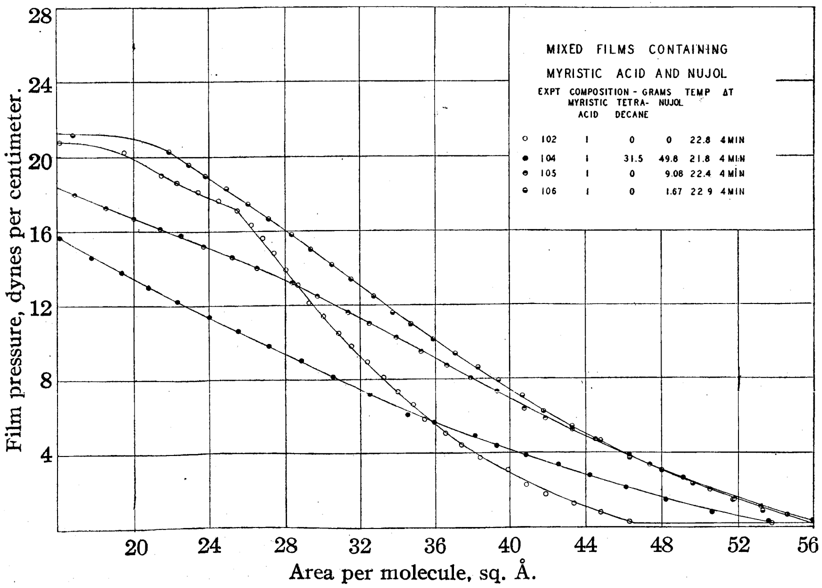

Fig. 3.—Poly- and mono-molecular films with myristic acid.

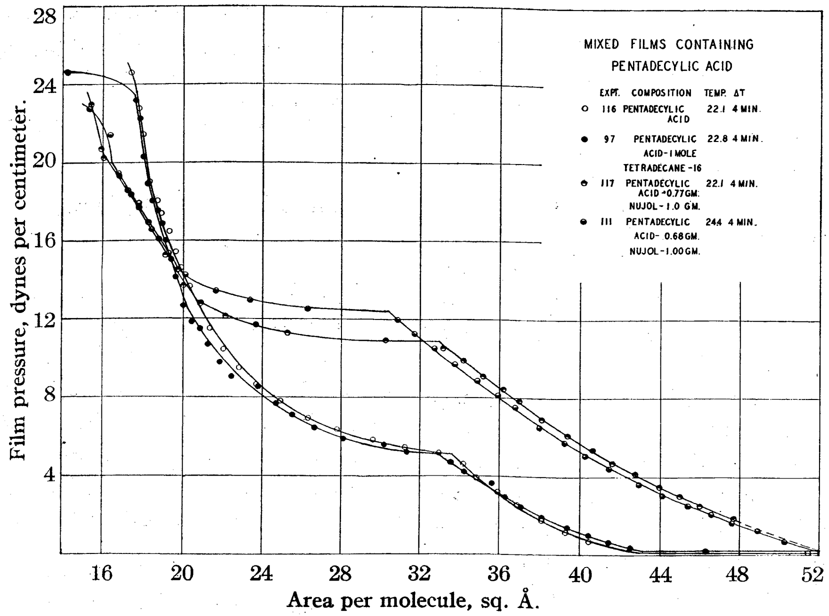

Fig. 4.—Poly- and mono-molecular films with pentadecylic acid.

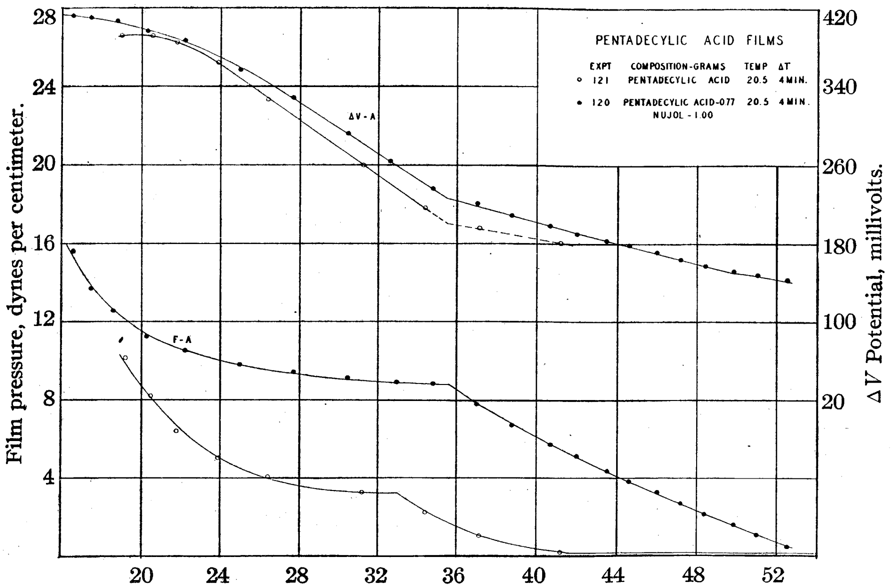

Fig. 5.—Surface potentials and areas of poly- and mono-molecular films of pentadecylic acid.

Polymolecular films exhibit many interesting relations, and many of these are under investigation in this Laboratory. At constant pressure many polymolecular, as well as monomolecular, films shrink with time. This shrinkage is very marked with pentadecylic acid at areas just below and pressures just above that of the kink in the curve.

University of Chicago
Chicago, Illinois
Received June 22, 1936

Micro Determination of Active Hydrogen with Deuterium Oxide

By Roger J. Williams

The usual methods of determining active hydrogen involving the use of a Grignard reagent, cannot be applied to highly water soluble materials which do not dissolve in ethers or other organic solvents.

We early suggested[1] the determination of active hydrogen by dissolving the unknown in deuterium oxide followed by a determination of the changed density of the water distilled off. Others[2,3] have independently made use of the principle.

An experimentally simple embodiment of the same principle has now occurred to us which consists merely in dissolving the substance to be analyzed in deuterium oxide, evaporating to dryness and determining the increase in weight due to the replacement of active hydrogen by deuterium. This method has been applied to two known substances and the results are given in the following table. Other experimental work along similar lines which need not be detailed here has convinced us of the applicability of the method. The substances in small weighing bottles were simply dissolved in 0.25 ml. of 99.5% deuterium oxide and then carefully evaporated and dried to constant weight in vacuum desiccators, and weighed again.

Substance analyzed	Hydroxyproline			Urea		
Sample, mg.	8.386			5.749		
After treatment, mg.	8.592			6.121		
Incr. after subtr. 5 γ blank	0.201			0.367		
Calcd. increases	2H	3H	4H	3H	4H	5H
	0.128	0.192	0.256	0.297	0.383	0.479

The theoretical increases were calculated on the basis of complete replacement by deuterium. This assumption would introduce practically no error in the first determination and a very slight error in the second. A small increase in weight, about 5 γ, is noted when a glass weighing bottle itself is treated with heavy water.

The method need not be limited to water soluble substances since interchange should occur in ether or pyridine solution. In case of compounds which do not dry readily, appropriate means will have to be taken to bring the material to the same degree of dryness before and after treatment with deuterium oxide. Since the principle is so simple and the manipulation involves nothing beyond drying and weighing, it appears that no serious difficulty should be involved in applying the method. We hope other investigators to whom this type of work is less incidental, will perfect and extend the method which has been experimented with in our laboratory only in a preliminary way.

CHEMISTRY DEPARTMENT
OREGON STATE COLLEGE
CORVALLIS, OREGON

RECEIVED MARCH 24, 1936

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[1] Roger J. Williams, "Introduction to Organic Chemistry," third edition, D. Van Nostrand Co., New York, 1935, p. 576.

[2] Bonhoeffer and Brown, *Z. physik. Chem.*, **B23**, 172 (1933).

[3] Hamill and Freudenberg, THIS JOURNAL, **57**, 1427 (1935).

Some Bismuth Derivatives of Diphenyl

BY DAVID E. WORRALL

Since the number of known organic compounds of bismuth is meager, previous work on diphenyl derivatives of the arsenic group has been extended to include this element.[1] Arylation was accomplished through the organo magnesium compound, for the Wurtz–Fittig method employing sodium, used so successfully with other members of the group, failed with bismuth.

Experimental

Tri-biphenylbismuth.—One hundred grams of *p*-bromodiphenyl was changed into the magnesium compound according to the directions of Bent.[2] After dilution with several volumes of ether, 36 g. of powdered bismuth chloride was added directly (in small lots) with shaking and the mixture allowed to stand overnight. The ether was removed by decantation, after which the residue was decomposed as usual. A small amount of dilute acid was added to remove basic salts. The black precipitate was then filtered, dried and extracted successively with hot alcohol and chloroform. A small amount of dibiphenyl separated from the chloroform extract on cooling, after which the filtrate was concentrated to a small volume. On the addition of an equal volume of alcohol a crystalline product formed; yield approximately 43 g.

Anal. Calcd. for $C_{36}H_{27}Bi$: C, 64.7; H, 4.0. Found: C, 65.0; H, 4.3.

It is insoluble in alcohol, but dissolves readily in chloroform, separating in the form of tiny flat needles that melt at 182–183°.

Tri-biphenylbismuth Dichloride.—To the above substance dissolved in carbon tetrachloride was added chlorine dissolved in the same solvent; yield nearly quantitative. The product was recrystallized from chloroform–alcohol mixture, from which it separated as small plates melting with decomposition at 198–200°, if heated slowly.

Anal. Calcd. for $C_{36}H_{27}BiCl_2$: Cl, 9.6. Found: Cl, 9.5.

The dibromide prepared in a similar manner formed pale yellow plates that melted indefinitely with decomposition when heated.

Anal. Calcd. for $C_{36}H_{37}BrBr_2$: Br, 19.3. Found: Br, 19.1.

Both halides dissolved in fuming nitric acid, forming nitro derivatives that deflagrated if heated quickly.

Di-biphenylbismuth Chloride.—This was prepared by the method of Challenger[3] using bismuth chloride with the

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[1] Worrall, THIS JOURNAL, **52**, 664 and 2046 (1930).

[2] Bent, THIS JOURNAL, **54**, 1398 (1932).

[3] Challenger, *J. Chem. Soc.*, **107**, 19 (1915).

triarylbismuth derivative in dry ether. A bright yellow powder rapidly separated out. It melted indefinitely when heated and probably contained some dichloride.

Anal. Calcd. for $C_{24}H_{18}BiCl$: Cl, 6.5. Found: Cl, 7.0.

Tri-biphenylbismuth Dinitrate.—Alcoholic silver nitrate solution was added to an equivalent amount of tri-biphenylbismuth dichloride suspended in a large volume of acetone. On concentrating the filtrate after removal of insoluble material, small plates were obtained that decomposed at approximately 162°, but deflagrated if heated quickly.

Anal. Calcd. for $C_{36}H_{27}BiO_6N_3$: Bi, 26.4. Found: Bi, 26.6.

PEARSON MEMORIAL LABORATORY
TUFTS COLLEGE, MASS.
RECEIVED JULY 7, 1936

Chile Seed

BY W. A. BUSH

The seeds of the Chile pepper (sometimes called pimento) obtained from the pods of the Southern Pacific Coast cultural variety of *Capsicum Annuum* have received little mention in the literature from the point of view of their composition.

A representative sample of a quantity of sixteen tons of dried seeds accumulated during a year from pods mostly of Californian origin gave results differing somewhat from those obtained by Ebert and Bailey[1] from Southeastern seed.

Yields from the seed by drying and extraction were: oil, 26.10%; moisture, 6.25%; dried extracted meal, 67.65%. Analysis of the meal, free from oil and moisture, shows: protein (N × 6.25), 28.92%; fiber, 29.10%; ash, 5.61%; N-free extract (carbohydrates), 36.37%. The constants of the oil, obtained by hot pressing (100°) and then filtering are

Specific gravity, 24.5°/25°	0.918
Refractive index at 25°	1.4738
Color (2.54 cm. column, Lovibond)	100 yellow—46 red
Acid number	2.18
Iodine number, Hanus	133.5
Acetyl number	7.0
Saponification number	192.0
Unsaponifiable matter	1.7%
Melting pt. of separated fatty acids	21.2°

The resemblance to tomato seed oil is striking.[2] However, the presence of colored veins on the outer edges of the seeds imparts to the oil the deep color noted above and a characteristic burning taste and paprika-like aroma.

LOS ANGELES, CALIF.
RECEIVED JULY 6, 1936

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(1) H. C. Ebert and H. S. Bailey, *Cotton Oil Press*, **7**, 35 (1924).

(2) Felice Sorgès, *Chim. Ind. Agr. Biol.*, **5**, 232 (1929); N. Barskii, *Masloboino-Zhirovoe Delo*, No. 6, 56 (1932).

COMMUNICATIONS TO THE EDITOR

MUREXIDE AND LEUCOMUREXIDE

Sir:

The recent publication of Kuhn and Lyman [*Ber.*, **69**, 1547 (1936)] concerning the oxidation–reduction potential of murexide prompts this report of results obtained in this field.

Preparation of Murexide.—The uncertainty in the preparation of murexide emphasized by previous writers including Kuhn and Lyman (who obtained only a 2% yield) has been removed by employing glacial acetic acid as the reaction medium. Furthermore, recrystallization has been effected without heating, by salting out at room temperature. Thus, 16.1 g. of finely powdered alloxantine suspended in 1600 cc. of boiling glacial acetic acid and treated with 80 g. of ammonium acetate with continued boiling for 1–2 minutes gave, on cooling, filtering, washing with acetic acid, alcohol and ether, and drying at 100°, 14.0 g. (calcd. 14.2 g.) of crude murexide. One gram of this dissolved in 900 cc. of water at 30° gave, on salting out the filtered solution with 60 g. of ammonium chloride, filtering, washing with 60% methanol and then with absolute methanol, and drying at 110°, about 75% of beautiful, reddish-brown crystals possessing a green reflex, which, on titration with sodium hydrosulfite, were found to be pure murexide.

Reduction of Murexide.—Leucomurexide has not been described previously, although postulated by Labes and Freisburger [*Arch. exptl. Path. Pharmakol.*, **156**, 226 (1930)] as well as by Kuhn and Lyman. One gram of pure murexide dissolved in 900 cc. of water at 30° was treated with a filtered solution of one g. of sodium hydrosulfite in a mixture of 20 cc. of water and 10 cc. of ammonia. In a few moments complete decolorization occurred. Salting out with 60 g. of ammonium chloride gave on filtering, washing with 60% methanol and finally with absolute methanol, and drying at 110°, 0.98 g. (98%) of a buff-colored microcrystalline powder which turned pink in the air. It contained the theoretical percentage of nitrogen for ammonium dihydropurpurate. Since its composition is identical with uramil (its molecular formula is simply twice that of uramil), a distinguishing test was sought. This was found in the action of potassium ferricyanide, which immediately converts leucomurexide to murexide, while uramil yields colorless oxidation products. Aeration of a dilute suspension of leucomurexide in water quickly regenerates murexide, 70% (by titration) having been obtained in one experiment after thirty minutes of aeration.

BROOKLYN COLLEGE DAVID DAVIDSON
BROOKLYN, N. Y.

RECEIVED JULY 24, 1936

RHEOPEXY IN BENTONITE

Sir:

Recently during the course of an investigation in the thixotropic properties of the clay mineral bentonite, gels showing pronounced rheopectic properties were observed. These gels are of particular interest inasmuch as Freundlich and Juliusburger in the original article describing rheopexy [*Trans. Faraday Soc.*, **31**, 920 (1935)] state that they were unable to find any evidence of rheopexy in bentonite.

The discovery of rheopexy in bentonite may be attributed to a new technique of fractionation which the authors have developed and described at the thirteenth Colloid Symposium at St. Louis, Mo., in June of 1936. Natural bentonite is dispersed in distilled water and then run through a high speed continuously fed centrifuge of the Sharples type. At various distances up the centrifuge bowl different particle size fractions of bentonite are removed and then refractionated. The finest fractions are a beautiful perfectly transparent golden-yellow color and completely amicronic while the coarser fractions are more opaque. There is a large percentage of amicronic particles present in the Wyoming Bentonite being used. By such a method of preparation the authors are establishing the influence of particle size upon thixotropy and rheopexy in bentonite.

Specifically 10 cc. of a very fine fraction (1.3% bentonite) was placed in a test-tube 1 cm. in diameter and 1 drop of saturated potassium chloride added. The setting time at 23° when the tube was kept perfectly still was twenty-five minutes, whereas slight tapping of the tube on a pad of rubber reduced the setting time to fifteen seconds. Additional potassium chloride makes it so stiff that it cannot be liquefied. Such a gel is perfectly transparent. In addition these fine bentonite fractions show pronounced streaking upon being stirred. This streaking phenomenon is greatly increased after electrodialysis. Altogether the bentonite fractions prepared in this manner act very similarly to the vanadium pentoxide system described by Juliusburger and Pirquet [*Trans. Faraday Soc.*, **32**, 445 (1936)].

From a consideration of the properties of a 1.3% bentonite gel in comparison to those gels of 10–20% concentration described by Freundlich, Schmidt and Lindau [*Kolloidchem. Beih.*, **36**, 43 (1932)], one is forced to the conclusion that particle size is of paramount influence in this case of thixotropy. In fact we have found evidences of gel structure at concentrations as low as 0.01% by wt. in the low colloidal range. It may be stated, however, that if hydrogen bentonite produced by electrodialysis is ever allowed to dry, it fails to exhibit thixotropy in low concentrations. This property can still be observed providing the material is never allowed to dry.

DEPARTMENT OF CHEMICAL ENGINEERING E. A. HAUSER
MASSACHUSETTS INSTITUTE OF TECHNOLOGY C. E. REED
CAMBRIDGE, MASS.

RECEIVED JULY 31, 1936

EXCHANGE BETWEEN SODIUM IODIDE AND ETHYL IODIDE*

Sir:

It was reported a few months ago in these columns [Hull, Schiflett and Lind, THIS JOURNAL,

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* This work was supported in part by the Fluid Research Fund of the Graduate School.

58, 535 (1936)] that while there is no exchange between radioactive iodine and ethyl iodide when heated together for fifteen minutes at 87°, as determined by the subsequent measurement of the activities of the two substances, yet in alcoholic solution at 100° a ready exchange takes place between sodium iodide and ethyl iodide. Further experiments on this latter reaction have shown the existence of a marked temperature effect.

The general procedure in these experiments has been as follows: A solution of 50 micro-moles of iodine in a liter of iodobenzene is irradiated with the neutrons from a Rn–Be source for a period of one and one-half hours or longer. After removal of the neutron source, the iodine is extracted and precipitated as silver iodide, which is then transformed into dry sodium radio-iodide. This is dissolved in 1–2 cc. of ethyl alcohol and mixed with 100 micro-moles of inactive ethyl iodide. This mixture is heated to the desired temperature for a stated interval of time and then quickly cooled. (In the one experiment carried out below room temperature both solutions were cooled before being mixed.) The two iodides are separated by shaking the solution with excess ether and water, and are transformed into silver iodide for measurement. The activity of each precipitate is measured by means of a tube counter. The results obtained in a series of experiments at different temperatures are given in tabular form.

Temp., °C.	Time, min.	Exchange
100	5	Complete
100	1	Complete
80	5	Complete
29	5	Partial
29	1	None
24	5	None
19	5	None

The authors are grateful to Dr. K. W. Stenstrom of the University Hospital for the gift of 150 millicuries of radon, and to Dr. J. H. Williams of the Department of Physics for the use of a low resistance amplifier [of the type described by Neher and Harper, *Phys. Rev.*, **49**, 940 (1936)], without which it would not have been possible to carry on this work during the recent hot weather.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINN.
D. E. HULL**
C. H. SCHIFLETT
S. C. LIND

** National Research Fellow.

RECEIVED AUGUST 22, 1936

THE PHOTOCHEMICAL DECOMPOSITION OF METHANE

Sir:

Methane at atmospheric pressure is photochemically decomposed when irradiated with the light which is transmitted by a thin fluorite window from a hydrogen discharge tube. The effective radiation would appear to lie near the limit of transmission of fluorite. Although no direct measurements of quantum yield have been made, a crude estimate based on a comparison with the rate of the ozone synthesis in the same cell indicates a value of the order of unity.

Among the products we have identified hydrogen and unsaturated hydrocarbons (probably ethylene) in the approximate molecular ratio of 4:1. Higher saturated hydrocarbons may also be produced but have not been detected. The large ratio of hydrogen to unsaturation in the products indicates that the decomposition

$$CH_4 + h\nu \longrightarrow CH_2 + H_2$$
$$2CH_2 \longrightarrow C_2H_4$$

cannot be the only process involved.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY, CALIF.
PHILIP A. LEIGHTON
ARNOLD B. STEINER

RECEIVED JULY 28, 1936

NEW SYNTHESIS OF GLYCOFURANOSIDES

Sir:

In the last decade considerable progress in sugar chemistry had been made from the study of the glycopyranosides. Further developments can likely be expected from a greater than our present knowledge of the glycofuranosides, or, as E. Fischer originally named them, γ-glycosides. The physical, chemical and biological properties, the conversion into the pyranosides under certain conditions, and the chemical structure in general, of these γ-glycosides should be thoroughly investigated. To be sure, such studies have already been made in the past, in a few isolated instances. However, a review of the literature reveals that only five or six γ-glycosides are known in pure crystalline form obtained mostly in small yields by cumbersome methods. The majority of the γ-glycosides described in the literature were prepared by the original method of E. Fischer [*Ber.*, **28**, 1145 (1895); **47**, 1980 (1914)] yielding only sirupy mixtures that could not be separated. Obviously, a general method which leads to well-defined, crystalline products, would constitute the first step toward a more extensive study of this class of sugar derivatives. We believe that we have found such a method. It represents a modification of a previous general procedure of one of us [Pacsu, *ibid.*, **58,** 509 (1925); Pacsu and Ticharich, *ibid.*, **62,** 3008 (1929)] by which the α-alkylpyranosides were prepared from the sugar mercaptals and mercuric chloride in the *boiling* solutions of the different alcohols. Taking, *e. g.*, galactosediethylmercaptal and ethanol, the reaction can be expressed by the following summary equation

$$C_6H_{12}O_5{\cdot}(SC_2H_5)_2 + 2HgCl_2 + C_2H_5OH = 2HCl + 2C_2H_5S{\cdot}HgCl + C_6H_{11}O_5{\cdot}OC_2H_5$$

This method was shown to yield almost pure (up to 92%) α-alkylpyranosides accompanied only by a slight quantity of the β-isomers. Now we have found that if the same reaction be carried out *at low temperature*, and the hydrochloric acid formed be neutralized at the moment of its development, an excellent yield of crystalline β-ethylgalactofuranoside can be obtained. The substance had m. p. 84.5–86° and $[\alpha]^{25}\text{D}$ −100.1° in water solution. Schlubach and Meisenheimer [*ibid.*, **67,** 429 (1934)] reported m. p. 86° (corr.) and $[\alpha]^{20}\text{D}$ −97.2° for the same compound obtained by a lengthy synthesis from the β-pentaacetate of galactofuranose of Hudson and Johnson. So far it has not been possible to find any isomer in the mother liquor. The same furanoside was obtained when dibenzylmercaptal had been used as starting material. For the instantaneous neutralization of the hydrochloric acid we have found the use of an excess of yellow mercuric oxide to be most excellent. It keeps the reaction mixture neutral during the whole process, and it provides for a desirable excess of the mercuric chloride up to the end of the reaction. For the removal of the mercuric chloride from the solution we have found that pyridine can be used most successfully. It seems very likely that these modifications can also be used with advantage in the procedures developed for the preparation of the open-chain methylated (Levene, 1926) and acetylated (Wolfrom, 1929) aldoses.

Since the formation of glycopyranosides by the original method has proved to be of general validity, we believe that by this modified procedure it will be possible to prepare the hitherto unknown or only difficultly available furanosides of the carbohydrates. It is our purpose to prepare by this method the alkylfuranosides and -thiofuranosides of the aldoses and ketoses from their mercaptals and acetonylated mercaptals. In the forthcoming first paper of this series of investigations conducted in this Laboratory, a detailed description of the procedure will be given.

FRICK CHEMICAL LABORATORY
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EUGENE PACSU
JOHN W. GREEN

RECEIVED AUGUST 14, 1936

NEW BOOKS

Colorimetric Methods of Analysis, Including Some Turbidimetric and Nephelometric Methods. Vol. I. Inorganic. By FOSTER DEE SNELL and CORNELIA T. SNELL. D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, N. Y., 1936. 766 pp. Illustrated.

In this second edition of Dr. Snell's treatise a much more comprehensive treatment of the field of colorimetry has been made. The book has been divided. This first volume covers general colorimetry and inorganic determinations; a second will deal with organic, biological and miscellaneous methods.

In its general plan and scope the book closely resembles Yoe's "Photometric Analysis." It differs in that nephelometric methods are treated with the colorimetric ones instead of in a separate volume and in that the bibliography occurs in footnotes instead of as a separate section at the end of the book. It contains, of course, methods and references which have appeared in the seven years since the publication of Yoe's book.

In the first nine chapters the general methods of colorimetry are discussed and the multitudinous forms of apparatus which have been devised for the measurement of color and of turbidity are illustrated and explained. Fifty-four chapters are then devoted to different methods for the determination of seventy-four elements or simple inorganic compounds. The last four chapters deal with the colorimetric determination of hydrogen ions. As many as ten or twelve methods are given for some elements. The treatment is well balanced in that the more important methods are given more space while other methods of less value are dismissed with a reference and a brief description.

The book, however, is by no means simply a reference list but rather an excellent working text. In general, after an introductory discussion of each method, the preparation of samples is detailed. This should be one of the most attractive features of the book to the practical worker. Next directions for making up reagents are given and then details of the analytical procedure. Finally there are directions for preparing standards suitable for the method.

Although the treatment is comprehensive rather than critical, this text represents a distinct contribution to the literature of analytical chemistry. It is a reference book which should be on the shelves of every chemist who has occasion to take advantage of the ease and rapidity of colorimetric methods.

CHARLES H. GREENE

Protoplasm. By WILLIAM SEIFRIZ, Ph.D., Professor of Botany, University of Pennsylvania. McGraw-Hill Book Co., Inc., 330 West 42d Street, New York, N. Y., 1936. x + 584 pp. 179 figs. 15.5 × 23.5 cm. Price, $6.00.

This is a delightful volume, a storehouse of information, and should be on the desk of every biologist, biochemist and biophysicist. If only all chemists teaching general chemistry, organic chemistry and especially physical chemistry would read this book they would gain a clear insight into the role which chemistry plays in the phenomena of life.

The author is Professor of Botany in the University of Pennsylvania but the book reads almost as though it were written by a physical chemist. It is a far cry from the "plant physiology" of a generation ago to this discussion of "protoplasm," the ultimate living matter of all cells. The author is to be congratulated on his accomplishment in bringing together in a unified whole so many interesting and diverse series of information.

Of the twenty-seven chapters only five may be said to be primarily biological and even these contain much chemistry and physics. The first chapter deals with "The Living Substance." This is followed with "The Cell"; "Model Making," "Micrurgy" (micromanipulation within living cells) and "Tissue Culture." The last chapter "The Origin of Living Matter" sums up the volume and presents a philosophical consideration of how life possibly came to be.

The other 22 chapters are fundamentally chemical and deal with "The Colloidal State," "Emulsions," "Hydrophilic Sols and Gels," "Surface Tension," "Adsorption," "Osmosis," "Imbibition," "Viscosity," "Elasticity," "The Structure of Protoplasm and Organic Colloidal Matter," "Permeability," "Acidity," "Electrophysiology," "Electrokinetics," "Radiant Energy," "The Role of Water," "Salts," "Carbohydrates," "Fats," "Proteins," and "Regulatory Substances," but into the chemistry and physics of these chapters is woven the experience of years of reading and teaching biological principles so that they are a mine of information uniting abstract chemical and physical laws with cell behavior.

As is to be expected in the first edition of a volume of this size there are some unfortunate typographical errors, some omissions and some inaccuracies. Furthermore, it is perhaps too much to hope that everyone will agree with the author in his interpretation of certain biological processes, certainly the reviewer does not agree in all points, but any and all shortcomings of the book are easily condoned in the light of the magnificent accomplishment which the author has achieved.

A few of the more serious errors are here noted, not as criticisms but to assist prospective purchasers: p. 56, "microvolts" is incorrectly used for millivolts; p. 82, glutathione is stated to be a dipeptide, it is a tripeptide, glutamyl-cysteinyl-glycine; p. 82, amino acids are not the "hydration" products of proteins, rather the products of hydrolysis; pp. 92, 94 and 118, the Tyndall phenomenon is discussed and statements made that it is perhaps the most characteristic property of colloids. Since the Tyndall phenomenon depends upon the refraction of light from an interface it is evident that a solid immersed in a liquid, both having the same index of refraction, will show no Tyndall phenomenon. The absence of "optical properties" in certain protein sols is well known and does not mitigate against their being truly colloidally dispersed. On p. 93 the author states that the word peptization is derived from "peptone, itself a peptizing agent." This is incorrect. Graham coined the word "peptization" and states that it "may be looked upon as analogous to the solution of insoluble organic colloids witnessed in animal digestion. . . . Liquid silicic acid may be represented as the 'peptone' of gelatinous silicic acid—etc." Accordingly "peptization" is derived from pepsin and the process is likened to enzymatic action. On p. 144 there is an erroneous statement as to the osmotic pressure developed by an 0.1 molar sucrose solution. On p. 153 the reference in the text to Fig. 91 should be to Fig. 92. On p. 174 Traube's rule is stated with no indication that it depends upon the nature of the interface and that it is reversed for a polar substance, *e. g.*, SiO_2, in water. On p. 175 there is an unfortunate error in the formula of the Freundlich adsorption isotherm. On p. 199 in the discussion of the osmotic pressure of the blood and body fluids, no mention is made of colloid osmotic pressure and the role it plays in urine secretion. On p. 287 the unfortunate statement is made that a low surface tension means a "loose arrangement of surface molecules and therefore a more permeable membrane." On p. 361 the apparatus figured is that of Freundlich and Rona, not that of Kruyt. On p. 418 metabolic water is stated to arise in part from the "polymerization" of compounds. On p. 429 is given a list of the elements found in protoplasm and the statement that the first 10 are essential. In the first ten sodium is included and iron is omitted! On p. 431 the term "phosphoproteins" is used for the correct "nucleoproteins." On p. 431 in a discussion of the being an integral part of the chlorophyll molecule. That it is present in chlorophyll is noted in another connection on a later page. This type of "omission" occurs in a number of places in the book, thus in discussing vitamin C on p. 514 no mention is made of ascorbic acid although ascorbic acid comes in later in another connection on p. 519. On p. 432 a typographical error gives the sulfhydryl group the formula, SH_2 and on the same page the unfortunate statement occurs that the sulfur bacteria "use sulfur instead of carbon in the synthesis of higher foods"; of course what the author meant was that elemental sulfur was used by the sulfur bacteria as an *energy* source and that by the oxidation of the sulfur they secured energy for the synthesis of carbon compounds. Likewise on p. 432 the cystine discussion is ambiguous. On p. 451 pernicious anemia is confused with nutritional anemia. On p. 477 Sørensen is stated to have found the molecular weight of egg albumin by the freezing point method to be 14,000. This is incorrect. By direct osmotic pressure measurements he found (*Compt. rend. trav. Lab. Carlsberg*, Vol. 12) a mol. function of magnesium in plants no mention is made of its wt. for egg albumin of 34,000. On p. 514 "night blindness," an hereditary affliction, is confused with lack of Vitamin A. On. p. 508 Northrup instead of Sumner is credited with the crystalline enzyme urease.

Apparently the author (in common with most biologists and chemists) is confused (p. 478) with Svedberg's use of the term "molecular weight" as it applies to proteins. It is unfortunate that Svedberg has used this term instead of the more exact (from the chemists' viewpoint) term of "particle weight." Svedberg's "molecular weights" are used in the physical sense and defines "a molecule as a unit which will acquire from thermal vibrations an average of $^1/_2\ kT$ ergs of energy for each of three translational degrees of freedom, neglecting quantum restrictions. The size and weights of these molecules may change with temperature, rate of sheer, and other factors" (personal communication from Prof. J. W. Williams).

Svedberg's use of the term does not necessarily connote that the "molecule" is the smallest unit of that primary substance that can be obtained. Consequently he speaks of the "decomposition" of molecules and later the reversal of the "decomposition" process so that the original "molecular weight" was regained. Obviously this cannot be accomplished if the term "molecular" were used in the older chemical sense.

Again I recommend this volume to all biologists, physicists and chemists who are interested in the phenomena of life in its manifold manifestations.

ROSS AIKEN GORTNER

Handbuch der biologischen Arbeitsmethoden. Edited by EMIL ABDERHALDEN. Abt. IV, Angewandte chemische und physikalische Methoden, Teil 1, Heft 9. (**Handbook of Biological Methods.** Section IV. Applied Chemical and Physical Methods. Part I, Vol. 9.) Fermentforschung. Urban and Schwarzenberg, Friedrichstrasse 105 B, Berlin N 24, Germany, 1935. 245 pp. 17.5 × 25.5 cm. Price, RM. 13.50.

This volume is of interest to those devoted to research in enzyme chemistry and related fields. It gives a comprehensive review of the following subjects:

In the first two articles the method of carrying out the Abderhalden reaction with immersion refractometer according to the method described by Pregl–de Crinis, is given. The estimation of protective enzymes by the use of the interferometer is described by Paul Hirsch.

The preparation of crystalline pepsin, trypsin and chymotrypsin is presented by John H. Northrop and M. Kunitz. The crystalline pepsin is prepared from the amorphous commercial product and is obtained (after recrystallization) in colorless microscopic crystals. The trypsin is obtained from pancreas and finally the chymotrypsin from the pancreas of cattle through the intermediate preparation of crystalline chymotrypsinogen.

The ketonaldehydmutase, an enzyme having the property of converting the alpha-keto aldehydes into alpha-hydroxy acids, is described by Carl Neuberg and E. Simon. This enzyme is widely distributed in nature and functions in the metabolism of living organisms. The most important reaction of this kind is the conversion of methyl glyoxal into lactic acid. The various derivatives of methyl glyoxal such as phenyl glyoxal and methyl glyoxal acetic acid react similarly. The article gives a comprehensive treatment of these reactions.

Emulsin is described by Karl Tauböck. The enzyme preparation consists mainly of β-*d*-glucosidase. It cleaves the β-*d*-glucosides both natural and synthetic, but not the *l*-glucosides. It has been observed that some preparations also cleave various galactosides or mannosides, but the question as to whether this is due to some other enzyme such as alpha-*d*-galactosidase or alpha-*d*-mannosidase, or the β-glucosidase alone has not been determined. This subject is under investigation at the present time.

The method of studying dehydrogenases is presented by Torsten Thunberg in great detail. A complete bibliography is given with each article.

G. BRAUN
C. N. FREY

Die Allotropie der chemischen Elemente und die Ergebnisse der Röntgenographie. (The Allotropy of the Chemical Elements and the Results of X-Ray Analysis.) By M. C. NEUBURGER. Verlag von Ferdinand Enke, Stuttgart W, Germany, 1936. 106 pp. 32 figs. 16 × 24 cm. Price, RM. 9.30; RM. 8.20, for subscribers.

This is Number 30 of a series of monographs on chemistry and chemical technology. The author has written a number of works on crystal chemistry and x-ray diffraction. Each year he writes the annual summary of lattice constants for the *Zeitschrift für Kristallographie.*

The possible allotropic forms and crystal structures of 69 elements, 23 of which actually have several modifications, are discussed. In addition, there is an introduction in which the criteria for distinguishing allotropic forms are discussed. There are chapters on the influence of foreign atoms on allotropy; the relations between allotropy, crystal structure and atomic properties; and transformation mechanisms and the kinetics of allotropic changes.

Crystal structure is chosen as the most unambiguous criterion of allotropic change and x-ray data as the most direct evidence. Although the author is in a position to write authoritatively and his judgment is generally good, a number of criticisms must be made.

In a book of this nature we should expect to find a short review of the literature for each element, giving all important ideas which have been put forth with references. The author should weigh these facts critically and sum up his conclusions distinguishing between what is thoroughly established and what is merely probable and mention possibilities which have not been verified. Neuburger's book falls below this standard. He ignores considerable data, good and bad, and often gives only his conclusions without specifically indicating their source or their relative probability. To get a good idea of the status of work on a given element it is still necessary to consult the original literature.

The author fails completely to mention the fact that cobalt is hexagonal at high temperatures, which has been verified by a number of authors and never disputed. On phosphorus, he ignores the fact that a number of contradictory x-ray patterns have been reported. He mentions the work of Frost [*J. Russ. Phys.-Chem. Soc.*, **62,** 2235 (1930)] which shows that red and violet phosphorus have different structures without giving credit or listing the reference. The best work on the transformation point of iron [by Wells, Ackley and Mehl (1935)] is not mentioned; perhaps it is too recent for inclusion.

The references, instead of being conveniently listed under each element, are placed at the end of the volume. The first 920 of them are alphabetically arranged according to author, but 82 more follow (not the most recent ones) in irregular order. The reference numbers are hard to find since they are not conspicuously printed and separate lines are not given to each reference. A great deal of space could have been saved by omitting data such as lattice constants which are conveniently found elsewhere. A few good tables would advantageously take the place of much of the discussion.

On the whole, the book bears evidence of hasty preparation. However, it is the first book on this subject and provides a summary, usually well chosen, of data to be found only by a search of the literature. It should be a useful reference work.

RALPH HULTGREN
ALDEN B. GRENINGER

Organic Chemistry. By ROBIN CHARLES BURRELL, Ph.D., Associate Professor of Agricultural Chemistry, The Ohio State University. McGraw-Hill Book Company, Inc., 330 West 42d Street, New York, N. Y., 1936. xii + 336 pp. 34 figs. 14 × 20.5 cm. Price, $2.75.

A more specific title for this textbook would be more appropriate in view of its rather extensive discussion of the biologically important substances and its more restricted treatment of some of the other subjects, such as methods of synthesis which are less pertinent to its purpose. The text is especially designed for a semester course in organic chemistry for students of home economics, agriculture and biological sciences. The choice of subject matter was largely based upon the consensus of the opinions of a number of authorities on nutrition.

The fundamental concepts and the most important types of compounds are adequately discussed. The aliphatic and the aromatic hydrocarbons are presented in the same chapter. About one-half of the book is devoted to the treatment of substances of direct biochemical importance—lipides, carbohydrates, proteins and their components, and miscellaneous natural substances. A concise account of the digestion and assimilation of each of the three important classes of food substances is also included.

The book is quite accurate and up-to-date; however, the following errors ought to be noted: "ethyl nitrile" for C_2H_5CN (p. 115); the boiling point of lactic acid is given as 122°C. (p. 154); the consideration of alcoholic fermentation as "a type of biological oxidation" (p. 176); and the formulas for hydroxyproline (p. 216) and nicotine (p. 281). The classification of the types of isomers that is given (p. 45) and the likening of esters to salts (p. 111) are not in accord with modern concepts.

The book is well organized and written in a clear and concise manner. It is well suited for the purpose for which it was intended.

EDWARD A. PRILL

BOOKS RECEIVED

July 15, 1936–August 15, 1936

ÉTIENNE AUDIBERT. "Les Carburants. I. L'Essence." Gauthier-Villars, Éditeur, 55 Quai des Grands-Augustins, Paris, France. 181 pp. Fr. 45.

F. R. BICHOWSKY AND F. D. ROSSINI. "The Thermochemistry of the Chemical Substances." Reinhold Publishing Corporation, 330 West 42nd St., New York, N. Y. 460 pp. $7.00.

G. DUPONT. "Cours de Chimie Industrielle. Vol. III. Métallurgie." Gauthier-Villars et Cie., Éditeur, 55 Quai des Grands-Augustins, Paris, France. 357 pp. Fr. 65.

HEINRICH FINCKE. "Handbuch der Kakaoerzeugnisse." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 568 pp. RM. 55.

O. A. HOUGEN AND K. M. WATSON. "Industrial Chemical Calculations. The Application of Physico-Chemical Principles and Data to Problems of Industry." Second edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 487 pp. $4.50.

KATHLEEN LONSDALE. "Simplified Structure Factor and Electron Density Formulae for the 230 Space Groups of Mathematical Crystallography." Published for the Royal Institution by G. Bell and Sons, Ltd., York House, Portugal St., London W. C. 2, England. 181 pp. 10s./- net.

S. SABETAY. "Progrès Récents dans la Chimie des Parfums et des Huiles Essentielles." Gauthier-Villars, Éditeur, 55 Quai des Grands-Augustins, Paris, France. 77 pp.

KARL SCHULTZE. "Das Ausblühen der Salze." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 99 pp. RM. 4.

JOHN C. WARE. "The Chemistry of the Colloidal State. A Textbook for an Introductory Course." Second edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 334 pp. $3.75.

HARRY BOYER WEISER. "Colloid Symposium Monograph. Papers Presented at the Twelfth Symposium on Colloid Chemistry, Ithaca, N. Y., June, 1935." The Williams and Wilkins Company, Mt. Royal and Guilford Aves., Baltimore, Md. 156 pp. $3.00.

"Gmelins Handbuch der anorganischen Chemie. System-Nummer 4, Stickstoff." Lieferung 4. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 184 pp. RM. 25.15.

"Gmelins Handbuch der anorganischen Chemie. System-Nummer 23, Ammonium." Lieferung 1. Verlag chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 242 pp. RM. 28.

"Bucher der Anstrichtechnik. Vorträge in Veranstaltungen des Fachausschusses." Erstes Buch. Herausgegeben vom Fachausschuss für Anstrichtechnik beim Verein deutscher Ingenieure und Verein deutscher Chemiker durch die Gruppe "Verbreitung anstrichtechnischen Kenntnisse." VDI Verlag G. m. b. H., Dorotheenstrasse 40, Berlin N. W. 7, Germany. 99 pp. RM. 7.50.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Entropy of Deuterium Oxide and the Third Law of Thermodynamics. Heat Capacity of Deuterium Oxide from 15 to 298°K. The Melting Point and Heat of Fusion

BY EARL A. LONG[1] AND J. D. KEMP

Aside from its usual thermodynamic utility, the entropy of deuterium oxide is of considerable interest in connection with the entropy discrepancy in ordinary water, first pointed out by Giauque and Ashley,[2] in which the calorimetric entropy does not agree with entropies calculated from the band spectrum and from reaction data. Explanations of this discrepancy have been discussed by Giauque and Ashley, and more recently by Pauling.[3]

In order to test these explanations, Giauque and Stout[4] have carried out a calorimetric investigation on ordinary water.

Since the substitution of deuterium for hydrogen in the water molecule does not appreciably change the internuclear distances, and probably has little effect on the nature of the bond forces, it seemed that an experimental investigation of the entropy of deuterium oxide would be valuable in any discussion of the entropy discrepancy in water. A calorimetric entropy value for heavy water should provide an additional test to distinguish between the theory of molecular rotation and the Pauling theory of random bond orientation, as has been pointed out by Giauque and Stout.[4]

Apparatus.—The measurements were made with the same copper calorimeter and auxiliary apparatus used by Giauque and Stout in their investigation of ordinary water. Although we did not have a sufficient quantity of pure heavy water to fill the calorimeter as completely as desired, the precision of the measurements was not seriously affected, and we feel that the use of the same calorimeter and temperature standard for hydrogen and deuterium oxide should lead to more accurate comparisons between the two isotopic forms.

The details of the apparatus and the method of making the measurements and calculations have been described previously.[5]

Purification of Deuterium Oxide.—The sample was taken from a preparation kindly supplied to us by Prof. H. L. Johnston. It had a density of 1.10781, corresponding to a deuterium content of 99.92 atomic per cent.,[6] if we compare our density with the maximum density of 1.1079 given by Taylor and Selwood.[7] The remaining 0.08 atomic per cent. of hydrogen does not affect our measurements, since the isotopes should of course form a perfect solution, and the thermal quantities are of nearly the same magnitude.

The heavy water container was broken in an

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[1] National Research Fellow.

[2] Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

[3] Pauling, THIS JOURNAL, **57**, 2680 (1935).

[4] Giauque and Stout, *ibid.*, **58**, 1144 (1936).

[5] (a) Giauque and Wiebe, *ibid.*, **50**, 101 (1928); (b) Giauque and Johnston, *ibid.*, **51**, 2300 (1929); (c) Giauque and Stout, *ibid.*, **58**, 1144 (1936).

[6] We are informed by Prof. Johnston that the sample contains not more than 0.01% above the normal concentration of the heavier oxygen isotopes, on the basis of the electrolytic separation coefficient 1.008 for the concentration of O^{18} by electrolysis with iron electrodes, determined by Johnston [*ibid.*, **57**, 484 (1935)].

[7] Taylor and Selwood, *ibid.*, **56**, 998 (1934).

atmosphere of pure helium, and the water was distilled at low pressures through a series of three bulbs, in order to eliminate a small amount of alkali in the original sample. After each distillation the solid was cooled with liquid air and the system was evacuated to a pressure of 10^{-5} mm. in order to get rid of traces of dissolved gas. The water was then transferred through a small german silver tube into the copper calorimeter. The calorimeter was filled with helium gas at one atmosphere pressure, the german silver tube was pulled out, and the very small opening was sealed with Wood's metal.

In order to determine the amount of liquid-soluble, solid-insoluble impurity, a series of short heat capacity runs was made in the temperature region just below the melting point. From the observed premelting effect in these runs, we estimate the soluble impurity to be less than 0.003 of one mole per cent. This is of course exclusive of the 0.08 atomic per cent. hydrogen content of the sample, as the presence of another isotopic form would not cause premelting.

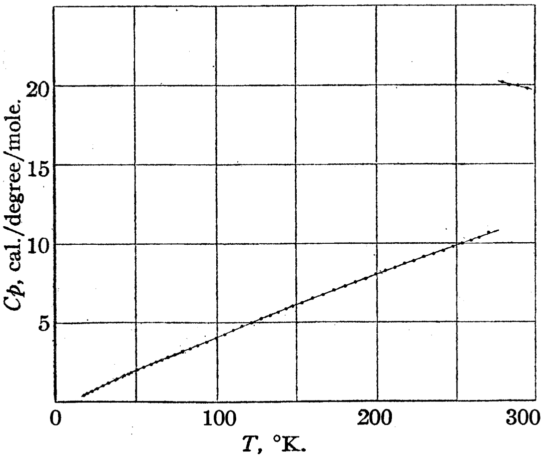

Fig. 1.—Heat capacity of deuterium oxide.

The Heat Capacity of Deuterium Oxide

The results of the heat capacity measurements are given in Table I, and are shown graphically in Fig. 1.

TABLE I

HEAT CAPACITY OF DEUTERIUM OXIDE

Molecular weight, 20.0284. 0°C. = 273.10°K.

T., °K.	ΔT	C_p, cal./deg./mole	Series
14.81	3.652	0.243	I
17.56	2.189	.403	I
19.89	2.874	.532	I
22.60	3.160	.660	I
25.97	3.645	.831	I
29.56	3.115	1.027	I
32.96	3.114	1.194	I
37.06	4.685	1.376	I
38.07	5.145	1.434	III
41.44	3.795	1.577	I
42.87	4.253	1.664	III
45.14	3.347	1.764	I
46.98	3.730	1.844	III
50.70	3.668	2.016	III
54.64	3.831	2.174	III
59.23	5.226	2.354	III
59.32	2.448	2.374	II
62.37	3.307	2.504	II
65.96	3.737	2.643	II
69.77	3.773	2.813	II
73.99	4.535	2.988	II
78.61	4.612	3.179	II
83.16	4.345	3.359	II
87.92	4.860	3.541	II
93.51	6.211	3.776	II
99.32	5.340	4.005	II
104.57	5.051	4.254	II
110.10	5.749	4.519	II
115.67	5.092	4.781	II
121.44	6.276	4.996	II
127.51	5.736	5.236	II
133.17	5.313	5.428	II
138.40	4.932	5.634	II
143.23	4.509	5.861	II
147.79	4.182	6.011	II
153.38	6.911	6.217	II
159.98	6.156	6.534	II
166.27	6.175	6.741	II
173.10	7.065	7.027	II
180.00	6.588	7.275	II
186.59	6.136	7.539	II
192.88	5.769	7.747	II
199.19	5.875	8.029	II
205.36	5.754	8.270	II
211.45	5.934	8.456	II
217.19	5.641	8.711	II
223.11	5.401	8.894	II
229.34	5.538	9.138	II
235.39	5.681	9.324	II
241.57	5.594	9.519	II
247.69	5.671	9.785	II
253.87	6.034	9.999	II
259.50	5.020	10.18	II
264.81	5.159	10.36	II
270.52	5.756	10.69	II
276.92	Melting point		
279.46	3.561	20.17	IV
283.91	4.558	19.99	IV
289.45	5.700	19.98	IV
295.16	5.497	19.78	IV

In the calculations, one 15° calorie was taken as equal to 4.1832 international joules. The calorimeter contained 32.708 g. of deuterium oxide. For the calculation of the molecular weight we used the value 2.01471 given by Aston[8] for the atomic weight of deuterium, and the factor 1.00025 for conversion from the physical to the chemical scale.

We took no special precautions in cooling the sample, as the first series of measurements showed no evidence of bad thermal equilibrium. For ordinary water, Giauque and Stout[4] observed slow attainment of thermal equilibrium in the region from 85 to 100°K. However, their experiments on different rates of cooling showed no appreciable effect on the heat capacities. If, as Giauque and Stout suggest, this lag in equilibrium is caused by the initial stages of excitation of new degrees of freedom connected with the motion of the hydrogen atoms, it is not surprising that the phenomenon does not appear in deuterium oxide, when one considers the great difference between the masses of hydrogen and deuterium.

TABLE II

HEAT CAPACITY OF DEUTERIUM OXIDE

Molecular weight, 20.0284. 0°C. = 273.10°K. Values taken from smooth curve through data.

T., °K.	C_p, cal./deg./mole	Ratio $C_{p\mathrm{D_2O}}/C_{p\mathrm{H_2O}}$	Deviations Brown, Barnes and Maass − This research %
15	0.272		
20	.532	1.086	
30	1.043	1.060	
40	1.524	1.040	
50	1.977	1.043	
60	2.403	1.043	
70	2.821	1.044	
80	3.234	1.052	
90	3.629	1.052	
100	4.047	1.066	
110	4.508	1.092	
120	4.931	1.112	
130	5.325	1.126	
140	5.709	1.143	
150	6.100	1.159	
160	6.500	1.171	
170	6.895	1.174	
180	7.282	1.186	
190	7.666	1.187	
200	8.050	1.194	−4.1
210	8.422	1.187	−3.9
220	8.802	1.191	−3.2
230	9.158	1.185	−1.9
240	9.500	1.186	+0.2
250	9.842	1.178	+2.6
260	10.19	1.179	+5.2
270	10.54	1.173	+8.0
276.92	Melting point		
280	20.15	1.115	
290	19.91	1.106	+2.4
295	19.78	1.100	

In Table II are listed values of the heat capacity at even temperatures, as read from a smooth curve through the data. These values are compared with those of Brown, Barnes and Maass,[9] who measured the total change in heat content from various initial temperatures to 25°, and have derived from these data values for the specific heats. In making this comparison we have used 20.0284 as the molecular weight.

We have also included in Table II values for the ratio of the molal heat capacities D_2O/H_2O over the whole temperature region, calculated from our data and those of Giauque and Stout.[4] For the heat capacity of liquid H_2O, the values given in the "International Critical Tables"[10] were used.

The Melting Point and Heat of Fusion.—The melting point was determined with various percentages of the D_2O melted. In each measurement the temperature was observed for several hours after heat input, until readings on the sensitive resistance thermometer indicated that thermal equilibrium had been attained. From these measurements, the melting point was selected as 276.92 ± 0.05°K. (3.82°C.), after taking into account the slight freezing point depression due to the 0.003 mole per cent. of soluble impurity present.

Table III summarizes the measurements of the melting point by various observers.

TABLE III

MELTING POINT OF DEUTERIUM OXIDE

0°C. = 273.10°K.

	M. p., °K.
Lewis and Macdonald[11]	276.9
La Mer and Baker[12]	276.90
Taylor and Selwood[13]	276.92
This research	276.92 ± 0.05

The heat of fusion was determined by the usual procedure of starting heat input at a temperature slightly below the melting point and heating to a temperature a little above. In this case, due to the fact that the less dense ice floated on top of the melted material, it was necessary to heat to almost 11° above the melting point in order to obtain sufficiently rapid thermal equi-

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(8) Aston, *Nature*, **137**, 357 (1936).

(9) Brown, Barnes and Maass, *Can. J. Research*, (a) **12B**, 699 (1935); (b) **13B**, 167 (1935).

(10) "Int. Crit. Tables," McGraw-Hill Book Co., Inc., New York, 1926, Vol. V, p. 113.

(11) Lewis and Macdonald, THIS JOURNAL, **55**, 3057 (1933).

(12) La Mer and Baker, *ibid.*, **56**, 2641 (1934).

(13) Taylor and Selwood, *ibid.*, **56**, 998 (1934).

librium after energy input. This necessitated a larger $\int C_p dT$ correction, which, however, could be applied with high accuracy.

The measurements are summarized in Table IV. Column two gives the heat input per mole, corrected for all experimental factors, but not including the $\int C_p dT$ correction, given in column three. A small correction for premelting is also included in the $\int C_p dT$ correction to the total energy. The last column gives the molal heat of fusion. We have also included in Table IV values for the heat of fusion given by other workers. These include the value of Bartholomé and Clusius, a direct determination with an ice calorimeter; that of Jacobs, an extrapolated value from heat of fusion measurements on equilibrium mixtures of light and heavy water; and indirect determinations by La Mer and Baker, and by Brown, Barnes and Maass.

In this connection it is of interest to point out that the heat of fusion of H_2O measured by Giauque and Stout[4] in the same calorimeter agreed with the accepted value within 0.1%.

TABLE IV

HEAT OF FUSION OF DEUTERIUM OXIDE

Molecular weight, 20.0284

Temp. interval, °K.	Corr. total heat input, cal./mole	$\int C_p dT$ +premelting/mole	ΔH fusion cal./mole
274.07–288.43	1872.7	373.5	1499.2
273.84–285.43	1796.4	293.5	1502.9
274.97–287.06	1818.3	317.8	1500.5
		Mean value	1501 ± 3
Bartholomé and Clusius[14]			1522
Brown, Barnes and Maass[9a]			1484
La Mer and Baker[15]			1510
Jacobs[16]			1525

The Entropy of Deuterium Oxide.—The entropy between 18 and 273.10°K. was obtained by graphical integration of our measured heat capacities. The entropy between 0 and 18°K. was calculated from the Debye equation, using $\theta = 185$.

The only direct value for the heat of vaporization of D_2O is that of Bartholomé and Clusius,[14] who determined the heat of sublimation at 0° using an ice calorimeter. They give 630.9 calories per gram as the mean of three determinations, with an average deviation of 0.4 cal./gram. Converting this to a molal basis, using our molecular weight (20.0284), we obtain 12,636 cal./mole as the heat of sublimation at 0°. The vapor pressure of D_2O at 0° is given by Bartholomé and Clusius as 3.65 ± 0.05 mm. The entropy correction to the ideal gas state should be negligible at this low pressure.

A summary of the entropy calculation at 273.10°K. is given in Table V.

TABLE V

ENTROPY OF DEUTERIUM OXIDE AT 273.10°K.

0–18°K., Debye function, $\theta = 185$	0.135
18–273.10°K., graphical	10.099
Sublimation at 273.10°K., 12636/273.10	+46.269
Compression $R \ln (3.65/760)$	−10.61
Entropy of the hypothetical perfect gas at 273.10°K. and 1 atmosphere pressure	45.89 ± 0.1 E. U.

Table VI summarizes the calculation of the entropy of *liquid* deuterium oxide at 298.10°K.

TABLE VI

CALORIMETRIC ENTROPY OF LIQUID DEUTERIUM OXIDE AT 298.10°K.

0–18°K., Debye function, $\theta = 185$	0.135
18–276.92°K., graphical	10.247
Fusion at 276.92°K., $\frac{1501}{276.92}$	5.420
276.92–298.10°K., graphical	1.472
Calorimetric entropy of liquid D_2O at 298.10°K.	17.27 ± 0.05 E. U.

For use in thermodynamical calculations, 0.806 E. U. should be added to the value in Table VI, giving 18.08 E. U., on the basis of Pauling's theory, discussed in a later section.

The Entropy from Spectroscopic Data.—The entropy was calculated from the well-known equation

$$S = 3/2\, R \ln M + 4R \ln T + R/2 \ln I_A I_B I_C - R \ln \sigma + 265.35 + S_{\text{vibrational}}$$

The vibrational fundamentals $\nu_1 = 2784$ cm.$^{-1}$, $\nu_2 = 2666$ cm.$^{-1}$, $\nu_3 = 1179$ cm.$^{-1}$ given by Barker and Sleator[17] and Rank, Larsen and Bordner[18] were used in the calculation of the vibrational entropy. At 273.10°K., this amounts to only 0.02 E. U.

As there exist no experimental values for the moments of inertia of deuterium oxide, a calculation of these was made from the corresponding moments of inertia for hydrogen oxide in the

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(14) Bartholomé and Clusius, *Z. physik. Chem.*, **B28**, 167 (1935).

(15) La Mer and Baker, THIS JOURNAL, **56**, 2641 (1934).

(16) Jacobs, *Trans. Faraday Soc.*, **31**, 813 (1935).

(17) Barker and Sleator, *J. Chem. Phys.*, **3**, 660 (1935).

(18) Rank, Larsen and Bordner, *ibid.*, **2**, 464 (1934).

ground state (non-rigid molecule) given by Freudenberg and Mecke.[19]

In this calculation, it was assumed that the root mean square distance between the D atoms in D_2O was the same as the root mean square distance between the H atoms in H_2O; it was also assumed that the root mean square distance between the O atom and the line connecting the D atoms was the same as the corresponding distance between the O atom and the line connecting the H atoms. Thus

$$I_{A_{D_2O}} = \left[\frac{\dfrac{2DO}{2D + O}}{\dfrac{2HO}{2H + O}}\right] I_{A_{H_2O}} \qquad (1)$$

$$I_{B_{D_2O}} = \frac{D}{H} \times I_{B_{H_2O}} \qquad (2)$$

$I_{C_{D_2O}}$ was calculated assuming that the distance between the D and O atoms in D_2O was the same as the distance between the H and O atoms in H_2O, and that this distance r is determined by the expression

$$I_{C_{H_2O}} = 2Hr^2\left(1 - \frac{1}{9}\cos^2\frac{\alpha}{2}\right)$$

The valence angle α is determined by

$$\tan\frac{\alpha}{2} = \frac{2}{3} \times \sqrt{2\frac{I_{B_{H_2O}}}{I_{A_{H_2O}}}}$$

Then

$$I_{C_{D_2O}} = \frac{D\left(1 - \dfrac{2}{10}\cos^2\dfrac{\alpha}{2}\right)}{H\left(1 - \dfrac{1}{9}\cos^2\dfrac{\alpha}{2}\right)} I_{C_{H_2O}}$$

The following values were obtained for the moments of inertia of deuterium oxide (in g.-cm.^{2}):

$$I_A = 1.790 \times 10^{-40} \qquad I_B = 3.812 \times 10^{-40}$$
$$I_C = 5.752 \times 10^{-40}$$

Then, at 273.10°K. and one atmosphere pressure

$$S_{D_2O} = \frac{3}{2} R \ln 20.0284 + 4 R \ln 273.10 + \frac{R}{2} \ln (1.790 \times 10^{-40} \times 3.812 \times 10^{-40} \times 5.752 \times 10^{-40}) - R \ln 2 + 265.35 + 0.02 = 46.66 \text{ E. U.}$$

in accordance with the usual custom of neglecting entropy due to nuclear spin. At 298.1°K. and one atmosphere, the spectroscopic entropy for D_2O is 47.46 E. U.

A comparison of this spectroscopic value with the calorimetric entropy given in Table V shows a difference of 0.77 E. U. A corresponding discrepancy of 0.82 E. U. at 298.1°K. was found by Giauque and Stout[4] in the case of hydrogen oxide.

Two explanations of the hydrogen oxide discrepancy have been made. Giauque and Ashley[2] offered an explanation which assumed that the ortho and para states in gaseous water persisted in the solid state at low temperatures. This theory, as pointed out by Giauque and Stout,[4] leads to a calculated discrepancy of $1/3\ R \ln 2 = 0.459$ E. U. for deuterium oxide, as compared to a calculated discrepancy of 1.033 E. U. for hydrogen oxide.

Pauling[3] has offered an alternative explanation which ascribes the discrepancy to the random orientation of the hydrogen bonds in the crystal. His theory leads to a calculated discrepancy of $R \ln 6/4 = 0.806$ E. U. This discrepancy, in Pauling's explanation, is identical for both forms of water.

In the case of hydrogen oxide, Giauque and Stout[4] have pointed out that while the discrepancy is quantitatively explained by Pauling's theory, the ortho–para explanation is not absolutely excluded, as a partial attainment of equilibrium between ortho and para forms would lead to a discrepancy somewhat lower than 1.033 E. U. The ortho–para explanation becomes still more improbable for the discrepancy in deuterium oxide, as it predicts a discrepancy of about 0.31 E. U. lower than its measured value. Thus, the agreement between our experimental discrepancy and that calculated by Pauling, together with the similar agreement found by Giauque and Stout for hydrogen oxide, gives strong support to the Pauling theory of random bond orientation.

We are indebted to Professor H. L. Johnston, who suggested the problem to one of us (E. A. L.) and kindly loaned us the pure deuterium oxide used in this investigation, and to Professor W. F. Giauque for the use of the vacuum calorimeter, and for many helpful conversations.

Summary

The heat capacity of solid and liquid deuterium oxide has been determined over their respective ranges from 15 to 298°K.

The melting point has been found to be 276.92°K. The heat of fusion of deuterium oxide is 1501 cal./mole.

The calorimetric entropy of liquid deuterium oxide at 298.1°K. is 17.27 E. U. The value which should be used in thermodynamic calculations is 0.806 E. U. higher, or 1808 E. U., on the basis of Pauling's theory.

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[19] Freudenberg and Mecke, *Z. Physik*, **81**, 465 (1933).

Using our measured heat capacities and the heat of sublimation of deuterium oxide given by Bartholomé and Clusius, we find the calorimetric entropy for $D_2O_{(g)}$ to be 45.89 E. U. at 273.10°K. and one atmosphere pressure. The entropy from spectroscopic data is 46.66 E. U., giving a discrepancy of 0.77 E. U. between the calorimetric and spectroscopic values. This is in good agreement with the theoretical discrepancy 0.806 calculated by Pauling from the assumption of random orientation of the hydrogen bonds in the crystal. This agreement, along with the similar agreement for hydrogen oxide found by Giauque and Stout, is evidence for the correctness of Pauling's theory.

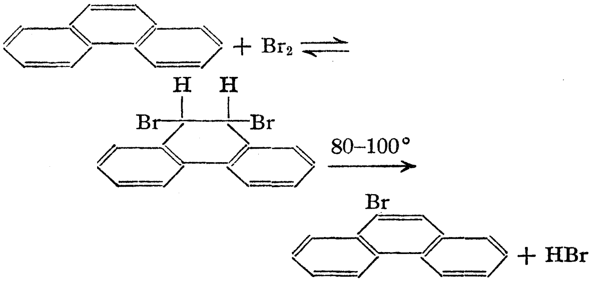
BERKELEY, CALIF. RECEIVED JULY 2, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Study of the Phenanthrene–Bromine Addition Reaction

BY CHARLES C. PRICE

Although it has been recognized since the discovery of phenanthrene[1] that the hydrocarbon forms a crystalline dibromide sufficiently stable to be isolated, the interesting reaction has received but little attention and the dibromide has been studied only as an incidental intermediate in the preparation of 9-bromophenanthrene,[2] loss of hydrogen bromide occurring when the substance is gently heated.



Since the reaction affords a model for the widely considered hypothesis that aromatic substitutions in general involve an addition–elimination mechanism, it was thought that a study of the kinetics of both of the above reactions in the presence and absence of halogenation catalysts might cast some light on the broad problem of substitution. That dibromides can be isolated from phenanthrene and anthracene but not from the other common aromatic hydrocarbons is no indication that these substances are different in kind from the others. It probably is merely a consequence of the greater reactivity of the central nucleus of the tricyclic hydrocarbons and of the stabilization of the dihydrobenzenoid nucleus of the addition product by the terminal, aromatic rings.

It was soon found in preliminary experiments that the reaction between phenanthrene and bromine in non-aqueous solvents is reversible, and that the position of the equilibrium and the rate of its establishment are both measurable by analytical methods. Consequently a study was made of the rate and equilibrium of the first reaction, the original problem being reserved for future investigation.

Analysis for bromine by titration was first tried and found to give approximate but unsatisfactory results, and the final measurements were made by colorimetric analysis for bromine with a Keuffel and Esser spectrophotometer. This proved to be a convenient and reliable method of attack. The experimental deviation of ±5% in the equilibrium constants determined by this method represents an error of only ±0.5% in the determination of the bromine concentration.

The phenanthrene used was a sample from coal tar (Gesellschaft für Teerverwertung) further purified by treatment with maleic anhydride,[3] distillation, and crystallization, m. p. 98.2–98.8°, corr. Pure bromine was prepared according to the directions of Scott,[4] dried over resublimed phosphorus pentoxide, and distilled. The purification of the carbon tetrachloride used as solvent was most satisfactorily accomplished by washing commercial material three times with one-tenth volume of concentrated potassium hydroxide in 50% alcohol at 60°, three times with water, three times with one-tenth volume of concentrated sulfuric acid at 25°, thorough washing with water, a

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(1) Fittig and Ostermayer, *Ber.*, **5**, 933 (1872); *Ann.*, **166**, 361 (1873); Graebe, *Ber.*, **5**, 861, 968 (1872); *Ann.*, **167**, 131 (1873).

(2) Hayduck, *Ann.*, **167**, 181 (1873); Anschütz, *Ber.*, **11**, 1217 (1878); Austin, *J. Chem. Soc.*, **93**, 1763 (1908); Sandqvist, *Ann.*, **398**, 126 (1913); Henstock, *J. Chem. Soc.*, **123**, 3097 (1923); Bachmann, THIS JOURNAL, **56**, 1365 (1934).

(3) Clar, *Ber.*, **65**, 852 (1932).

(4) Scott, *J. Chem. Soc.*, **103**, 847 (1913).

preliminary drying over calcium chloride, and distillation from phosphorus pentoxide, b. p. 76–76.5°. The use of sodium as a final drying agent, recommended by several investigators,[5] gave a product containing a slight amount of bromine-absorbing impurity (0.004–0.006%), determined by the decrease in the absorption coefficient with increasing dilution.

The rate as well as the equilibrium for the addition of bromine to phenanthrene follow quite as would be expected from the equation of the reaction

$$C_{14}H_{10} + Br_2 \underset{k_1}{\overset{k_2}{\rightleftharpoons}} C_{14}H_{10}Br_2$$

The equilibrium constant K is defined as follows:

$$K = \frac{[C_{14}H_{10}Br_2]}{[C_{14}H_{10}][Br_2]} = \frac{k_2}{k_1}$$

where k_1 and k_2 represent the rate constants for the reactions as indicated.

The rate constant for the bimolecular forward reaction, k_2, is calculated from the expression for a bimolecular forward reaction corrected for a monomolecular back reaction

$$dx/dt = k_2(a - x)(b - x) - k_1x$$

Substitution for k_1 of its value as determined from the expression for the equilibrium constant, $k_1 = k_2/K$, and integration lead to the following expression for k_2.

$$k_2 = \frac{2.303}{t\sqrt{-q}}\left[\log\frac{2x - (a + b + 1/K) - \sqrt{-q}}{2x - (a + b + 1/K) + \sqrt{-q}} - \log\frac{-(a + b + 1/K) - \sqrt{-q}}{-(a + b + 1/K) + \sqrt{-q}}\right]$$

where $a = [Br_2]_{i\,(\text{initial})}$, $b = [C_{14}H_{10}]_i$, $x = [Br_2]_i - [Br_2]_{t\,(\text{at time t})}$, and $-q = (a+b+1/K)^2 - 4ab$.

The experimentally determined values for these constants at 15.7, 25.0 and 39.0° are shown in Tables I and II. On plotting log K at these three temperatures against $1/T$, the points are observed to fall accurately on a straight line. The rate constants are all calculated from the starting time. In the determination of the rate constants for expts. 1–6 the light of the spectrophotometer was on during the entire course of the reaction, the rate constants increasing steadily due to catalysis by the light. In the remaining experiments the light was on for only about thirty seconds of every five minutes, and this seemed to have no appreciable effect on the rate of the reaction, the rate constants showing no systematic deviation either with the concentration or amount

TABLE I

EQUILIBRIUM AND RATE CONSTANTS FOR THE ADDITION OF BROMINE TO PHENANTHRENE AT 25.0°

Expt.	$[Br_2]_i$[a]	$[C_{14}H_{10}]_i$	K	k
1	0.00696	0.00476	239	23–36[b]
2	.00555	.00456	236	26[b]
3	.00555	.00727	226	24–26[b]
4	.00699	.00871	229	. . .
5	.00699	.00692	218	10–27[b]
6	.00699	.01087	213	9–18[b]
7	.00845	.00431	224	10–12.4
8	.00845	.01043	219	11–14
9	.00845	.01495	225	. . .
10	.00845	.00824	230	. . .
12	.03405	.02997	241	11–12.6
13	.03405	.00889	223	12–13.5
14	.03405	.02268	219	7–8
15	.00655	.01188	241	9–13.5
18	.00655	.00900	237	. . .
19[c]	.00841	.00904	236	9–11.5
20	.00841	.01181	221	8–11.5
25	.00873	.01433	240	9–13
32	.00542	.01202	232	6–6.5
96[d]	.00788	.01063	224	. . .
97[d]	.00782	.00839	240	. . .
		$K_{25}{}^{\circ} =$	230	

[a] Concentrations expressed in moles per liter. [b] Spectrophotometer light on during entire course of experiment. [c] Oxygen removed from solvent by boiling under diminished pressure.[6] [d] Synthetic phenanthrene of Fieser and Hershberg, THIS JOURNAL, 57, 2192 (1935), used in these experiments after further selenium dehydrogenation and recrystallization, m. p. 100.7–101°, corr.

TABLE II

EQUILIBRIUM AND RATE CONSTANTS FOR THE ADDITION OF BROMINE TO PHENANTHRENE AT 39.0 AND 15.7°

Expt.	$[Br_2]_i$	$[C_{14}H_{10}]_i$	K	k
33	0.01042	0.00892	132	7–9.5
34	.01042	.00714	134.5	8–11
35	.00628	.00440	139	9.5–10.5
36	.00628	.01004	132.5	6.5–8
37	.00628	.00656	134.5	7.5–9
38	.00628	.00718	132	10–11
		$K_{39}{}^{\circ} =$	134	
39	.00946	.00890	322	6.5–8.5
40	.00946	.00648	358	8.5–9.5
		$K_{15.7}{}^{\circ} =$	340	

TABLE III

SUMMARY OF THE EQUILIBRIUM DATA FOR THE ADDITION OF BROMINE TO PHENANTHRENE

Temp., °C.	K	$-\Delta F$ (cal.)	$-\Delta H$ (cal.)	ΔS (cal./deg.)
15.7	340 (±8)	3350 (±10)		
25.0	230 (±6)	3220 (±15)	7350 (±250)	13.8
39.0	134 (±2)	3040 (±15)		

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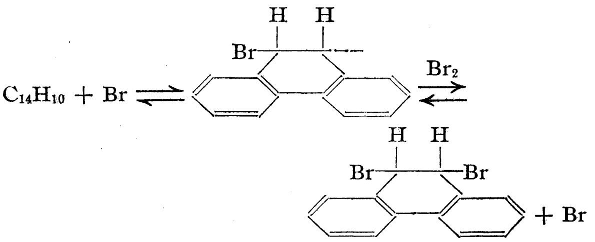
[5] Berthoud and Béraneck, *J. chim. phys.*, **24**, 213 (1927); Bauer and Daniels, THIS JOURNAL, **56**, 378 (1934).

of reaction. Table III summarizes the equilibrium data, including ΔF, ΔH and ΔS, for the addition of bromine to phenanthrene. The limits indicated are calculated from the average deviation of the equilibrium constants.

The inhibitory effect of oxygen noted by Bauer and Daniels[6] in a study of the addition of bromine to cinnamic acid was not noticeable in this reaction (expt. 19). Benzoyl peroxide also had no effect on either the rate or the equilibrium, nor did the antioxidant β-naphthol. It was discovered, however, that such antioxidants as diphenylamine, hydroquinone, tetrabromohydroquinone and tetrabromocatechol are very effective inhibitors of the reaction, even in relatively small amounts. It appears significant that the distinctive feature of these inhibitors is the fact that they may readily donate *atoms* of hydrogen and revert to stable compounds, namely, tetraphenylhydrazine or a quinone.

These facts all find ready explanation on the basis of a chain mechanism for the addition of bromine to phenanthrene, propagated by bromine atoms and free radicals as follows



a type of mechanism which has been proposed by several investigators studying photochemical bromination reactions.[7] It is suggested that the inhibitor functions by interaction with the bromine atoms, yielding hydrogen bromide and either tetraphenylhydrazine or a quinone. Lauer,[8] in a recent series of papers on the bromination of various aromatic hydrocarbons does not seem to consider fully the possibility of a chain mechanism in the deduction of his conclusions.

This inhibitory effect not only indicates that the reaction proceeds through a chain mechanism but makes possible an estimation of the length of the chain, a determination which usually is made only through a photochemical study of quantum yield. If, for instance, the concentration of the inhibitor is one-tenth that of the phenanthrene, it may be assumed that the chain length is approximately ten, since the chances are ten to one in favor of a bromine atom colliding with a molecule of phenanthrene, thus propagating the chain rather than hitting a molecule of inhibitor and interrupting the chain. Multiplication of the ratio of phenanthrene to inhibitor by the ratio of the uninhibited rate to inhibited rate will then give the length of the chain in the case of the uninhibited reaction. The validity of the above assumption regarding the chain length of the inhibited reaction depends chiefly on two conditions, namely, the equality of the activation energy for the reactions between bromine atoms and phenanthrene or inhibitor, and the equivalence of the steric factors involved in these two reactions. The assumption implies that the fraction of effective collisions between bromine atoms and molecules of inhibitor is the same as that for the collisions between bromine atoms and phenanthrene. The quantitative identity of the results using diphenylamine, tetrabromocatechol, and tetrabromohydroquinone seems to substantiate the validity of the assumption, and to indicate the probability that all of the above collisions result in reaction, since if either a steric effect or activation energy were a factor it would not be expected to be the same in each case.

It should be pointed out that in the determinations of the chain length by this method, the inhibitor was added in quantity sufficient so that the ordinary chain-stopping process could be neglected as compared with the interruption of the chain by the inhibitor. The results of the experiments at 25° are shown in Table IV. In each case the experiment with less inhibitor gave a lower value for the chain length, possibly due to decrease in inhibitor concentration by reaction with bromine atoms, an effect which would natu-

TABLE IV

EFFECT OF VARIOUS INHIBITORS ON THE RATE OF ADDITION OF BROMINE TO PHENANTHRENE AT 25 AND 36°

Inhibitor	$[C_{14}H_{10}]$/ [Inhib.]	k	Chain length
Diphenylamine	38.8	0.18	2500[a]
Diphenylamine	144	.85	1850[a]
Tetrabromocatechol	33.6	.18	2050[a]
Tetrabromocatechol	105	.84	1400[a]
Tetrabromohydroquinone	43	.25	1900[a]
Tetrabromohydroquinone	105	.70	1650[a]
Tetrabromohydroquinone	70.6	.67	1000[b]
Tetrabromohydroquinone	145	1.2	1200[b]

[a] Calculated for $k_{25°} = 11$. [b] Calculated for $k_{36°} = 10$.

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(6) Bauer and Daniels, THIS JOURNAL, **56**, 2014 (1934).

(7) Berthoud and Béraneck, *J. chim. phys.*, **24**, 213 (1927); Wachholtz, *Z. physik. Chem.*, **125**, 1 (1928).

(8) Lauer, *Ber.*, **69**, 141, 146, 851, 978, 1061 (1936).

rally be increasingly noticeable with decreasing concentration of inhibitor. For this reason the higher values are perhaps the more nearly correct.

It is necessary to reconcile the interpretation of the results in terms of a chain mechanism with the observed second order kinetics. In studies of photochemical brominations,[5,7] which apparently proceed by chain reactions, the initiating reaction is the photochemical dissociation of bromine molecules to atoms, the experimentally determined rates being proportional to the first power of the bromine concentration alone. That the rate in the present case is dependent also upon the concentration of phenanthrene can be accounted for by assuming that the chain initiating reaction is

$$C_{14}H_{10} + Br_2 \longrightarrow C_{14}H_{10}Br + Br$$

It is further necessary to assume that the length of the chain remains sensibly constant during the course of the reaction. A calculation of the variation of this factor with changing concentrations of the reactants was made on the basis of the following mechanism, the same as that proposed by Berthoud and by Wachholtz[7] for the addition of bromine to ethylenic double bonds, except that in the present case the chain-initiating reaction is not the photochemical dissociation of bromine.

$$\begin{array}{lll}
(1) & C_{14}H_{10} + Br_2 \longrightarrow C_{14}H_{10}Br + Br & k_1 \\
(2) & C_{14}H_{10} + Br \longrightarrow C_{14}H_{10}Br & k_2 \\
(3) & C_{14}H_{10}Br + Br_2 \longrightarrow C_{14}H_{10}Br_2 + Br & k_3 \\
(4) & C_{14}H_{10}Br + Br \longrightarrow C_{14}H_{10}Br_2 \text{ (or } C_{14}H_{10} + Br_2) & k_4 \\
(5) & C_{14}H_{10}Br \longrightarrow C_{14}H_{10} + Br & k_5 \\
(6) & C_{14}H_{10}Br_2 + Br \longrightarrow C_{14}H_{10}Br + Br_2 & k_6 \\
(7) & C_{14}H_{10}Br_2 + Br_2 \longrightarrow C_{14}H_{10}Br + Br_3 \text{ (or } Br + Br_2) & k_7
\end{array}$$

Reaction 7 is included since a solution of phenanthrene dibromide alone is quite stable and its dissociation proceeds only on the addition of a small amount of bromine.

If now the chain length, α, is placed equal to the ratio of the chain-propagating reactions to the chain-interrupting reactions

$$\alpha = \frac{k_2[C_{14}H_{10}][Br] + k_3[C_{14}H_{10}Br][Br_2]}{k_4[C_{14}H_{10}Br][Br]}$$

it is necessary only to obtain the concentrations of the intermediates, $C_{14}H_{10}Br$ and Br, in terms of the reactants by setting up and solving the equations of the steady state in order to obtain an expression for the chain length in terms of definitely determinable quantities. Making the one simplifying assumption that $k_6[C_{14}H_{10}Br_2]$ is negligible as compared with $k_2[C_{14}H_{10}]$, since the rate of the forward reactions must be greater than the back reactions due to the position of the equilibrium and since the concentration of the dibromide is at most equal to that of the phenanthrene at the dilution in question, the following expression can be derived:

$$\alpha^2 = 3\,\frac{k_2k_3}{k_1k_4} + \frac{k_2k_5}{k_1k_4}\,\frac{1}{[Br_2]} + \frac{k_2k_3^2}{k_1k_4}\left(\frac{[Br_2]}{k_3[Br_2] + k_5}\right)$$

A two- or three-fold change in bromine concentration, as was the case in the measurements, should have but little effect on α^2, even less on α itself.

A probable reason for the lack of temperature coefficient was indicated by the results of determinations of the chain length at 36°. At this temperature the chain-initiating reaction should have approximately twice the rate at 25°, but compensating for this factor it was found that the chain length had decreased from about 2000 to 1000. The results of these experiments are shown in Table IV.

One other very interesting phenomenon discovered in the course of the work was the phenanthrene-induced bromination of dioxane, and the observations offer further support for the proposed mechanism for the initiation of the bromine–phenanthrene reaction. A solution of bromine in dioxane was found to be completely stable at room temperature or slightly above, but the addition of phenanthrene causes a rapid absorption of bromine, not only by addition to phenanthrene ($^1/_3$) but by bromination of the dioxane ($^2/_3$). The phenomenon has not been thoroughly investigated but the results suggest the following mechanism:

$$\begin{array}{rl}
C_{14}H_{10} + Br_2 & \longrightarrow C_{14}H_{10}Br + Br \\
C_{14}H_{10}Br + Br_2 & \longrightarrow C_{14}H_{10}Br_2 + Br \\
C_4H_8O_2{\cdot}Br_2 + 2Br & \longrightarrow C_4H_6Br_2O_2 + 2HBr \\
 & \qquad\quad \big\downarrow H_2O \\
 & \qquad 2CH_2OH{\cdot}CHO + 2HBr
\end{array}$$

This accounts for the observed ratio of hydrogen bromide produced to bromine absorbed. A positive Fehling's test showed the presence of an aldehyde. The reaction is to be studied further.

The author wishes to express his grateful appreciation to Professor Louis F. Fieser both for proposing the problem and for inspiration to its successful completion. Acknowledgment is also due Dr. Paul D. Bartlett for much helpful advice and criticism.

Summary

1. The rate and equilibrium for the addition of bromine to phenanthrene have been measured.
2. Evidence for a chain mechanism has been presented, as well as a method for the determination of its length.

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CAMBRIDGE, MASS.
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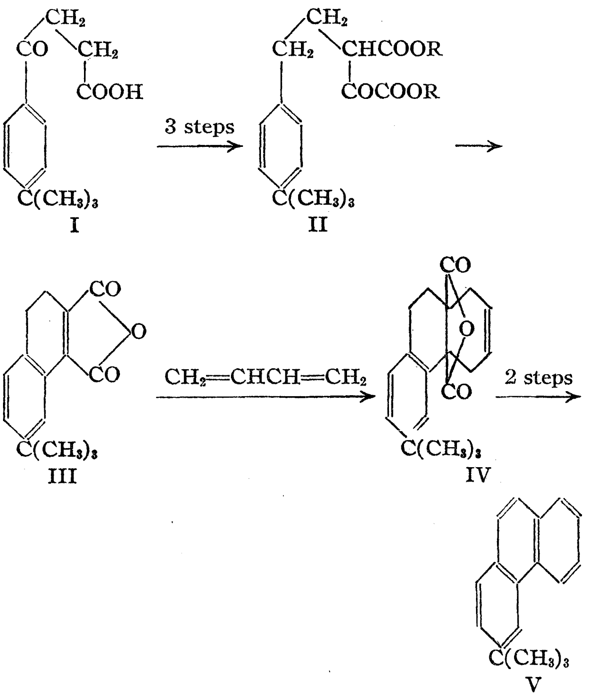
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Effect of Substituents on the Phenanthrene–Bromine Addition Reaction

BY LOUIS F. FIESER AND CHARLES C. PRICE

Following the observation[1] that the addition of bromine to phenanthrene proceeds to a measurable equilibrium at a conveniently measurable rate, it became of interest to investigate the effect of substituent groups in the terminal rings on the free energy and rate of the reaction. It seemed desirable to study compounds having substituents belonging to the three types distinguished by the nature of the directive influence which they exert on aromatic substitutions, and attention was directed first to 2- and 3-substituted phenanthrene derivatives since these are more readily available than the 1- and 4-isomers. As representative compounds with meta-directing groups the 2- and 3-carboxylic esters of phenanthrene were selected and found satisfactory. Halogen atoms constitute a special class of substituent since they retard substitution in the benzene ring like meta groups yet direct to the ortho–para positions, but of the compounds desired only 3-chlorophenanthrene[2] had been described at the time our work was undertaken. The 2- and 3-halophenanthrenes, however, were conveniently obtained from the acetyl compounds[3] through the oximes, acetylamines and amines, a method which has been reported by Bachmann and Boatner[4] in a preliminary communication published since the completion of our work.

It was a more difficult matter to find suitable 2- and 3-phenanthrene derivatives having ortho–para directing groups of the type that facilitate aromatic substitutions. A too powerfully directing group would lead to substitution in the terminal nucleus rather than 9,10-addition, and this apparently is the case with the methoxy- and acetylamino-phenanthrenes for they rapidly absorb more than one mole of bromine irreversibly in carbon tetrachloride solution. The same observation was made with 3-ethylphenanthrene, and it is possible that in this case the principal reaction is a side-chain substitution. The phenanthryldimethyl carbinols were investigated but they proved to be too unstable. Finally the tertiary butyl compounds were synthesized and found entirely satisfactory for the purpose. 3-*ter.*-Butylphenanthrene (V) was obtained by the synthetic method of Fieser and Hershberg[5] starting with the keto acid I resulting from the condensation of *ter.*-butylbenzene with succinic anhydride.



The structure was established by conversion to *p*-*ter.*-butylbenzoic acid and terephthalic acid. The addition of butadiene to III and the remaining steps all proceeded very satisfactorily, affording

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[1] Price, THIS JOURNAL, 58, 1834 (1936).

[2] Sandqvist, *Ann.*, 396, 116 (1909).

[3] Mosettig and van de Kamp, THIS JOURNAL, 52, 3704 (1930).

[4] Bachmann and Boatner, *ibid.*, 58, 857 (1936).

[5] Fieser and Hershberg, *ibid.*, (a) 57, 1851 (1935); (b) 57, 2192 (1935).

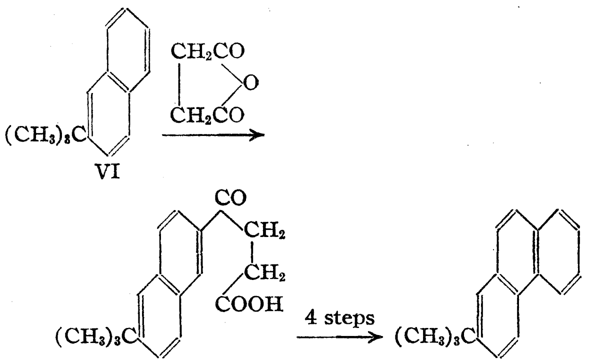
TABLE I

EQUILIBRIUM AND RATE DATA FOR THE PHENANTHRENE–BROMINE-ADDITION REACTION FOR VARIOUS PHENANTHRENE DERIVATIVES IN CARBON TETRACHLORIDE SOLUTION AT 25 AND 36°

Compound	$K_{25°}$	$K_{36°}$	$k_{25°}$	$k_{36°}$	$-\Delta F_{25°}$ (cal.)	$-\Delta H$ (cal.)	ΔS (cal./deg.)
2-Carbethoxyphenanthrene	168	88	2.0–7.0	3–7	3070	10,400	24.6
3-Carbethoxyphenanthrene	93	59	1.5–3.0	1.5–5	2690	7,200	14.9
2-Carbomethoxyphenanthrene	167	81	0.4–0.7	0.5–1	3030	11,300	27.8
3-Carbomethoxyphenanthrene	129	63	3–8	0.75–1.25	2880	11,250	28.2
2-Chlorophenanthrene	159	54	0.02–0.05	0.015–0.025	3000	16,900	46.6
3-Chlorophenanthrene	170	67	0.3–0.7	0.5–1.5	3040	14,300	37.7
2-Bromophenanthrene	152	59	0.02–0.05	0.02–0.05	2980	14,800	39.6
3-Bromophenanthrene	152	69	....	0.3–1.0	2990	12,800	32.9
Phenanthrene	230	148	7–11	7–11	3220	7,350	13.8
2-*ter.*-Butylphenanthrene	320	262*	1–4	2–5	3420	3,350	0
3-*ter.*-Butylphenanthrene	467	191*	7–11	5–7	3640	12,900	31.1

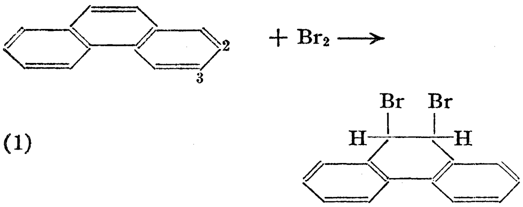
(* 37.4°.)

an easily purified hydrocarbon. The synthesis of the 2-isomer was patterned after Haworth's syntheses and based upon his observation[6] that in nitrobenzene solution succinic anhydride condenses with β-methyl- and β-isopropyl-naphthalene in the 6-position. β-*ter.*-Butylnaphthalene was found to react in the same way, giving the keto acid VII. On reduction, cyclization and conversion to an aromatic hydrocarbon, the product was found to be a phenanthrene derivative isomeric with 3-*ter.*-butylphenanthrene and yielding on oxidation an ortho quinone with the substituent still intact, hence a *ter.*-butyl-9,10-phenanthrenequinone. Theoretically VI could give rise to 2-, 3- or 9-*ter.*-butylphenanthrene, and since the last two structures are eliminated the substance obtained is the 2-isomer and the keto acid (VII) has the structure shown.



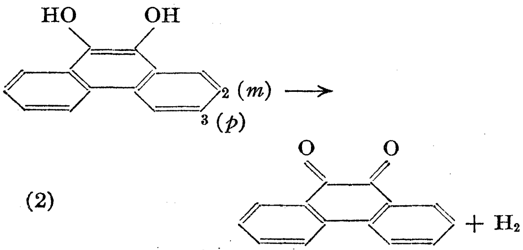
VI VII VIII

The bromine-addition reaction was studied in carbon tetrachloride solution by the method employed for phenanthrene[1] and the results are summarized in Table I. On comparing the equilibrium constants at 25 and 36° with the values for phenanthrene it is seen that the constants at the two temperatures are roughly parallel for the pairs of isomers except in the case of the two alkyl compounds. It is quite interesting that halogen substituents fall into line with the typically meta-directing carboxylate groups in decreasing the free energy of the bromine-addition, while an alkyl group has just the opposite effect. This relationship is exactly that found for the effect of groups of these three types on the oxido-reduction potentials of quinone-hydroquinone systems,[7] and it is of interest to compare the reactions:



(1)

$-\Delta F_{25°}$ = 3220 cal.



(2)

$-\Delta F_{25°}$ = 21,736 cal.[8]

As applied to the oxidation of a hydroquinone (Reaction 2), a rule previously stated[7] in terms of potentials may be phrased as follows: groups which facilitate substitution in the benzene ring increase the free energy of oxidation, while those which retard benzene-substitution, including meta-directing groups and halogen atoms, have the opposite influence. It is clear from the present re-

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(6) Haworth, Letsky and Mavin, *J. Chem. Soc.*, 1784 (1932).

(7) Fieser and Fieser, THIS JOURNAL, **57**, 491 (1935).

(8) From the normal potential in 95% alcoholic solution, Fieser, *ibid.*, **51**, 3101 (1929).

sults that the rule applies equally well to Reaction 1. In each case the reaction involves the conversion of the central, benzenoid ring into a dihydrobenzenoid nucleus, and substituents in a terminal ring exert similar influences in the two processes. The free energy change in the bromine-addition is much less than in the oxidation, but a substituent has nearly the same proportionate influence in each case, as can be seen from the comparisons given in Table II. Although the effect of a 3-*ter*.-butyl group on the free energy of oxidation is not known, it can be inferred from other data[7,8] that such a group probably would increase the free energy change to about twice the extent that a bromine atom decreases it. This again corresponds to the findings regarding Reaction 1.

TABLE II

EFFECT OF SUBSTITUENTS IN CALORIES ON $-\Delta F$

Substituent	Reaction 1	Reaction 2
3-Bromo	230 (7.1%)	1292 (5.9%)
3-Carbomethoxy	340 (10.0%)	2677 (12.3%)

With regard to the effect of the position of the substituent in the phenanthrene nucleus, it has been observed[8] in the case of Reaction 2 that the effect of a group in either the positive or negative direction is greater when it is situated in the 3-position para to the 10-hydroxyl group than when it is located at the meta position 2. The present results are hardly extensive enough to show whether or not this is true also of Reaction 1. With the halogen compounds the differences in the values of $-\Delta F$ for the isomers are too slight to be significant. The ester groups are invariably more effective in the 3-position, and the differences are quite noticeable. Considering the free energy changes at 25°, the same relationship holds for the *ter*.-butyl group, but in this case there is a curious reversal at the higher temperature and more data will be required to establish the analogy.

Comparing the rate constants for the bromine-addition to the substituted phenanthrenes (Table I), it may be said that there is no striking deviation from the behavior of phenanthrene, and no significant difference between isomers, except in the case of the halogen compounds. A halogen atom at either the 2- or 3-position definitely retards the addition reaction, and there is a decided difference between the isomers. The rate constants for 2-bromo- and 2-chlorophenanthrene are only about one-fortieth as great as the constants for the 3-isomers. Considering that the 2-position is meta to one of the unsaturated carbon atoms concerned in the addition reaction while a 3-substituent occupies a para position with respect to this group, it may be said that halogen is somewhat inhibitory to the addition of bromine in any event but that it exerts a pronounced and specific inhibiting influence when in the meta (2-) position. This suggests a possible explanation of the peculiar fact that halogen atoms stabilize the benzene ring like the common meta-directing groups but nevertheless direct substituents into the ortho–para positions. In the present study halogen is classed with the meta-type groups with respect to its effect on the equilibrium (stabilizing effect) but is found to differ from other groups in specifically decreasing the rate of a reaction at a center with respect to which it occupies the meta position.

Experimental Part[9]

The phenanthroic esters were prepared according to Mosettig and van de Kamp[3] and the melting points were as follows: 2-methyl 95–96°, 2-ethyl 72.5–73.5°, 3-methyl 93.5–94.5°, 3-ethyl 55–56°. Incidentally, 3-acetophenanthrene on purification through the picrate was found to melt at 73.5–74.5°; picrate, m. p. 123–125°. In the hypochlorite oxidation of the acetophenanthrenes the time of reaction was shortened greatly by providing vigorous mechanical stirring. 3-Ethylphenanthrene[3] was purified through the picrate, m. p. 120–122°, and distilled. The halophenanthrenes employed had the following melting points: 2-chloro 86.5–87.5°, 2-bromo 97–98°, 3-chloro 82–83°, 3-bromo 82–83°. In view of the announcement of Bachmann and Boatner[4] the preparations and analyses will be omitted, but it may be noted that 2-acetophenanthrene-oxime (m. p. 193–195°, crystallized with excess hydroxylamine) and the 3-isomer were obtained in 83–95% yield, rearranged with phosphorus pentachloride in dry ether and converted to the phenanthrylamine hydrochlorides in about 70% yield. The Sandmeyer reaction proceeded best (45% yield) when the diazonium salt was added to the boiling cuprous halide solution.

2-Phenanthryldimethyl carbinol was prepared by adding a solution of 2-acetophenanthrene in benzene to an ethereal solution of methylmagnesium iodide and refluxing. On allowing a solution of the crude product (80% yield) in petroleum ether to evaporate at room temperature the substance was deposited as long silky needles, m. p. 90–92°, dec., and as cubes, m. p. 97–99°, dec.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.44; H, 6.95. Found: (needles) C, 86.66; H, 6.85; (cubes) C, 86.12; H, 6.94.

3-Phenanthryldimethyl carbinol was obtained, after purification through the picrate, as an oil which crystallized from petroleum ether in a bath of solid carbon dioxide and alcohol but melted again at room temperature. The

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[9] Analyses by Mrs. G. M. Wellwood.

picrate separated from methyl alcohol as bright orange crystals, m. p. 107–110°, dec.

Anal. Calcd. for $C_{17}H_{16}O \cdot C_6H_3O_7N_3$: C, 59.32; H, 4.13. Found: C, 59.50; H, 4.11.

On recrystallization from alcohol the melting point rose eventually to 160–163°, dec., and apparently dehydration had occurred giving 3-isopropenylphenanthrene picrate (calcd. C, 61.7; H, 3.8. Found: C, 62.5; H, 3.7).

Synthesis of 3-*ter*.-Butylphenanthrene

β-(*p-ter*.-Butylbenzoyl)-propionic Acid (I).—*ter*.-Butylbenzene (17 g.) was added slowly to a mixture of succinic anhydride (13 g.), aluminum chloride (36 g.), and carbon bisulfide (100 cc.), and after refluxing for one hour the mixture was cooled and decomposed with ice and hydrochloric acid. After removing the solvent with steam the product solidified (20 g.) and on crystallization from 50% acetic acid it was obtained as colorless crystals, m. p. 121–122°; yield 16.5 g. (55%). The substance crystallizes from dilute alcohol as lustrous plates and from benzene–ligroin as large cubes; both forms melt at 121–122°.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.75; H, 7.73. Found: C, 71.46; H, 7.30.

The acid was converted by oxidation with potassium hypochlorite into *p-ter*.-butylbenzoic acid, m. p. 165–166°, corr., and this with dilute nitric acid gave terephthalic acid, identified as the dimethyl ester, m. p. 140.5–141°, corr., by comparison with an authentic sample.

γ-(*p-ter*.-Butylphenyl)-butyric acid was obtained in 72% yield from the keto acid by Martin's modification[10] of the Clemmensen method as already reported.[10] After refluxing for fifteen hours the product was collected and dried in ether and distilled, b. p. 164–167° (5 mm.), m. p. 57–60°. Recrystallized from petroleum ether the acid formed small crystals, m. p. 59.5–60.5°.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.30; H, 9.17. Found: C, 76.30; H, 9.04.

The **ethyl ester** was conveniently prepared by distilling off the toluene at the end of the reduction, extracting with ether, esterifying the crude acid with absolute alcohol and hydrogen chloride, and distilling the ester. It was obtained as a colorless liquid, b. p. 145–147° (5 mm.), in 70% yield.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.41; H, 9.68. Found: C, 77.38; H, 10.19.

7-*ter*.-Butyl-Δ¹-dihydronaphthalene-1,2-dicarboxylic Anhydride (III).—Ethyl γ-(*p-ter*.-butylphenyl)-butyrate (63 g.) was condensed with ethyl oxalate in the presence of sodium ethylate by the procedure of Fieser and Hershberg[5a] and the crude oxalyl derivative (II), obtained as a light reddish oil after removal of the ether at diminished pressure, was cyclized by stirring a mixture of the oil with twenty parts by volume of 80% sulfuric acid at room temperature, heating the deep red solution to 60° and maintaining this temperature for ten minutes. The anhydride separated as a yellow solid which was collected after cooling on a sintered glass funnel and washed with fresh acid and with water. The yield of microcrystalline material was 55 g. (85%). Crystallized from benzene–ligroin the anhydride formed nearly colorless, flat needles, m. p. 143–145°.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.97; H, 6.28. Found: C, 75.36; H, 6.28.

The sulfuric acid liquor on standing deposited a second substance (0.8 g.) which after two crystallizations formed faintly yellow needles, m. p. 174–175°. The substance has the same composition as the chief reaction product (found: C, 75.19, 75.19; H, 6.33, 6.25) and it may arise from a small amount of an isomer present in the starting material.

7-*ter*.-Butylnaphthalene-1,2-dicarboxylic anhydride was obtained in good yield by heating the dihydro compound with the calculated amount of sulfur at 330–340° for one hour and distilling the product. Long, pale yellow needles, m. p. 146.5–147.5°, were obtained from benzene–ligroin.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.56; H, 5.55. Found: C, 75.71; H, 5.70.

6-*ter*.-Butyl-1,4,9,10,11,12-hexahydrophenanthrene-11,12-dicarboxylic anhydride (IV) was obtained by heating a mixture of 12.2 g. of the anhydride and 31.8 g. of butadiene at 150° for thirty-six hours. On distillation at 1 mm. pressure (bath at 240–260°) there was obtained 12.8 g. of colorless material which fluoresced bright blue in ultraviolet light. Crystallized from benzene–ligroin it formed stout, colorless needles, m. p. 85.5–86.5°; yield 10 g. (68%).

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.36; H, 7.16. Found: C, 77.43; H, 7.20.

3-*ter*.-Butylphenanthrene.—The diene addition product (5 g.) was heated with 10 g. each of potassium hydroxide and water in the manner described,[5b] and after driving off the water the bath temperature was brought to 330–360°, when 2.5 g. (about 65%) of hydrocarbon collected as a colorless distillate (oil). A portion of the distillate (2.2 g.) was heated under nitrogen with 4 g. of selenium, added in portions, for thirty-six hours and the product was extracted with petroleum ether and vacuum distilled from a small bit of sodium. The pale yellow distillate soon solidified, m. p. 49–52°, yield 1.5 g. The hydrocarbon crystallized from alcohol as colorless, centimeter-long, prismatic needles fluorescing bright blue in ultraviolet light, m. p. 54–55°.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.24; H, 7.76. Found: C, 92.30, 92.00; H, 7.55, 7.99.

The **picrate**, once recrystallized from alcohol, formed orange needles, m. p. 142–143°.

Anal. Calcd. for $C_{18}H_{18} \cdot C_6H_3O_7N_3$: C, 62.17; H, 4.58. Found: C, 61.79; H, 4.26.

The **quinone** was obtained by heating the hydrocarbon with chromic anhydride in acetic acid solution at 80–90° for one hour, the product separating as bright orange needles on cooling (77% yield). Recrystallized from alcohol it formed slender orange needles, m. p. 186–187°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.78; H, 6.10. Found: C, 81.51; H, 6.15.

Synthesis of 2-*ter*.-Butylphenanthrene

β-*ter*.-Butylnaphthalene.—A mixture of 330 g. of naphthalene and 251 g. of *ter*.-butyl chloride was warmed at

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[10] Martin, THIS JOURNAL, **58**, 1438 (1936).

50–60° until the solid had dissolved and 10 g. of aluminum chloride was added in small portions with stirring in about one and one-half hours. The reaction was largely over when about half of the aluminum chloride had been added. After a further half-hour of stirring the material was washed and dried in benzene and distilled. About 100 g. of naphthalene came over up to 140° (12 mm.) and the main product distilled at 119–135° (6 mm.). Redistillation gave 140 g. (30%) of β-*ter.*-butylnaphthalene as a colorless oil, b. p. 127–131° (9 mm.), picrate, m. p. 99.5–100.5°. The picrate of the hydrocarbon obtained by other methods is reported to melt at 102–103°[11] and at 96°.[12]

Di-*ter.*-**butylnaphthalenes.**—The combined higher-boiling fractions from the above preparation on redistillation gave 100 g. of a fraction boiling at 150–170° (10 mm.) and promptly solidifying. This apparently consisted largely of a mixture of the two di-*ter.*-butylnaphthalenes described by Gump,[13] and in a preliminary examination it was found that the higher-melting isomer can be isolated easily by two crystallizations from methyl alcohol: thick, lustrous plates, m. p. 146–147°. As this isomer does not form a picrate in alcoholic solution whereas the lower-melting hydrocarbon does, the latter can be isolated easily from the mother liquor or from the original mixture as the picrate. This picrate was obtained as beautiful orange needles, m. p. 155.5–156.5°, but it was not analyzed successfully. The hydrocarbon regenerated from the purified picrate formed fine cottony needles from alcohol; it melted unsharply at 86–90° but had the expected composition.

Anal. Calcd. for $C_{18}H_{24}$: C, 89.93; H, 10.07. Found: (146–147°) C, 90.14; H, 10.39; (86–90°) C, 90.17; H, 9.92.

A quinone was obtained by refluxing a solution of the higher-melting hydrocarbon in glacial acetic acid with chromic anhydride for twenty minutes. It was purified with Norite in ether solution and crystallized from alcohol; slender, bright yellow needles, m. p. 83.5–84.5°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.22. Found: C, 79.98; H, 8.15.

β-(**6-*ter.*-Butylnaphthoyl-2)-propionic acid (VII)** was prepared by adding with stirring 140 g. of β-*ter.*-butylnaphthalene and 66 g. of succinic anhydride to a solution of 226 g. of aluminum chloride in 1.5 liters of nitrobenzene at 0°. After eight hours at 0° and one day at room temperature ice and hydrochloric acid were added and the solvent removed with steam. The dark brown mass remaining after decanting the aqueous liquor was treated with a small quantity of ether, as this dissolved a dark oil and left a fairly clean solid (92 g.). This was dissolved in glacial acetic acid and the solution was diluted with hot water until cloudy and treated with a liberal quantity of Norite. The filtered solution deposited glistening, colorless needles, m. p. 148–150°; total yield, 80 g. (37%).

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.07; H, 7.04. Found: C, 76.02; H, 7.11.

γ-(**6-*ter.*-Butylnaphthyl-2)-butyric Acid.**—The above keto acid was largely unchanged when submitted to reduction by the usual Clemmensen method or with added toluene (thirty hours) but, as already noted,[10] the reaction proceeded smoothly by Martin's method using toluene and a small amount of acetic acid, yield crude 78%. A portion of the acid was purified through the methyl ester, b. p. 185–187° (6 mm.), and after saponification crystallized from petroleum ether. It separated as long, slender needles which soon changed in part at least into short, stout needles. Apparently neither form was obtained as a pure individual, for the melting points were unsharp and varied from 87 to 95°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.94; H, 8.22. Found: C, 79.86; H, 8.36.

7-*ter.*-Butyl-1-keto-1,2,3,4-tetrahydrophenanthrene.—The above acid (20 g.) was warmed gently with purified thionyl chloride and the mixture was then heated on the steam-bath and the excess reagent removed by water pump suction. The acid chloride was dissolved in 150 cc. of carbon bisulfide and treated at 0° with 14.7 g. of aluminum chloride. The mixture was allowed to come to room temperature, refluxed for fifteen minutes, and worked up as usual. After distillation the product (12 g., 65%) remained as a pale yellow, viscous oil, and it was characterized as the picrate, which formed yellow needles from alcohol, m. p. 107–108°.

Anal. Calcd. for $C_{18}H_{20}O\cdot C_6H_3O_7N_3$: C, 59.85; H, 4.82. Found: C, 59.75; H, 5.01.

2-*ter.*-Butylphenanthrene.—The cyclic ketone (3.6 g.) was reduced by refluxing for fifteen hours with 17 g. of amalgamated zinc, 35 cc. of constant boiling hydrochloric acid, and 4 cc. of toluene, and the crude product was heated at 320–350° with 9 g. of selenium, added in portions, for sixty hours. The resulting hydrocarbon was extracted with petroleum ether, distilled in vacuum from a small piece of sodium, and the solid distillate (1.5 g.) crystallized twice from alcohol (0.85 g.). The hydrocarbon formed colorless, pearly plates, m. p. 99–100°, showing a brilliant purple fluorescence in ultraviolet light.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.24; H, 7.76. Found: C, 92.38; H, 7.71.

The **picrate** forms orange needles, m. p. 130–131°.

Anal. Calcd. for $C_{18}H_{18}\cdot C_6H_3O_7N_3$: C, 62.17; H, 4.58. Found: C, 62.29; H, 4.47.

The **quinone**, purified through the bisulfite addition product and crystallized from alcohol, formed bright orange needles, m. p. 129–130°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.78; H, 6.10. Found: C, 81.62; H, 6.34.

Summary

Carboxylic ester groups and halogen atoms in the 2- and 3-positions of phenanthrene decrease the free energy of the 9,10-addition of bromine, while the *ter.*-butyl group has the opposite effect. The results parallel those obtained in the study of the free energy of oxidation of 9,10-phenanthrenehydroquinones and there is a correlation between the observed effects of the groups and their influence in retarding or facilitating sub-

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[11] Barbot, *Bull. soc. chim.*, [4] **47**, 1314 (1930).

[12] Wegscheider, *Monatsh.*, **5**, 237 (1884).

[13] Gump, THIS JOURNAL, **53**, 380 (1931).

stitutions in the benzene ring. Of further bearing on the latter problem is the observation that halogen atoms in the 2(meta)-position specifically decrease the reaction rate.

2- and 3-*ter.*-butylphenanthrene were synthesized for use in the investigation.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Studies of the Reducing Action of Mercury. III. Hydrogen Peroxide Formation and the Copper-Catalyzed Autoxidation of Quinquivalent Molybdenum and Other Strong Reductants in Acid Solution

BY W. M. MURRAY, JR., AND N. HOWELL FURMAN

The first paper[1] of this series dealt with the formation of hydrogen peroxide when mercury and dilute hydrochloric acid are shaken in the presence of air. The second article[2] discussed the use of the mercury reductor in a new method for the determination of molybdenum and mention was made of the catalytic action of copper on the autoxidation of quinquivalent molybdenum.

It will be the object of this work to give data which show more clearly just what takes place in the mercury reductor when heavy metal ions are present and how it is possible to use the mercury reductor as an analytical tool even though the formation of hydrogen peroxide in the reductor is possible. Also, the question of the autoxidation of quinquivalent molybdenum solutions and the copper catalysis of this and of the analogous autoxidations of stannous, titanous and uranous solutions will be discussed more fully.

Hydrogen Peroxide in the Mercury Reductor.—Some of the work on the action of metallic mercury as a reducing agent was done by Schaffhaütl[3] and Carnegie,[4] although neither of these investigators undertook the subject from a quantitative standpoint. Later Borar[5] studied the stoichiometry of the reaction between mercury and potassium permanganate, potassium dichromate, ferric chloride and cupric sulfate.

McCay and Anderson[6] proposed the mercury reductor for use in the quantitative determination of ferric salts, and later they[7] studied the reduction of vanadic acid solutions by mercury. Finally, McCay[8] worked on the reduction of antimonic acid solutions by mercury as a quantitative method for determining antimony.

At present, then, mercury reduction has been proposed as a quantitative and efficient method for the determination of iron, vanadium, antimony and molybdenum. The reduction by mercury of solutions of these elements is always carried out in the presence of hydrochloric acid. It appears rather paradoxical that mercury can be used for the quantitative reduction of the above substances when we recall that mercury and hydrochloric acid will react rapidly with oxygen to form large amounts of hydrogen peroxide. The explanation of this seems to be largely a matter of competing rates, except in the case of antimony.

Solutions of iron, molybdenum, and vanadium salts are known to be good catalysts for the decomposition of hydrogen peroxide. It is then evident that if we shake a mixture of mercury and hydrochloric acid in the presence of oxygen and add small amounts of iron, vanadium or molybdenum salts to the mixture, the hydrogen peroxide should be decomposed catalytically by the heavy metal ions present. There would in such a case be two competing reactions: (a) the formation of hydrogen peroxide in the reaction between mercury, hydrochloric acid, and oxygen; (b) the catalytic decomposition of the hydrogen peroxide by the heavy metal ion. If reaction (a) is faster than reaction (b) we will be able to detect hydrogen peroxide in the mixture, but if step (a) is the slow one, then all the peroxide will be decomposed and will not be evident in the solution. However, the rate of reaction (b) will depend to some extent on the concentration of the heavy metal ion and the rate of its reduction by mercury since the decomposition of hydrogen peroxide by these ions is very probably an alternate oxidation and reduc-

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(1) Furman and Murray, THIS JOURNAL, **58**, 429 (1936).
(2) Furman and Murray, *ibid.*, **58**, 1689 (1936).
(3) Schaffhaütl, *Ann.*, **44**, 25 (1842).
(4) Carnegie, *J. Chem. Soc.*, **53**, 468 (1888).
(5) Borar, *ibid.*, **99**, 1414 (1911).
(6) McCay and Anderson, THIS JOURNAL, **43**, 2372 (1921).
(7) McCay and Anderson, *ibid.*, **44**, 1018 (1922).
(8) McCay, *Ind. Eng. Chem., Anal. Ed.*, **5**, 1 (1933).

tion of the ion as shown in the study of Haber and Weiss.[9]

To test these conclusions in a series of experiments, 25-ml. portions of mercury and 50 ml. of *N* hydrochloric acid were shaken with oxygen supplied from a buret for 150 minutes. The apparatus and technique were the same as in the previous study.[1]

In one pair of experiments 111 ml. of oxygen was consumed without any addition and 118 ml. when 5 mg. of vanadium was added as vanadic acid. A second pair gave 105 ml. without addition and 136 ml. with the addition of 0.5 mg. of iron as ferric chloride, while a third pair used 116 ml. of oxygen without addition and 163 ml. with the addition of 80 mg. of iron as ferric chloride. The effect of vanadium is negligible or very slight, while the iron perceptibly catalyzes the reaction.

The point of interest is the substances found in the solutions which contained iron and vanadium. In the cases where iron was present in amounts less than 0.005 g., hydrogen peroxide was detected with titanium sulfate, and the iron was found to be largely in the ferric state. In those cases where vanadium was present in amounts less than 0.005 g., the solution was of a deep red color which indicates the presence of pervanadic acid and hydrogen peroxide rather than the reduced vanadyl solution which is blue in color.

No experiments along this line were performed with molybdenum in the mercury reductor, for the quinquivalent molybdenum interferes with most of the color reactions given by hydrogen peroxide. However, it is assumed by analogy that molybdenum would behave quite similarly to iron and vanadium.

The case of antimony is different. McCay[8] found it necessary to carry out the reduction of antimony in an atmosphere of carbon dioxide, and this at once eliminates any interference from the hydrogen peroxide reaction. We have carried out experiments which show that even if very large samples (0.3 g.) of antimonic acid in 2 *N* hydrochloric acid are shaken with mercury in the presence of air, hydrogen peroxide is formed rapidly in large amounts.

Conclusions.—From the foregoing it is to be concluded that large samples (*ca.* 0.1 g.) of iron, vanadium or molybdenum decompose hydrogen peroxide as fast as it is formed in the mercury reductor and the mercury keeps these metal ions in the reduced state. However, when only very small samples (*ca* 0.005 g.) of these substances are taken, the mercury reduction method will not be reliable unless all oxygen is excluded. This means then that the mercury reductor would not be a practical tool for micro-analytical methods unless used in the absence of oxygen. This is in accord with the work of C. F. Fryling and F. V. Tooley,[10] who have found that the silver reductor yields large quantities of hydrogen peroxide when microsamples of iron are employed.

We determined the molybdenum in the Bureau of Standards Calcium Molybdate, which is certified to contain 35.3% of molybdenum by the accepted Jones reductor method and by gravimetric technique. Using samples varying between 0.4 and 1.0 g. we obtained, by the mercury reduction method, respectively, 34.65, 34.80, 34.43, 33.90 and 33.74%, with an average of 34.3%. Iron and titanium were removed prior to the reduction of the solution by mercury.[11] We detected copper in the solution at this point. Electrolytic and colorimetric estimations of the copper gave 0.05, 0.06, 0.04, 0.06 and 0.07%, average 0.05%. The presence of copper is not mentioned on the certificate of analysis.

We believe that this error in the value for molybdenum is caused by the copper which is in the solution at the time it is reduced by mercury. When the quinquivalent molybdenum solution from the mercury reductor is filtered in the presence of air, the traces of cuprous ion present are oxidized by the air and hydrogen peroxide is formed. The hydrogen peroxide then oxidizes some of the quinquivalent molybdenum, which causes the results to be low.

The formation of the hydrogen peroxide in the reaction between cuprous solutions and molecular oxygen has been studied many times since the original observation of Traube.[12] Our idea is then that we have a cyclic reaction in which hydrogen peroxide oxidizes the quinquivalent molybdenum. It will be shown presently that under certain conditions quinquivalent molybdenum is able to reduce cupric ions to the cuprous state and this makes it possible for the cycle to continue, oxidizing more quinquivalent molybdenum in each step. Such a cycle might be pictured as follows:

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[9] Haber and Weiss, *Proc. Roy. Soc.* (London), **147A**, 332 (1934).

[10] Fryling and Tooley, THIS JOURNAL, **58**, 826 (1936).

[11] The standard procedure of double precipitation by ammonia was used according to Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," John Wiley & Sons, Inc., New York, 1932.

[12] Traube, *Ber.*, **15**, 659 (1882).

$$Cu^2 + Mo^5 = Cu^1 + Mo^6 \qquad (1)$$
$$2H^+ + 2Cu^1 + O_2 = 2Cu^2 + H_2O_2 \qquad (2)$$
$$2H^+ + 2Mo^5 + H_2O_2 = 2Mo^6 + 2H_2O \qquad (3)$$

With such a cyclic mechanism in mind, we have studied many conditions under which the autoxidation of the molybdenum solutions is apparently catalyzed by copper and all of the results of these experiments seem to verify the mechanism which we have postulated.

Experimental Studies on the Copper-Catalyzed Autoxidation of Quinquivalent Molybdenum Solutions.—First, in order to show that it is actually copper which causes the error in the determination of molybdenum by mercury reduction, we studied the effect of traces of copper sulfate on the determination of molybdenum in a standard ammonium molybdate solution. The ammonium molybdate solution was standardized by the silver molybdate method.[13] Copper was added in the form of a very dilute cupric sulfate solution. Total volume of solution at time of shaking was 30 ml. Hydrochloric acid concentration at time of shaking was 3 *N*.

TABLE I

EFFECT OF COPPER ON THE DETERMINATION OF MOLYBDENUM IN A STANDARD MOLYBDATE SOLUTION BY THE MERCURY REDUCTION METHOD

Copper added, mg.	0	0	0.1	0.4	0.7	1.1
Error, mg.	−0.2	+0.1	− .7	−1.1	−1.4	−1.7

If the mechanism for the autoxidation of the quinquivalent molybdenum is as indicated in equations (1), (2) and (3) the oxidation by air must take place while the solution is being filtered. This being the case, the volume of solution which passes through the funnel should have some effect on the amount of molybdenum oxidized. This was studied by taking equal samples of the ammonium molybdate solution and adding the same amount of cupric sulfate to each, then diluting the samples with 3 *N* hydrochloric acid to varying volumes before shaking with mercury. The results of this volume effect on the amount of molybdenum oxidized are shown in Table II.

TABLE II

DEPENDENCE OF COPPER AUTOXIDATION EFFECT ON VOLUME OF THE SOLUTION AT THE TIME OF FILTRATION

Copper added, g.	Total volume at time of filtering, ml.	Molybdenum Found, g.	Molybdenum Taken, g.	Error, mg.
....	30	0.2495	0.2494	+0.1
0.0005	30	.2483	.2494	−1.1
....	80	.2496	.2494	+0.2
.0005	80	.2463	.2494	−3.1
....	140	.2492	.2494	−0.2
.0005	140	.2450	.2494	−4.4

In all the experiments of Table II the copper was present at the time of reduction of the molybdenum with mercury. In order to study more fully the actual effect of the copper, we prepared a large quantity of quinquivalent molybdenum by reducing a concentrated molybdic acid solution with mercury. This reduced solution was then diluted with water and acid to yield a solution which was 0.1 *M* in molybdenum content and 2 *N* in hydrochloric acid. The solution was stored in a closed buret system under carbon dioxide and its normality with respect to the Mo^5—Mo^6 change was checked each day. Samples of this quinquivalent molybdenum solution were run into flasks, varying amounts of cuprous or cupric solutions added, then air bubbled through the mixture for a given length of time. In this way it was possible to change the copper and acid concentrations readily and also vary the time of contact of the solution with air.

The data of Table III were taken from a series of experiments run in this way, the rate of air bubbling being relatively constant throughout. These experiments prove definitely that copper is acting as a catalyst for the autoxidation of the quinquivalent molybdenum for here we are only bubbling air through a mixture of quinquivalent molybdenum and traces of copper. The HCl concentration was 1 *N* in all cases, total volume of solution being 150 ml.

TABLE III

EFFECT OF CUPRIC AND CUPROUS IONS UPON THE OXIDATION OF QUINQUIVALENT MOLYBDENUM SOLUTIONS BY AIR

Time of air bubbling, min.	Copper added, mg.	Error, mg.
15	...	+0.1
15	0.5 Cu^{++}	−1.1
15	1.0 Cu^{++}	−2.6
15	2.5 Cu^{++}	−3.2
30	...	±0.0
60	...	−0.4
30	1.0 Cu^{++}	−3.1
60	1.0 Cu^{++}	−3.4
15	0.5 Cu^{+}	−2.3
15	1.0 Cu^{+}	−2.5
30	1.0 Cu^{+}	−2.8

If the cyclic mechanism which we have postulated for the copper-catalyzed autoxidation of quinquivalent molybdenum is to be feasible, it must be shown that the first step as indicated by

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[13] McCay, THIS JOURNAL, **56**, 2548 (1934).

equation (1) is possible. This step involves the formation of cuprous ions from the reaction between cupric ions and quinquivalent molybdenum and is the starting point of the cycle. The graph of Fig. 1 shows the potentials of the two systems Mo^6/Mo^5 and Cu^2/Cu^1 plotted against acidity. The data for the copper system were taken from the work of Carter and Lea[14] and the data for the molybdenum system from the work of Foerster, Fricke and Hausswald.[15] These curves are for the equivalent mixtures of Mo^6/Mo^5 and Cu^2/Cu^1. If we consider the potentials of pure cupric solutions and pure quinquivalent molybdenum solutions, we must take into account the logarithmic concentration term in the equation

$$E = E_0 + \frac{0.059}{n} \log \frac{(\mathrm{Ox})}{(\mathrm{Red})} \qquad (4)$$

If we consider the ratio of (Ox)/(Red) as being of the order of $^1/_{1000}$ in the case of quinquivalent molybdenum and $^{1000}/_1$ in the case of cupric solution, then the concentration term will lower the molybdenum potential by 0.17 volt and raise the copper potential by 0.17 volt. This will then place the molybdenum potential more than 0.2 volt below that of the copper system. Under these conditions, quinquivalent molybdenum would readily reduce cupric ions in 1 N hydrochloric acid. However, this could not proceed for very long, for the molybdenum potential is rising and the copper potential dropping as the reaction proceeds.

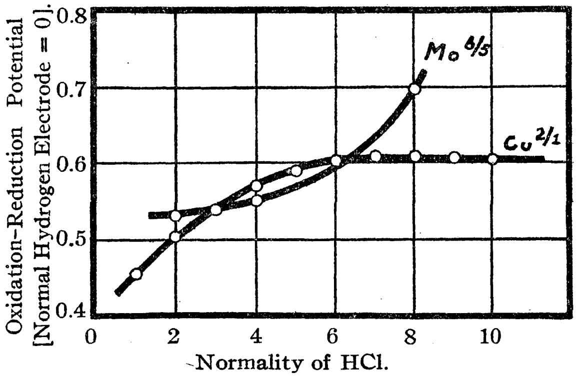

Fig 1.—Graphs of oxidation-reduction potentials of $Mo^{6/5}$ (25°) and Cu $^{2/1}$ (18°) systems as functions of acidity.

A portion of a freshly prepared quinquivalent molybdenum solution was mixed with a solution of cupric sulfate and the mixture adjusted to 1 N concentration of hydrochloric acid. A few ml. of potassium thiocyanate solution was then added. The mixture turned dark red in color due to the formation of the complex between the thiocyanate ion and quinquivalent molybdenum, but a heavy white precipitate was formed at the same time. This precipitate was filtered off and proved to be cuprous thiocyanate. This is therefore experimental proof that quinquivalent molybdenum can reduce cupric ions to the cuprous state in 1 N hydrochloric acid.

It is further evident from Fig. 1 that at an acid concentration of about 5 N the potential of the equilibrium mixture of Mo^6/Mo^5 is always below that of the Cu^2/Cu^1 system. This would suggest that in 5 N hydrochloric acid quinquivalent molybdenum should be rapidly and continuously autoxidized in the presence of traces of copper, since at this acidity the molybdenum will keep more of the copper reduced. The results of such an experiment are given in Table IV.

TABLE IV

EFFECT OF 1 MG. OF CUPRIC ION ON THE OXIDATION OF SOLUTIONS CONTAINING 0.2525 G. OF Mo^V IN 5 N HCl

Time of air bubbling, min.	30	15	30	30
Copper added, mg.	...	1.0	1.0	1.0
Error, mg.	±0.0	−23.2	−20.5	−20.5

Conclusions.—The data presented seem to verify our ideas of a cyclic autoxidation mechanism for quinquivalent molybdenum in which cuprous ions play the important role of first reacting with atmospheric oxygen to yield hydrogen peroxide. Such a reaction accounts for the difficulties in the determination of molybdenum by the mercury reduction method when small amounts of copper are present. Although it was not easily possible to detect hydrogen peroxide as an intermediate in this case, several instances are discussed in the next section which are quite analogous to this and in which hydrogen peroxide is readily detected.

Copper-Catalyzed Autoxidation of Reducing Substances in Acid Solution.—The autoxidation of cuprous ions in hydrochloric acid solution has been studied by Wieland and Franke,[16] Filson and Walton,[17] and others. Hydrogen peroxide is formed in this reaction in large amounts and no salt has been found so far which speeds up the autoxidation of the cuprous ion. Wieland

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[14] Carter and Lea, *J. Chem. Soc.*, 499 (1925).

[15] Foerster, Fricke and Hausswald, *Z. physik. Chem.*, **146**, 81 (1929).

[16] Wieland and Franke, *Ann.*, **473**, 289 (1929).

[17] Filson and Walton, *J. Phys. Chem.*, **36**, 740 (1932).

and Franke point out the fact that it is only in acid solution that hydrogen peroxide is formed during the autoxidation of the cuprous ion.

With these facts in view, we think that it may be said that the copper-catalyzed autoxidation of reducing substances in acid solutions possibly proceeds in most cases by a cyclic mechanism similar to that which we have postulated for the autoxidation of quinquivalent molybdenum.

Filson and Walton[17] and Haring and Walton[18] found copper salts to be excellent catalysts in the autoxidation of stannous chloride solutions and even detected hydrogen peroxide in the non-catalyzed reaction. The equations which they gave for the catalyzed reaction were

$$2CuCl_2 + SnCl_2 = 2CuCl + SnCl_4 \qquad (4)$$

$$4CuCl + 4HCl + O_2 = 4CuCl_2 + 2H_2O \qquad (5)$$

It is possible that equation (5) involves hydrogen peroxide as an intermediate according to our reasoning.

The copper-catalyzed autoxidation of ascorbic acid has been studied by Barron, De Meio and Klemperer[19] who found that in acid solution the reaction is dependent both on *p*H and copper concentration. They write a mechanism which is analogous to that postulated here and which includes hydrogen peroxide as an intermediate.

Luther and Michie[20] found that the rate of autoxidation of quadrivalent uranium solutions containing small amounts of sulfuric acid was increased markedly by the addition of traces of copper. This reaction was not thoroughly studied but it appears to be another case in which the cyclic mechanism involving hydrogen peroxide would apply.

We have studied qualitatively the effect of small amounts of copper on the rate of autoxidation of titanous chloride solutions which contained hydrochloric acid. The rate was increased greatly by the addition of cupric sulfate and when the red color of the titanous salt had disappeared, the solution rapidly became yellow, which was indicative of the presence of hydrogen peroxide.

Conclusions.—In all the cases cited a reducing agent capable of reducing cupric ions to the cuprous state has been employed. In this way a system is set up in which cuprous ions are available for autoxidation and with an excess of oxygen the cycle may proceed until either all the reducing agent has been oxidized or its potential has been raised so high that it can no longer furnish cuprous ions. From these facts and the instances in which hydrogen peroxide has been actually detected in such reactions, we think it probable that in general a cyclic reaction such as indicated in equations (1), (2) and (3) is the mechanism. This is not to be confused with the frequently studied chain reactions such as the sulfite oxidation which take place in nearly neutral or alkaline solution.

Summary

1. The mercury reductor gives satisfactory results when used for the determination of iron, vanadium and molybdenum on a macro scale, for these ions catalytically decompose any hydrogen peroxide formed. It could be used for microdeterminations only when oxygen was rigorously excluded. In the macro-determination of antimony, oxygen must be excluded because the hydrogen peroxide that is formed is not decomposed catalytically by the antimonite.

2. Quinquivalent molybdenum is rapidly autoxidized when small amounts of copper are present as catalyst. A mechanism for this reaction has been postulated which involves hydrogen peroxide as intermediate.

3. It is believed that the cyclic mechanism postulated will apply to most copper-catalyzed autoxidations which take place in acid solution as, for example, those of titanous, stannous and uranous ions.

PRINCETON, N. J. RECEIVED JULY 3, 1936

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(18) Haring and Walton, *J. Phys. Chem.*, **37**, 133 (1933).

(19) Barron, De Meio and Klemperer, *J. Biol. Chem.*, **112**, 625 (1936).

(20) Luther and Michie, *Z. Elektrochem.*, **14**, 826 (1908).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ROLLINS COLLEGE]

Thermodynamic Properties of Fused Salt Solution. IX. Lithium Chloride in Silver Chloride

BY EDWARD J. SALSTROM, THEODORE J. KEW AND THOMAS M. POWELL

The following is a continuation of the general program of investigating fused salts and their solutions.

The apparatus and details of procedure have been described previously.[1]

The silver chloride and lithium chloride used in the cells were of the highest purity obtainable commercially. A pure silver wire inserted through a glass tube in the bottom of the cell container served as the negative electrode. The positive electrode was created by bubbling chlorine gas over a treated graphite rod. This treatment consisted of heating the graphite rod at 600° for twenty-four hours in chlorine gas at several atmospheres pressure. Just before using the rod as an electrode it was heated to a bright yellow heat to free it from all volatile products. The chlorine gas for the electrode was obtained by electrolysis of fused lead chloride of highest purity. The fused chlorides of silver and lithium in the cells and of lead in the chlorine generator were freed from all traces of moisture and oxides by bubbling dry hydrogen chloride gas through the filled containers for not less than an hour.

Other investigators, notably Lorenz and coworkers,[2] Hildebrand and Ruhle,[3] and Wachter and Hildebrand,[4] have worked with the chlorine electrode in fused salts. With the exception of the latter work, all previous attempts involved polarization methods and hence uncertainties.

As in previous studies these cells involved thermoelectric effects of from four to seven millivolts due to the temperature gradient existing at each electrode. The results of the e. m. f. measurements upon the cells plus these thermal corrections are given in Table I, and are shown graphically in Fig. 1. The mean deviation of the points from the straight lines drawn through them is less than 0.2 millivolt, while the maximum deviation is about three times this value.

To obtain the relations of free energy to composition at 500 and 600°, the data in Table I were plotted on a large scale and the e. m. f. values at these temperatures determined. These values of the e. m. f. are given under **E** in Table II, together

TABLE I

E. M. F. VALUES OF THE CELL, Ag(s), LiCl IN AgCl(l), Cl_2(g)

Temp., °C.	E. m. f. obsd., volt
Cell A	
N_1 = 1.000	
498.1	0.9009
509.8	.8968
512.1	.8964
536.3	.8890
538.3	.8883
551.8	.8844
562.0	.8822
566.5	.8804
567.8	.8802
568.0	.8801
573.2	.8786
597.8	.8718
600.3	.8715
Cell B	
N_1 = 0.804	
551.8	0.8949
580.0	.8864
583.5	.8859
591.3	.8839
594.7	.8832
605.7	.8801
623.5	.8757
Cell C	
N_1 = 0.690	
503.3	0.9149
510.8	.9129
518.5	.9108
547.3	.9033
563.7	.8993
577.3	.8957
580.7	.8947
582.9	.8946
588.0	.8931
590.7	.8923
599.8	.8901
600.3	.8898
626.5	.8834
Cell D	
N_1 = 0.573	
529.0	0.9130
531.8	.9120
537.4	.9109
567.6	.9041
580.8	.9012
590.0	.8989
598.0	.8973
609.4	.8946
617.0	.8927
635.6	.8882
Cell E	
N_1 = 0.469	
545.5	0.9152
565.5	.9108
574.3	.9092
587.0	.9070
591.4	.9059
604.3	.9033
611.0	.9015
617.3	.9003
619.2	.9000
629.0	.8980
Cell F	
N_1 = 0.252	
552.5	0.9340
554.2	.9338
573.2	.9304
575.0	.9300
584.5	.9288
592.0	.9276
613.0	.9234
624.1	.9218
Cell G	
N_1 = 0.136	
592.5	0.9509
595.0	.9506
614.2	.9477
619.2	.9470
629.0	.9463
631.4	.9458

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(1) Salstrom and Hildebrand, THIS JOURNAL, **52**, 4641 (1930).

(2) Lorenz, "Die Electrolyze geschmolzener Salze," Dritte Teil, Elektromotorische Kräfte, Verlag Wilhelm Knapp, Halle a. S., 1906; *Z. physik. Chem.*, **62**, 119 (1908); **63**, 109 (1908); *Z. angew. Chem.*, **39**, 88 (1926).

(3) Hildebrand and Ruhle, THIS JOURNAL, **49**, 722 (1927).

(4) Wachter and Hildebrand, *ibid.*, **52**, 4655 (1930).

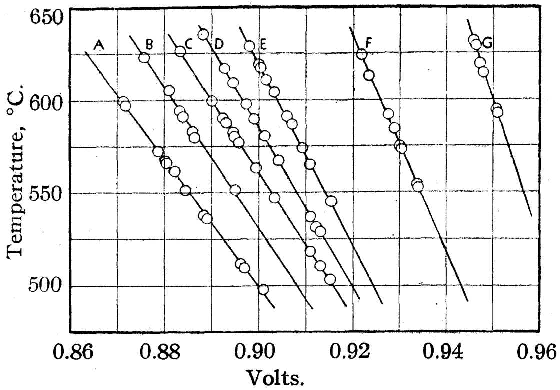

Fig. 1.—Temperature, e. m. f. and composition relations of the cells Ag, AgCl in LiCl, Cl_2. The mole fractions of cells A to G are 1.000, 0.804, 0.690, 0.573, 0.469, 0.252, 0.136, respectively.

with the values of d**E**/dT for the different cells. From these have been calculated the free energy of formation of silver chloride from silver and chlorine vapor, ΔF_1, the free energy of dilution of silver chloride by lithium chloride, $\bar{F}_1$, the entropy change, ΔS_1, the partial molal entropy, $\bar{S}_1$, the heat of formation, ΔH_1, the partial molal heat $\bar{H}_1$, the activity of silver chloride in the solutions, a, taking pure silver chloride as the standard state, and the activity coefficient of silver chloride, λ.

TABLE II

THERMODYNAMIC PROPERTIES OF SILVER CHLORIDE DILUTED WITH LITHIUM CHLORIDE AT 500°

Cell	A	B	C	D	E	F	G
N_1	1.000	0.804	0.690	0.573	0.469	0.252	0.136
log $1/N_1$	0	.095	.161	.242	.329	.599	.867
E, volt	0.9001	.9085	.9156	.9199	.9249	.9424	.9626
ΔF_1, cal.	−20770	−20960	−21130	−21230	−21340	−21750	−22210
$\bar{F}_1$, cal.	0	−190	−360	−460	−570	−980	−1440
ΔS_1, cal./deg.	−6.74	−6.21	−5.88	−5.40	−4.87	−3.78	−2.98
$\bar{S}_1$, cal./deg.	0	0.53	0.86	1.34	1.87	2.96	3.76
d**E**/dT, mv./deg.	− .292	− .269	−0.255	−0.234	−0.211	−0.164	−0.129
a_1	1.000	.884	.791	.741	.690	.529	.392
γ_1	1.000	1.099	1.147	1.294	1.471	2.097	2.881
At 600°							
E, volt	0.8709	0.8816	0.8901	0.8965	0.9038	0.9260	0.9497
ΔF_1, cal.	−20100	−20340	−20540	−20690	−20850	−21370	−21910
$\bar{F}_1$, cal.	0	−240	−440	−590	−750	−1270	−1810
a_1	1.000	0.824	0.775	0.712	0.649	0.487	0.352
γ_1	1.000	1.083	1.124	1.242	1.384	1.931	2.592
ΔH_1, cal.	−25980	−25760	−25680	−25400	−25100	−24670	−24510
$\bar{H}_1$, cal.	0	220	300	580	880	1310	1470

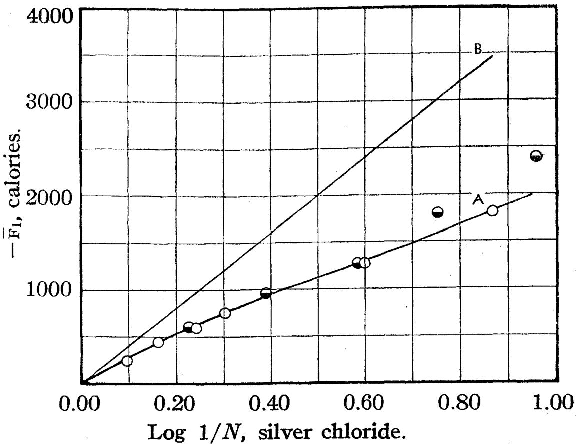

Fig. 2.—Change in free energy of silver chloride at 600° upon dilution with lithium chloride. Curve A shows the observed values, while B is that for a perfect solution. The shaded circles show the values previously obtained for the silver bromide–lithium bromide system.

Table II contains these calculated values while Fig. 2, curve A shows the partial molal free energy $-\bar{F}_1$, at 600° plotted against log $1/N_1$, where N_1 is the mole fraction of silver chloride. Curve B is that of a perfect solution where $a_1 = N_1$. Assumptions of no ionization or of complete ionization of both salts make no difference in the curve predicted by Raoult's law since in either case $a_1 = N_1$ and curve B results. There is then a marked positive deviation of the results from ideal behavior *i. e.*, in the direction of unmixing. This is in close agreement with the values previously obtained for the dilution of silver bromide by lithium bromide, shown in Fig. 2 by shaded circles except in the case of the highest concentration of added lithium chloride[1] (p. 4650).

A previous treatment of the deviations from ideality of solutions of silver bromide with alkali bromides[5] based upon Hildebrand's definition of regular solutions[6] thus holds equally well for this system. The excess of the partial molal free energy, $\bar{F}_1$, over the ideal, $\bar{F}_1^i$, given by $\bar{F}_1 - \bar{F}_1^i = RT \ln \gamma_1$, fits fairly well the relation, $\bar{F}_1 - \bar{F}_1^i = bN_2^2$, where N_2 is the mole fraction of lithium chloride, and the value of b in calories is 2100 compared to 1880 for the silver bromide-lithium bromide system. That b is practically independent of temperature is shown readily in Table III.

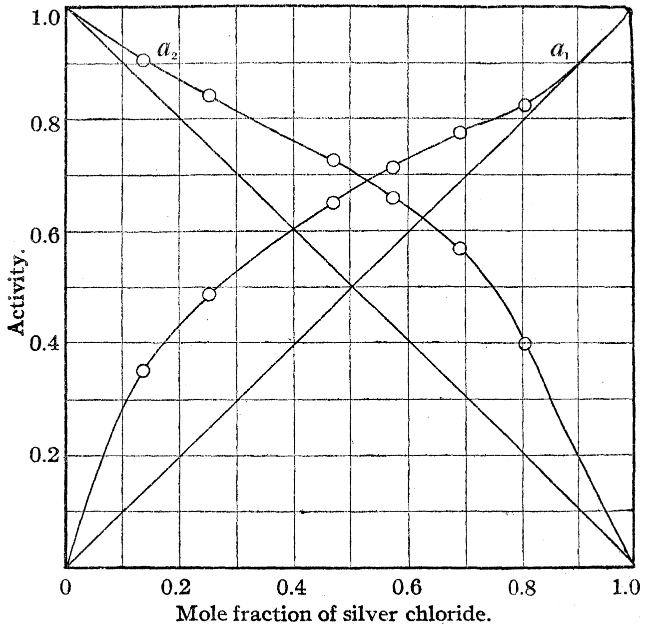

Fig. 3.—Relations of the activities of silver chloride, a_1, and lithium chloride, a_2, to their compositions at 600°.

TABLE III

N_1	1.000	0.804	0.690	0.573	0.469	0.252	0.136
$RT \ln \gamma_1$ at 500°	0	140	210	360	590	1140	1630
$RT \ln \gamma_1$ at 600°	0	140	200	380	560	1140	1650
bN_2^2	0	80	200	380	670	1170	1560

From this it may be concluded that the partial molal entropy is the same as it would be in an ideal solution, *i. e.*, $\bar{S}_1 = R \ln N_1$, indicating that the randomness of arrangement is the same in both cases. The bond between lithium and chloride ions may thus as before be regarded as being completely polar, while that between silver and chloride ions as tending to tighten into a non-polar bond, this tendency being hindered most by the presence of a small ion such as lithium, without in any case altering the simple cubic lattice arrangement which may probably be assumed to persist into the liquid state.

The activities and activity coefficients of the solute, lithium chloride, have been obtained by integrating graphically the equation given by the Duhem relationship

$$\log a_2/N_2 = -\int_0^{N_2} N_1/N_2 \; d \log a_1/N_1$$

In performing this integration the difficulty is encountered that N_1/N_2 rapidly approaches infinity as $\log a_1/N_1$ approaches zero. However, no change in the ratio between any two values of a_2/N_2 will be produced regardless of what method of extrapolation may be used. It thus becomes more convenient to calculate the activity of the solute by choosing the standard state of lithium chloride as the pure salt rather than the customary standard of infinite dilution. The partial molal free energy of lithium chloride was also obtained from its activity by use of the equation, $\bar{F}_2 = RT \ln a_2$. These values are given in Table IV while Fig. 3 shows the activities of silver chloride and lithium chloride plotted against the mole fraction of silver chloride at 600°.

TABLE IV

THERMODYNAMIC PROPERTIES OF LITHIUM CHLORIDE IN THE SOLUTIONS

Cell	A	B	C	D	E	F	G
N_2	0.00	0.196	0.310	0.427	0.531	0.748	0.864
a_2 at 500°	.00	.436	.614	.687	.740	.851	.912
γ_2 at 500°		2.22	1.98	1.61	1.39	1.14	1.06
$-\bar{F}_2$ at 500°	0	1280	770	580	460	250	140
a_2 at 600°	0.00	0.399	0.567	0.658	0.725	0.841	0.906
γ_2 at 600°		2.04	1.83	1.54	1.37	1.12	1.05
$-\bar{F}_2$ at 600°	0	1590	980	730	700	300	170

Summary

E. m. f. measurements of the cells, Ag (s), Ag Cl in LiCl (l), Cl_2 (g), have been made at mole fractions of silver chloride varying between 1.000 and 0.136 from temperatures of 500 to 635°.

Calculations of the activity, activity coefficient, free energy of formation and of dilution, entropy, and heat of formation of silver chloride have been made at 500 and 600°.

The activity, activity coefficient, and partial molal free energy of lithium chloride have been evaluated from the Duhem relationships.

A marked positive deviation of the activities of the salts in the solutions from ideality was found and has been discussed briefly.

WINTER PARK, FLORIDA RECEIVED JUNE 29, 1936

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[5] Hildebrand and Salstrom, THIS JOURNAL, **54**, 4257 (1932).

[6] J. H. Hildebrand, *ibid.*, **51**, 66 (1929).

[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES OF HARVARD UNIVERSITY]

The Surface Tension of Aqueous Solutions of Dipolar Ions

BY J. R. PAPPENHEIMER, M. P. LEPIE AND JEFFRIES WYMAN, JR.

I. Problem

It is a commonplace that the surface tension of aqueous solutions of practically all organic compounds is less than that of water, though a curious exception is afforded by certain sugars.[1,2] It was long ago pointed out by Traube[3] that the lowering of surface tension associated with a given molar concentration of the solute increases in a regular way with the number of carbon atoms in the members of a homologous series. On the other hand, the surface tension of solutions of inorganic salts, and indeed of most strong inorganic electrolytes, is greater than that of the solvent. This means of course, in accordance with Gibbs' theorem, that these ions, in contrast to the organic compounds, are negatively adsorbed at the liquid surface.[4]

Now there is a class of organic molecules, most familiarly represented by the amino acids, which exist in solution preponderantly as dipolar ions, or zwitter ions.[5] These dipolar ions are exceptional above all for their extremely large electric moments, which are the basis of much of their behavior. Although they bear no net charge they have affinities with strong electrolytes. In regard to their structure and phenomena associated with solubility, they are susceptible to treatment in accordance with the concepts of the Debye–Hückel theory for strong electrolytes, with some modifications.[6,7] Thus their partial free energy in dilute solution may be shown to be proportional to the first power, and not the square root, of the ionic strength of the medium, as for ordinary ions.[6,7] Clearly these dipolar ions are of interest in the matter of surface tension. This is especially true of the aliphatic amino acids, which, as organic compounds, belong to a well-defined homologous series, while at the same time they are ions of an exceptional class, owing to their zero net charge and extremely large electric moments. By suitable choice from members of this group it is possible on the one hand to try the effect of varying the electric moment without altering the molecule in any other way, as for example when we pass from an α- to a β-form, or on the other hand, keeping the moment constant, to alter the length of the hydrocarbon chain.

There appear to be but two studies in the literature dealing with this question. Jones and Lewis,[8] by means of Sugden's bubble pressure method, showed that the surface tension of aqueous solutions of glycine was somewhat greater than that of pure water and that the surface tension passed through a slight maximum between a *p*H of 4 and 7. Unfortunately their results are only presented in the form of a small scale graph. Errera and Milliau[9] also report that the surface tension of glycine solutions is slightly greater (about 1%) than that of water, but they say that solutions of leucine, alanine, aspartic acid and asparagine are indistinguishable from water. They give no figures. The present paper contains the results of measurements of the surface tension of aqueous solutions of seven amino acids of varying size and moment, and of one other substance, glycine betaine, which is known to be a zwitter ion.

II. Materials and Methods

The amino acids were all obtained from the Laboratory of Physical Chemistry of the Harvard Medical School and all had been purified by recrystallization before measurements were made. Recrystallization of α-aminocaproic acid and β-alanine was especially necessary in order to obtain reproducible results. The betaine was the same preparation, several times recrystallized, which was previously studied by Edsall and Wyman.[10] The importance of careful purification of materials in these studies is very great, since

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[1] Traube, *J. prakt. Chem.*, **31**, 177 (1885).

[2] Clark and Mann, *J. Biol. Chem.*, **52**, 157 (1922).

[3] Traube, *Ann.*, **265**, 27 (1891).

[4] Onsager and Samara, *J. Chem. Phys.*, **2**, 528 (1934), have recently developed a theory first put forward by Wagner, *Physik. Z.*, **25**, 474 (1924), to account for this behavior. In its bare outline the theory is based on the Gibbs adsorption theorem and on the unequal distribution of ions between the interior and the surface of the liquid, calculated, in accordance with Debye's treatment of strong electrolytes, taking account of ionic atmospheres and image charges at the air–liquid interface, from the difference of potential energy between an ion at the surface and one in the interior. Whether or not it is correct in detail, this theory accounts for the increase of surface tension and points to a general method of attack on the problem of the surface tension of strong electrolytes.

[5] For a discussion of dipolar ions, see Cohn, *Ann. Rev. Biochem.*, **4**, 93 (1935).

[6] Scatchard and Kirkwood, *Physik. Z.*, **33**, 297 (1932).

[7] Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

[8] Jones and Lewis, *Biochem. J.*, **26**, 638 (1932).

[9] Errera and Milliau, *J. chim. phys.*, **30**, 726 (1933).

[10] Edsall and Wyman, THIS JOURNAL, **57**, 1964 (1935).

minute traces of surface active impurities may have appreciable effects.

After a preliminary trial with Sugden's method it was decided to use the drop weight method as being simpler and giving more reproducible results.[11] The surface tension of the solutions was calculated from the weights of the drops of solution and of water falling from a given tip by means of the equation

$$\gamma = \frac{w}{w_0}\frac{\psi_0}{\psi}\gamma_0$$

in which γ denotes surface tension, w the weight of a single drop, ψ the corresponding correction factor as given by Harkins and Brown, and the subscript $_0$ refers to water. The surface tension of water was taken as 71.97 at 25°. For any particular case the value of ψ is determined by the ratio of the radius of the tip to the cube root of the volume of the drop, and in order to determine ψ it is therefore necessary to know the density of the liquid. The densities used in the calculation of the values of the surface tension given below were taken directly from the data given by Wyman and McMeekin[12] in the case of glycine and α-aminobutyric acid and were calculated from the partial molal volumes in the other cases—for betaine from the volume given by Edsall and Wyman;[10] otherwise from the figures of Cohn, McMeekin, Edsall and Blanchard.[13] In calculating the density of the solutions of ϵ-aminocaproic acid studied over a wide range of *p*H no attempt was made to distinguish between the isoelectric material and its salts since it was apparent that the effect of this on the values of the surface tension would be less than the experimental error. Indeed the tips were so chosen that ψ was relatively insensitive, and consequently varied but little between pure water and the most concentrated solution—the greatest variation was from 0.6022 to 0.6033, in the case of α-aminobutyric acid.

Three different tips were used, one of monel metal, one of Pyrex, and one of fused quartz. The radii of these were 0.4701 ± 0.0003, 0.476 ± 0.002 and 0.4770 ± 0.0003 cm., respectively. The monel metal and quartz tips were turned or ground so as to be of accurately circular cross section; the Pyrex tip was made from a selected piece of Pyrex rod and was less exact; yet on the whole it gave the best results and was used in the majority of the determinations. The fact that it was less round than the others did not appear to affect the consistency of the results and any possible error in the calculation of the surface tension arising from uncertainty as to the proper value to use for the radius in reckoning the values of ψ was negligible. The monel metal tip was difficult to clean and there was often trouble in getting the liquids to wet the face of the tip. It was found that this tip did better if the face was electrolytically coated with a light deposit of platinum black. It proved difficult to grind the face of the quartz tip sufficiently rough to provide for good wetting without chipping the edges. This problem of ensuring that the drops, particularly the first one, completely wet the tip proved to be the most troublesome feature of the manipulations, more so than that of adjusting the rate of drop formation.

The measurements were all made at 25° and the apparatus containing the liquid was always placed in the thermostat at least fifteen minutes before the first drop was formed in order to make sure of temperature equilibrium.

All hydrogen-ion concentrations were determined with a glass electrode, in connection with a circuit similar to that described by DuBridge and Brown,[14] making use of a type F. P. 54 General Electric tube. The electrode was calibrated with standard buffers before or after measurements.

III. Results

The results obtained on six isoelectric amino acids and on isoelectric betaine, are given below in Table I and are shown graphically in Fig. 1. Except in one case, each point is based on several determinations which agree to about 0.1% or better. It may be seen from Fig. 1 that in every case the relation between surface tension and concentration is linear within the limits of error. At their worst the experimental points depart from the straight lines by slightly more than 0.1%.

Glycine, α-alanine, β-alanine, and β-aminobutyric acids all behave like inorganic salts in that the surface tension of their solutions is greater than that of water. The effect however is less pronounced than in the case of most of the latter substances. Thus even for glycine the increment

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[11] For a discussion of this method see Harkins and Brown, This Journal, **38**, 246 (1916), and **41**, 520 (1919).

[12] Wyman and McMeekin, *ibid.*, **55**, 908 (1933).

[13] Cohn, McMeekin, Edsall and Blanchard, *ibid.*, **56**, 784 (1934).

[14] DuBridge and Brown, *Rev. Sci. Instruments*, **4**, 532 (1933).

TABLE I

SURFACE TENSION OF SOLUTIONS OF ISOELECTRIC MATERIALS AT 25°

Concentrations are expressed in moles per liter. Values of $\Delta\gamma/\Delta c$, the increment of surface tension per mole of solute, reckoned from the straight lines in Fig. 1, are given in parentheses after the name of each compound. The surface tension of water is 71.97

Glycine[a] ($\Delta\gamma/\Delta c = +0.92$)

c	0.502	1.035	1.185	1.360	1.517
γ	72.43	72.86	73.14	73.15	73.47

α-Alanine[b] ($\Delta\gamma/\Delta c = +0.58$)

c	0.50	1.00	1.39
γ	72.27	72.54	72.79

α-Aminobutyric acid[b] ($\Delta\gamma/\Delta c = -0.41$)

c	0.38	0.845	1.185	1.245
γ	71.80	71.63	71.49	71.43

α-Aminocaproic acid[b,c] ($\Delta\gamma/\Delta c = -23$)

c	0.025	0.051
γ	71.23	70.90

Betaine[b] ($\Delta\gamma/\Delta c = -0.14$)

c	0.44	0.88
γ	71.95	71.79

β-Alanine[b] ($\Delta\gamma/\Delta c = +0.77$)

c	0.237	0.475	0.949	1.390
γ	72.19	72.36	72.62	72.99

β-Aminobutyric acid[b] ($\Delta\gamma/\Delta c = +0.05$)

c	0.5	1.0	1.5
γ	72.03	72.04	72.04

ε-Aminocaproic acid[b] ($\Delta\gamma/\Delta c = -0.25$)

c	0.545	0.763	1.09
γ	71.88	71.80	71.66

[a] Measurements with monel metal tip. [b] Measurements with Pyrex tip. [c] Measurements with quartz tip.

of surface tension per mole of solute[15] is but 0.97 as compared with a value of 1.64 for sodium chloride or a value of 3.04 for magnesium chloride, a uni-divalent salt; for β-aminobutyric acid it is but 0.05.

If we compare the four α-amino acids, or the two β-acids, studied, it is clear that increasing the length of the carbon chain when the electric moment is kept constant has the effect of depressing the molar increment of surface tension, as in the case of other homologous series; and the data on the α-acids indicate that the depressing effect of each additional carbon atom increases geometrically, at least approximately so, with the number of atoms introduced, as has been observed in other series more extensively studied.[16] In this connection the behavior of betaine is of interest. Betaine ($(CH_3)_3{}^+NCH_2COO^-$) differs from glycine owing to the substitution of three methyl groups for the three hydrogens attached to the positively charged nitrogen atom. It therefore contains three more CH_2 groups than glycine, and since its electric moment is known to be very nearly if not quite the same as that of α-amino acids,[10] it might be supposed that it would behave like α-aminovaleric acid. Although we have not determined the surface tension–concentration curve for this amino acid, it is safe to predict that it lies between curves of α-aminobutyric and α-aminocaproic acids. Actually the curve for betaine lies well above that for α-aminobutyric acid. The implication of this is that a CH_2 group which is itself a part of the structure of a changed group contributes quite differently to the properties of the molecule than one which belongs to a hydrocarbon residue.

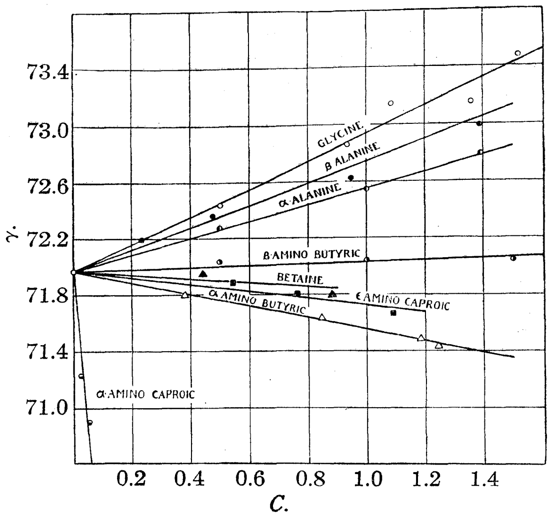

Fig. 1.—Graph of data in Table I.

The effect of increasing the dipole moment without otherwise altering a molecule is to increase the molar increment of surface tension,

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(15) In what follows this quantity is referred to as the molar increment of surface tension, for brevity.

(16) Szgszkowski's data [*Z. physik. Chem.*, **64**, 385 (1908)] on normal fatty acids show that in dilute solutions, where the surface tension may be regarded as linear in the concentration, the molar surface tension increments decrease geometrically with the number of CH_2 groups in the molecule, the ratio for the series being about 3.4. This is equivalent to the statement that the differences, taken as positive, between the molar surface tension increments of successive members of the series increase in the same ratio, 3.4. In the case of the α-amino acids the molar surface tension increments themselves change from positive to negative values so that we must consider the differences. Data for one member of the series, α-aminovaleric acid, are lacking, which leaves only three differences to be considered. These may be fitted moderately well by assuming a ratio of 3.8. If we use a value of 0.30 instead of the observed value of 0.34 for the first difference, we may calculate expected values of the molar surface tension increments as +0.92, +0.62, −0.52, −21.4. These are in fairly good agreement with the values given in Table I.

that is, to rotate the curve counter-clockwise and make the substance behave more like an inorganic salt. This may be seen by comparing the curves for α- and β-alanine, α- and β-aminobutyric acid, or, better still, α- and ε-aminocaproic acid.

In Table II and Fig. 2 are given data showing the change of surface tension with *p*H for a solution of ε-aminocaproic acid containing 0.2431 mole per liter. Figure 2 also contains, in the upper portion, a graph of the titration data obtained incidentally in the course of these measurements. The full curve, with which the experimental points are in fairly good agreement, is calculated from the two *pK* values of 4.43 and 10.75 given for this amino acid by Edsall and Blanchard.[17]

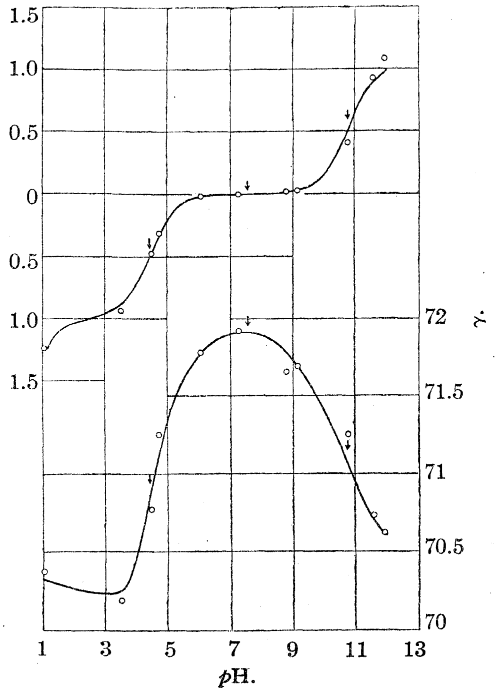

Fig. 2.—Lower curve: Surface tension of a 0.2431 molar solution of ε-aminocaproic acid as a function of *p*H. Upper curve: Titration of ε-aminocaproic acid (0.2431 molar). The ordinates give moles of acid or base per mole amino acid. The smooth curve is based on *pK* values of 4.43 and 10.75. The isoelectric point (7.59) and the *pK* values are indicated by arrows.

TABLE II

SURFACE TENSION OF ε-AMINOCAPROIC ACID SOLUTIONS AS A FUNCTION OF *p*H AT 25°

The total concentration of amino acid is 0.2431 mole per liter throughout. In column 1 the amount of acid or base present is expressed in terms of moles per mole of amino acid.

Amount of acid (−) or base (+)	*p*H	γ
−1.234	1.05	70.38
−0.944	3.52	70.19
− .474	4.50	70.77
− .308	4.74	71.24
− .021	6.07	71.78
0	7.26	71.92
+ .019	8.80	71.65
+ .020	9.16	71.69
+ .405	10.80	71.25
+ .925	11.58	70.73
+1.091	11.90	70.62

The data extend over somewhat more than the full titration range and show that the surface tension is a maximum at or close to the isoelectric point (*p*H = 7.59). There is a marked drop of surface tension with addition of acid or base amounting to about 2.4% when the isolectric material is converted completely into the hydrochloride, and a drop of about 1.7% when it is converted to the sodium salt. This is in general agreement with the results of Jones and Lewis[8] on glycine. As nearly as can be judged from their small scale graph there is roughly a 1% decrease in the surface tension of a 1.5 molar solution when the isoelectric amino acid is converted into the hydrochloride or sodium salt.[18]

This phenomenon is of interest since it shows the effect of the dipole moment as contrasted with the single charge of the anion or cation on the molar increment of surface tension. The increment is greater for the dipolar ion than for the simple ion, the more so for ε-aminocaproic acid where the moment is large than for glycine where it is relatively much smaller. In fact it appears from the figures given above, rough as they are in the case of glycine, that the increase in the surface tension increment of a 1 molar solution due to converting the cation or anion into the dipolar ion is about six times as great for ε-aminocaproic acid as for glycine. It is worth bearing in mind here the great size of the moments involved. Thus the moment of glycine has been estimated as in the neighborhood of 15×10^{-18} e. s. u. That of the caproic acid is much larger.[5]

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(17) Edsall and Blanchard, THIS JOURNAL, **55**, 2337 (1933).

(18) Jones and Lewis [*Biochem. J.*, **26**, 632 (1932)] have shown that the surface tension of dispersions of lecithin in water, though less than that of water, is a maximum at *p*H = 2.8. This is close to the estimated isoelectric point of lecithin, which presumably exists as a dipolar ion. The surface tension of solutions of proteins and peptones is less than that of water, but there is disagreement among observers as to whether it is a maximum or a minimum at the isoelectric point. See Johnston, *ibid.*, **21**, 1314 (1927); Botazzi, in Alexander, "Colloid Chemistry," D. Van Nostrand Co., New York, 1919, Chap. VII; Berczeller, *Biochem. Z.*, **53**, 215 (1913); Errera and Milliau;[9] Loebel, *J. Phys. Chem.*, **32**, 763 (1928); Artom, *Arch. Sci. Biol.* (Ital.), **14**, 327 (1930).

It is striking that the molar increment of surface tension of the hydrochloride or sodium salt of ε-aminocaproic acid is very much less negative than that of isoelectric α-aminocaproic acid and therefore *a fortiori* presumably less negative than that of its salts. This is an illustration of the fact pointed out by Cohn[5] on the basis of a systematic study of solubilities that the effect of a CH_2 group situated between polar groups (whether or not they bear a free charge) is different from that of one located in a hydrocarbon residue in the molecule.

As a result of the application of a new and exceedingly accurate method of measuring surface tension Jones and Ray[19] report a very curious phenomenon shown by aqueous solutions of inorganic salts. The surface tension–concentration curves, which are linear at ordinary concentrations, do not continue straight back to the ordinate axis, but dip down so as to show negative surface tension increments when the solutions are very dilute. It would be of importance in any theoretical interpretation of surface tension to know whether or not dipolar ions behave in the same way, and it is hoped in the future to study the problem by this more accurate method.

Summary

Measurements of the surface tension of aqueous solutions of seven amino acids of differing size and moment and of glycine betaine have been made with the drop weight method. In the case of four of the amino acids the surface tension is greater than that of water; in the other cases it is less. In these dipolar ions there appears to be an antagonism between the effect of the electric moment which tends to increase the surface tension, and the size and number of organic groups in the molecule which tend to lower it. The effect of converting an amino acid into its hydrochloride or its sodium salt is to lower the surface tension of the solution.

CAMBRIDGE, MASS. RECEIVED JULY 10, 1936

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[19] Jones and Ray, THIS JOURNAL, **57**, 957 (1935).

The Electromotive Force of the Cell Zn-Hg (2 phase) | $ZnSO_4$ (m) $PbSO_4$ (s) | Pb-Hg (2 phase) and its Temperature Coefficient at 25° and Concentrations from 0.05 to 1.5 Molal[1]

BY JACOB KIELLAND[2]

Determinations of the e. m. f. of the cell

$$\text{Zn-Hg (2 phase)} \mid ZnSO_4\ (m)\ PbSO_4\ (s) \mid \text{Pb-Hg (2 phase)} \quad (1)$$

corresponding to the chemical reaction

$$\text{Zn (satd. amalg.)} + PbSO_4\ (s) = ZnSO_4\ (m) + \text{Pb (satd. amalg.)} \quad (2)$$

have been reported by Bray[3] at 25° for molalities from 0.0005 to 3.5, and by Cowperthwaite and La Mer[4] at 0, 12.5, 25, 37.5 and 50° for molalities from 0.0005 to 0.01, also 0.02 and 0.05 molal at 0, 25 and 50°.

In the present paper are given some e. m. f. measurements on cell (1) for the molalities 0.0512, 0.150, 0.510 and 1.501 at the temperatures 15, 25 and 35°.

Experimental Part

Preparation of Materials.—Lead sulfate of definite crystalline form was prepared from *pro analysi* reagents in the way recommended by Bray[3] and stored under doubly distilled water until needed. Zinc sulfate stock solution was made up from Kahlbaum "zur analyse" reagents and doubly distilled water, and analyzed by the zinc ammonium phosphate method as well as by weighing in the form of zinc sulfate after evaporation and heating on addition of some drops of sulfuric acid.

Four per cent. lead amalgam and 4% zinc amalgam were made up with *pro analysi* metals and redistilled mercury as described by Cowperthwaite and La Mer,[4] filtered hot through capillary tubings and stored under a slight excess pressure of purified nitrogen.

Tank nitrogen was purified from oxygen by the wet combustion method described by Van Brunt,[5] using a nitrogen lift pump to circulate the ammonia–ammonium carbonate solution over the copper wire gauze filling of the absorption tower.

Experimental Method.—The cell was similar to that used by Cowperthwaite and La Mer,[4] with

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[1] This work was aided by a grant from "Anna Paus's Legat."

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[3] U. B. Bray, THIS JOURNAL, **49**, 2372 (1927).

[4] I. A. Cowperthwaite and V. K. La Mer, *ibid.*, **53**, 4333 (1931).

[5] C. Van Brunt, *ibid.*, **36**, 1448 (1914).

the exception that the electrodes were inserted at the top, using well ground glass joints. The solutions and the cell were freed from oxygen by running purified nitrogen through the whole system for four hours. The method of filling the cell with amalgams and solutions, and sealing off with mercury, was essentially the same as used by Cowperthwaite and La Mer.

The cleaning of cells and electrodes was effected by washing with concentrated sulfuric acid, distilled water, and then with a weak alcoholic solution of potassium hydroxide. They were then rinsed ten times with doubly distilled water, steamed out for an hour and subsequently dried at 110°.

Constant e. m. f. was ordinarily obtained one to four hours after the cell was prepared, and was controlled by readings after fifteen to twenty hours. It was found that a constant potential was far more rapidly obtained by passing from higher to lower temperatures than *vice versa.*

Apparatus.—The measurements were carried out with an Otto Wolff Potentiometer 5881 and a Hartmann and Braun Reflecting Galvanometer No. 1528. A Weston element calibrated by "Polytechnisches Reichsanstalt" served as the standard cell. The regulation of the thermostat temperature was maintained to a precision of ±0.02° by means of mercury regulators.

Results

The observed values of e. m. f. ($E_{\text{obsd.}}$) and of $E^{0\prime}$, computed from the equation

$$E^{0\prime} = E_{\text{obsd.}} + (\nu RT/nF) \ln m \qquad (3)$$

are given in Table I. The corrections necessary owing to the solubility of lead sulfate at the concentrations stated in the present paper, are less than 0.01 mv., and are therefore not taken into account.

TABLE I

OBSERVED E. M. F. AND COMPUTED VALUES OF $E^{0\prime}$

Molality, m	$E_{\text{obsd.}}$	$(\nu RT/nF)$ ln m	$E^{0\prime}$
Temperature 15°			
0.0512	0.53425	−0.07378	0.46047
.150	.51955	− .04710	.47245
.510	.50551	− .01671	.48880
1.501	.49195	+ .01008	.50203
Temperature 25°			
0.0512	0.52830	−0.07635	0.45195
.150	.51350	− .04873	.46477
.510	.49915	− .01729	.48186
1.501	.48500	+ .01043	.49543
Temperature 35°			
0.0512	0.52215	−0.07891	0.44324
.150	.50740	− .05037	.45703
.510	.49285	− .01787	.47498
1.501	.47800	+ .01078	.48878

The values of the mean practical[6] stoichiometric activity coefficient for zinc sulfate, given by the equation

$$\ln \gamma_{\pm} = \frac{E^0 - E_{\text{obsd.}}}{\nu RT/nF} - \ln m = \frac{E^0 - E^{0\prime}}{\nu RT/nF} \qquad (4)$$

are collected in Table II, using the best values for E^0 obtained by Cowperthwaite and La Mer.[4]

TABLE II

MEAN PRACTICAL STOICHIOMETRIC ACTIVITY COEFFICIENTS OF ZINC SULFATE

Molality, m	$t = 15°$ ($E^0 = 0.4215_5$)	$t = 25°$ ($E^0 = 0.41086$)	$t = 35°$ ($E^0 = 0.3992$)
0.0512	0.209	0.202	0.190
.150	.128	.123	.113
.510	.0667	.0631	.0569
1.501	.0392	.0372	.0342

Discussion

The agreement between the values presented here and those given by the measurements of Cowperthwaite and La Mer[4] up to 0.05 molal is very good.

The activity coefficients given previously by Bray[3] are all higher than those found by Cowperthwaite and La Mer and by the present author. This discrepancy can be traced back to Bray's measurements in the most dilute concentration range.[7] Using Cowperthwaite and La Mer's $E^0_{298.1} = 0.41086$, which hitherto is the most reliable value given for the normal potential of the cell (1), the activity coefficients given by Bray were recalculated. The results are shown in Table III.

TABLE III

MEAN PRACTICAL STOICHIOMETRIC ACTIVITY COEFFICIENTS OF ZINC SULFATE AT 25°, RECALCULATED FROM BRAY'S MEASUREMENTS

m	0.005	0.01	0.02	0.05		
$\gamma_{\pm}$	0.477	0.387	0.298	0.202		
m	0.08	0.1	0.2	0.3	0.5	0.8
$\gamma_{\pm}$	0.162	0.148	0.104	0.0837	0.0634	0.0491
m	1.0	1.5	2.0	2.5	3.0	3.5
$\gamma_{\pm}$	0.0439	0.0368	0.0354	0.0368	0.0409	0.0476

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(6) *Cf.* practical and rational activity coefficients by E. A. Guggenheim, *Phil. Mag.*, **19**, 588 (1935).

(7) The uncertainty of Bray's extrapolation was already pointed out by Gronwall, La Mer and Sandved [*Physik. Z.*, **29**, 390 (1928)], who found a somewhat different value, with "a" = 4.0 Å. Cowperthwaite and La Mer's "a" = 3.64 is however the most reliable, since cryoscopic measurements also give "a" = 3.6. Bray's measurements at the highest dilutions consequently should not be taken into account.

These recalculated coefficients are in good agreement with Cowperthwaite and La Mer's at concentrations 0.005 to 0.05 *m*, and with the author's at 0.05 to 1.5 *m*. Log $\gamma_{\pm}$ *vs.* $\sqrt{m}$ are shown in Fig. 1.

It would be of great interest to obtain values of the partial molal heat of dilution of zinc sulfate at concentrations here studied, on account of the difference between the calorimetric values given by Lange and collaborators[8] and the results of La Mer and Cowperthwaite, obtained by application of the Gibbs–Helmholtz equation.[9] But as $\overline{L}_2$ in the case of zinc sulfate depends about equally upon the precision with which $(E^{0\prime} - E^0)$ and $\mathrm{d}(E^{0\prime} - E^0)/\mathrm{d}T$ can be determined, it is obvious that more than the three temperatures investigated in the present paper, are necessary to obtain values of $\overline{L}_2$ which are sufficiently accurate[10] to be compared with those determined calorimetrically. The final answer to the questions must therefore await a more extended investigation.[11]

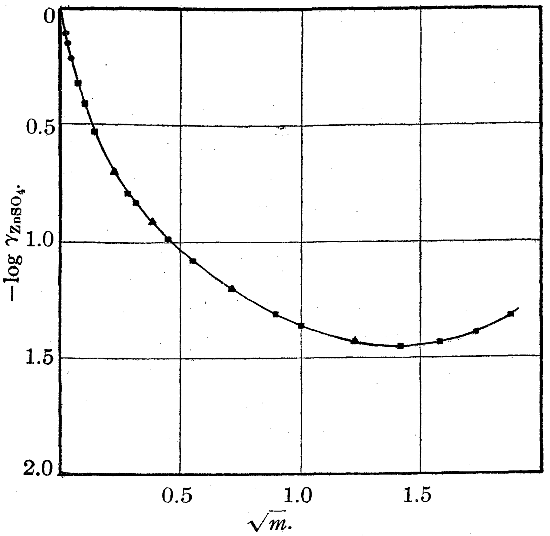

Fig. 1.—Mean stoichiometric activity coefficients of zinc sulfate at 25°: ●, Measurements of Cowperthwaite and La Mer; ■, Bray; ▲, Kielland.

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Summary

The electromotive force of the cell Zn (satd. amalgam) | $ZnSO_4(m)$, $PbSO_4(s)$ | Pb (satd. amalgam) has been measured at 15, 25 and 35° for concentrations of zinc sulfate of 0.0512, 0.150, 0.510 and 1.501 molal. The activity coefficients of zinc sulfate are given for these concentrations and temperatures.

OSLO, NORWAY RECEIVED JUNE 2, 1936

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[8] E. Lange, J. Monheim and A. L. Robinson, THIS JOURNAL, **55**, 4733 (1933).

[9] V. K. La Mer and I. A. Cowperthwaite, *ibid.*, **55**, 1004 (1933).

[10] The partial molal heat of dilution varies considerably with the temperature, according to some unpublished calculations of $\overline{C}_p - \overline{C}_p^0$ for zinc sulfate at concentrations studied; hence it is necessary to make use of a sufficient number of temperatures.

[11] According to a communication from Professor La Mer, W. H. Wood, working with Dr. Cowperthwaite, has been reinvestigating the e. m. f. of the cell at 5° temperature intervals from 0 to 50° from high dilution to one molal; the results have not yet been published.

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Studies in the Phenanthrene Series. XIII. 9,10-Dihydrophenanthrene and Amino Alcohols Derived from It[1,2]

BY ALFRED BURGER AND ERICH MOSETTIG

The important investigations of Schroeter and his co-workers[3] have shown that phenanthrene yields by catalytic hydrogenation (elevated temperature and pressure) and by reduction with sodium and amyl alcohol, three well-defined hydrogenation products, namely, 9,10-dihydrophenanthrene, 1,2,3,4-tetrahydrophenanthrene and 1,2,3,4,5,6,7,8-octahydrophenanthrene, in amounts which depend upon the mode of reduction. These investigators determined the structure of the hydrocarbons beyond any doubt by synthetic methods, thus ridding the literature of the great confusion prevailing in the series of hydrogenated phenanthrenes up to that time. While the octahydro[4] and tetrahydro compounds may be isolated quite conveniently from the

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[1] The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

[2] See preliminary note, THIS JOURNAL, **57**, 2731 (1935).

[3] Schroeter, *Ber.*, **57**, 2025 (1924); Schroeter, Müller and Huang, *ibid.*, **62**, 645 (1929).

[4] For a convenient preparative method of octahydrophenanthrene, see van de Kamp and Mosettig, THIS JOURNAL, **57**, 1107 (1935).

reaction mixture and purified easily, the isolation and purification of the dihydro compound offers considerable difficulty. Neither the known reductive methods nor the synthetic method[3] is practicable for the preparation of 9,10-dihydrophenanthrene, which was needed in large amounts for systematic chemical and pharmacological investigations.

Through the extensive studies of Adkins and his collaborators on catalytic hydrogenation,[5] the great practical value of the "chromite" catalyst has been demonstrated. Copper–chromium oxide (or copper–chromium–barium oxide) proves to be particularly useful in cases where only partial or selective hydrogenation is desired. It has been known for a long time that the 9,10-double bond in phenanthrene is characteristically different from the other double bonds in this ring system. It behaves, to some extent, like an olefinic double bond (bromination, nitration), and it could be expected, therefore, that by employing the chromite catalyst in the reduction of phenanthrene, only or chiefly the 9,10-double bond would be attacked, leaving the benzenoid double bonds of the terminal nuclei intact. This expectation is fully realized; phenanthrene, reduced at 220° under a pressure of 2000–3000 lb./sq. in. (136–204 atm.), using copper–chromium–barium oxide as catalyst, yields practically pure 9,10-dihydrophenanthrene in very satisfactory amounts (up to 80%). The rate of reduction is apparently dependent to some extent upon the age of the catalyst. Phenanthrene can be recovered easily in the form of the picrate, and no higher hydrogenated phenanthrenes can be found in the reaction mixture. Efforts to bring the reduction to completion by varying experimental conditions were without success.

We found that anthracene, which is well known to be more reactive on the meso-positions than phenanthrene, is reduced under similar conditions, using chromite catalyst, at a decidedly lower temperature (160°) and in a considerably shorter time, yielding 9,10-dihydroanthracene only. The hydrogenation of anthracene at room temperature and atmospheric pressure, using noble catalysts, has been investigated carefully by Fries and Schilling.[6] The reduction of phenanthrene under similar conditions has not been reported, as far as we know. Phenanthrene, purified by the method of Cohen and Cormier,[7] distilled over sodium, treated with maleic anhydride,[8] recrystallized and resublimed, resists catalytic reduction under ordinary conditions (platinum oxide in glacial acetic acid). Synthetic phenanthrene, prepared by Pschorr's method, however (or as we later found, phenanthrene purified through the stages, 9-bromophenanthrene ⟶ 9-cyanophenanthrene ⟶ 9-phenanthroic acid ⟶ phenanthrene), absorbs hydrogen readily under those conditions.[9] We are now engaged in reinvestigating the course of the catalytic reduction of phenanthrene and of partially hydrogenated phenanthrenes under various conditions, a study that seems to be of interest as a complement to the investigation of Fries and Schilling[6] on the course of the reduction of anthracene. It may also be of importance in connection with the 1,4-dihydrophenanthrene (from the lithium addition product) of Schlenk and Bergmann,[10] for the structure of which, in our opinion, sufficient proof has not been offered.

The Friedel–Crafts reaction on 9,10-dihydrophenanthrene, employing acetyl and propionyl chlorides, proceeds smoothly in nitrobenzene solution as well as in carbon disulfide, giving in very satisfactory yields the expected ketones. It should be recalled that the same reaction on phenanthrene itself can be carried out successfully only in nitrobenzene solution, while in carbon disulfide chiefly oily and uncharacterizable products are obtained.[11] The formation of these is undoubtedly due to the interference of the 9,10-double bond.[12] Another remarkable difference between phenanthrene and 9,10-dihydrophenanthrene lies in their power to direct substituents. Whereas with phenanthrene in the Friedel–Crafts reaction, the acetyl or propionyl group enters mainly the 3-position, substitution in position-2 being a minor side reaction,[12,13] in 9,10-dihydrophenanthrene these groups are directed solely into the 2-position. Dihydrophenanthrene behaves in this respect as a diphenyl rather than as phenanthrene. The

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[5] Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931); Adkins and Folkers, *ibid.*, **53**, 1095 (1931); Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932); Folkers and Adkins, *ibid.*, **54**, 1145 (1932); Adkins, Wojcik and Covert, *ibid.*, **55**, 1669 (1933).

[6] Fries and Schilling, *Ber.*, **65**, 1494 (1932).

[7] Cohen and Cormier, THIS JOURNAL, **52**, 4363 (1930).

[8] Clar, *Ber.*, **65**, 852 (1932).

[9] Mosettig and Krueger, unpublished results.

[10] Schlenk and Bergmann, *Ann.*, **463**, 84 (1928).

[11] Mosettig and van de Kamp, THIS JOURNAL, **52**, 3704 (1930).

[12] See Mosettig and van de Kamp, *ibid.*, **54**, 3328 (1932).

[13] Mosettig and Czerwin, unpublished results.

structural proof for the acylation products mentioned was carried out by converting them into 2-acetyl-9,10-phenanthrene quinone and 2-propionyl-9,10-phenanthrene quinone, respectively.

Name of compound Derivatives of 9,10-dihydrophenanthrene	Solvent	Appearance	Yield, %	M. p., °C. (all hydrochlorides with dec.)	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
2-ω-Chloroacetyl—[a]	Petrol. ether	Pale yellow		100–101	$C_{16}H_{13}OCl$	74.84	74.53	5.11	4.88		
2-Propionyl—	MeOH	Colorless prisms	74	62–63	$C_{17}H_{16}O$	86.39	86.54	6.83	6.85		
-Semicarbazone	EtOH	Colorless needles		213–214	$C_{18}H_{19}ON_3$					14.33	14.49
2-α-Bromopropionyl—	Ether–petr. ether	Pale yellow	84	85–86	$C_{17}H_{15}OBr$	64.75	64.60	4.80	5.09		
2-[2-(Dimethylamino)-1-oxo-ethyl]—·HCl	EtOH–Et_2O	Yellow	60	213–215	$C_{18}H_{20}ONCl$					4.64	4.71
2-[2-(Diethylamino)-1-oxo-ethyl]—·HCl	EtOH–Et_2O	Yellow	94	173–176	$C_{20}H_{24}ONCl$					4.25	4.36
2-[2-Piperidino-1-oxo-ethyl]—	Dil. MeOH	Pale yellow		86–87	$C_{21}H_{23}ON$					4.59	4.32
-Hydrochloride	EtOH–Et_2O	Colorless	98	240–252	$C_{21}H_{24}ONCl$					4.10	4.36
2-[2-(1,2,3,4-Tetrahydroisoquinolino)-1-oxo-ethyl]—·HCl[b]	EtOH–Et_2O	Yellow	64	238–239	$C_{25}H_{24}ONCl$					3.60	3.62
2-[2-(Dimethylamino)-1-oxo-propyl]—·HCl	EtOH–ether	Colorless	86	210–214	$C_{19}H_{22}ONCl$					4.44	4.59
2-[2-(Diethylamino)-1-oxo-propyl]—·$HClO_4$	EtOH–Et_2O	Almost colorless	57	138–140	$C_{21}H_{26}O_5NCl$					3.44	3.55
2-[2-Piperidino-1-oxo-propyl]—·HCl	EtOH–Et_2O	Colorless		208–213	$C_{22}H_{26}ONCl$					3.94	4.05
2-[2-(1,2,3,4-Tetrahydroisoquinolino)-1-oxo-propyl]—·$HClO_4$	EtOH	Almost colorless	47	230–231	$C_{26}H_{26}O_5NCl$					3.00	3.06
2-[2-(Dimethylamino)-1-hydroxy-ethyl]—·HCl	EtOH–Et_2O	Colorless	98	170–172	$C_{18}H_{22}ONCl$	71.14	71.30	7.31	7.38	4.61	4.54
2-[2-(Dimethylamino)-1-acetoxy-ethyl]—·HCl	EtOH–Et_2O	Colorless		216–217	$C_{20}H_{24}O_2NCl$					4.05	3.93
2-[2-(Diethylamino)-1-hydroxy-ethyl]—·HCl	EtOH–Et_2O	Colorless	95	184–186	$C_{20}H_{26}ONCl$	72.36	71.97	7.90	7.79	4.22	4.12
2-[2-(Diethylamino)-1-acetoxy-ethyl]—·HCl	EtOH–Et_2O	Colorless		145–150	$C_{22}H_{28}O_2NCl$					3.73	3.98
2-[2-Piperidino-1-hydroxy-ethyl]—	EtOH	Colorless needles		124	$C_{21}H_{25}ON$	82.03	82.22	8.20	8.18	4.56	4.69
-Hydrochloride	EtOH–Et_2O	Silky leaflets	86	242	$C_{21}H_{26}ONCl$					4.08	3.90
2-[2-Piperidino-1-acetoxy-ethyl]—·HCl	EtOH–Et_2O	Colorless		212–213	$C_{23}H_{28}O_2NCl$					3.63	3.75
2-[2-(1,2,3,4-Tetrahydroisoquinolino)-1-hydroxy-ethyl]—	Dil. MeOH	Colorless		101–102	$C_{25}H_{25}ON$	84.46	84.47	7.10	7.10		
-Hydrochloride	MeOH	Colorless	75	244–246	$C_{25}H_{26}ONCl$	76.59	76.81	6.69	6.95	3.58	3.81
2-[2-(1,2,3,4-Tetrahydroisoquinolino)-1-acetoxy-ethyl]—·HCl	EtOH–Et_2O	Colorless		197–199	$C_{27}H_{28}O_2NCl$					3.23	3.36
2-[2-(Dimethylamino)-1-hydroxy-*n*-propyl]—	EtOH–water	Colorless		90–91	$C_{19}H_{23}ON$	81.08	81.19	8.24	8.29	4.98	5.04
-Hydrochloride	EtOH–Et_2O	Glittering rods	99	225–227	$C_{19}H_{24}ONCl$					4.41	4.41
2-[2-(Dimethylamino)-1-acetoxy-*n*-propyl]—·HCl	EtOH–Et_2O	Glittering rods		210–211	$C_{21}H_{26}O_2NCl$					3.90	4.02
2-[2-(Diethylamino)-1-hydroxy-*n*-propyl]—·HCl	EtOH–Et_2O	Silky leaflets	90	209–210	$C_{21}H_{28}ONCl$	72.90	73.24	8.16	8.11	4.05	4.01
2-[2-(Diethylamino)-1-acetoxy-*n*-propyl]—·HCl	EtOH–Et_2O	Colorless		189–190	$C_{23}H_{31}O_2NCl$					3.61	3.61
2-[2-Piperidino-1-hydroxy-*n*-propyl]—	Dil. MeOH	Colorless needles		104–106	$C_{22}H_{27}ON$	82.18	81.80	8.47	8.55	4.36	4.54
-Hydrochloride	EtOH–Et_2O	Colorless		249–250	$C_{22}H_{28}ONCl$					3.92	4.06
2-[2-Piperidino-1-acetoxy-*n*-propyl]—·HCl	EtOH–Et_2O	Colorless		192–194	$C_{24}H_{30}O_2NCl$					3.51	3.53
2-[2-(1,2,3,4-Tetrahydroisoquinolino)-1-hydroxy-*n*-propyl]—	EtOH	Colorless		136–138	$C_{26}H_{27}ON$					3.79	4.10
-Hydrochloride	EtOH–Et_2O	Colorless	90	226–228	$C_{26}H_{28}ONCl$	76.90	76.54	6.96	7.15	3.45	3.59
2-[2-(1,2,3,4-Tetrahydroisoquinolino)-1-acetoxy-*n*-propyl]—·HCl	EtOH–Et_2O	Colorless		190–192	$C_{28}H_{30}O_2NCl$					3.13	3.28

[a] Obtained in poor yield by Friedel–Crafts reaction with chloroacetyl chloride.

[b] As a by-product in the exchange of the bromine with tetrahydroisoquinoline a red resin is formed, which on treatment with dilute alkali, yields 9,10-dihydrophenanthrene-2-carboxylic acid. Compare Mosettig and Robinson, THIS JOURNAL, **57**, 2188 (1935), footnote g.

In addition, the methyl ester of the carboxylic acid obtained by oxidation of the acetyl derivative with sodium hypochlorite was dehydrogenated with selenium, whereby 2-phenanthroic acid was formed.[14]

From the 2-acetyl- and 2-propionyl-9,10-dihydrophenanthrenes, amino alcohols of the type —$\mathrm{CHOHCH_2NR_2}$ and —$\mathrm{CHOHCH(CH_3)NR_2}$ were synthesized, *via* the bromo ketones and amino ketones, in a manner described previously in communications of this series. The pharmacological study of these compounds in comparison with their non-hydrogenated analogs, is expected to give some information concerning the influence of saturation of the 9,10-double bond on the physiological effectiveness in this series.

Experimental

Preparation of 9,10-Dihydrophenanthrene.[15]—One hundred and twenty grams of phenanthrene in 260 cc. of absolute alcohol with 10 g. of chromite catalyst was heated to 220° and kept at this temperature for eight to ten hours under a hydrogen pressure of 2000–3200 lb./sq. in. (136–218 atm.). Phenanthrene was removed from the reaction mixture as the picrate; the crude dihydrophenanthrene was purified by vacuum distillation (b. p. at 60 mm., 212–213°, yield 78–84%). This product was used for further reactions. By freezing it (5° overnight) and treating it with methyl alcohol at the same temperature, a pure dihydrophenanthrene was obtained. It is advantageous to use freshly prepared catalyst, since it was observed that with a catalyst that had been stored for about a year, the reduction proceeded considerably slower, and more catalyst had to be added to attain the same results.

2-Acetyl- and 2-Propionyl-9,10-dihydrophenanthrene.—A cold solution of 2 moles of aluminum chloride in 800 cc. of dry nitrobenzene was added gradually to an ice-cold solution of 1 mole of dihydrophenanthrene and 1.2 moles of acetyl or propionyl chloride, respectively, in 360 cc. of nitrobenzene. The mixture was allowed to stand at room temperature overnight, poured onto ice and hydrochloric acid and worked up in the customary way. The crude ketones were distilled in an oil pump vacuum and purified through the semicarbazones or oximes.

Structural Proofs.—Three grams of the acetyl compound was heated for four hours, with an excess of dilute sodium hypochlorite solution at 70°; yield of carboxylic acid, 1.9 g. One gram of the oily methyl ester (prepared from the acid with diazomethane) was heated with 2 g. of selenium in a sealed tube to 280–300° for twenty hours. The reaction product was treated with ether, and the ethereal solution was extracted with cold dilute potassium hydroxide solution. The acid obtained was identified as 2-phenanthroic acid by direct comparison with an authentic specimen of this acid (mixed melting point of acids and methyl esters).

One gram of the acetyl compound in 10 cc. of warm glacial acetic acid was treated with a solution of 1.2 g. of chromic acid in 2 cc. of water. After a few minutes the quinone crystallized out and was purified by high vacuum sublimation, m. p. 223–224° (dec.). The mixed melting point with an authentic sample of 2-acetyl-9,10-phenanthrene quinone showed no depression.

The propionyl-9,10-dihydrophenanthrene was oxidized in the same manner. The orange-red quinone was sublimed in a high vacuum; m. p. 215–217° (dec.).

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.24; H, 4.58. Found: C, 77.25; H, 4.81.

The mixed melting point with 2-propionyl-9,10-phenanthrene quinone of the same m. p. (obtained by chromic acid oxidation of 2-propionylphenanthrene)[13] showed no depression.

Preparation of Amino Alcohols.—The bromination of the ketones was carried out in absolute ether (cooling with cold water). The yield of the bromoacetyl compound was 55%, that of the bromopropionyldihydrophenanthrene, 84%. The exchange of the bromine atom with the amino groups was effected by allowing the reactants to stand in benzene solution overnight. The hydrochlorides of the amino ketones (in two cases the perchlorates) were readily hydrogenated in 90% alcohol or methyl alcohol solutions, using a platinum oxide catalyst. The amino alcohols were acetylated in pyridine solution with acetic anhydride.

Summary

A convenient large scale method for the preparation of 9,10-dihydrophenanthrene by catalytic reduction of phenanthrene at elevated temperature and pressure, using chromite catalyst, is described.

By the Friedel–Crafts reaction, 2-acetyl- and 2-propionyl-9,10-dihydrophenanthrenes are obtained in good yields.

From the acetyl and propionyl derivatives amino alcohols of the type $\mathrm{C_{14}H_{11}CHOHCH_2NR_2}$ and $\mathrm{C_{14}H_{11}CHOHCH(CH_3)NR_2}$ ($\mathrm{NR_2}$ being the dimethylamino-, the diethylamino, the piperidino and the 1,2,3,4-tetrahydroisoquinolino group) have been synthesized for pharmacological studies.

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RECEIVED AUGUST 12, 1936

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[14] The cleavage of the ester groups in this process is remarkable. Similar observations with selenium dehydrogenation of esters have been made recently also by Ruzicka [*Helv. Chim. Acta*, **19**, 419 (1936)].

[15] Additional experimental data, reference 2.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Synthesis of Acetylenic Ketones from Acetylenic Grignard Reagents[1]

BY J. W. KROEGER AND J. A. NIEUWLAND[2]

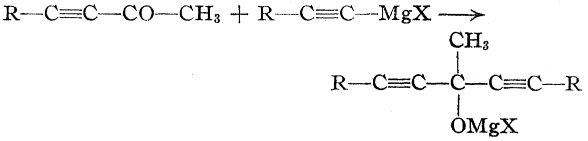
In connection with some of the work carried on in this Laboratory[3] it was found necessary to prepare acetylenic ketones of the type $R{-}C\equiv C{-}CO{-}CH_3$. The principal method reported in the literature consists in treating the sodium salt of an acetylenic hydrocarbon with an acyl halide.[4] This method was found to be unsatisfactory from the point of view both of yields and quality of products since traces of halogen were always present in the resulting ketone. This report concerns an entirely successful solution of the problem involving the use of acetylenic Grignard reagents.

A number of compounds have been reported to react with Grignard reagents to form ketones.[5] Of these, acetonitrile, acetamide, acetyl chloride and acetic anhydride were investigated. The first two compounds were found to be inert toward acetylenic Grignard reagents while, of the latter two, acetic anhydride gave the best results.

The ketone which is formed in accordance with the reaction

$$R{-}C\equiv C{-}MgX + (CH_3{-}CO)_2O \longrightarrow R{-}C\equiv C{-}CO{-}CH_3 + CH_3{-}CO{-}OMgX$$

may react further, as follows



$$R{-}C\equiv C{-}CO{-}CH_3 + R{-}C\equiv C{-}MgX \longrightarrow R{-}C\equiv C{-}\underset{OMgX}{\overset{CH_3}{C}}{-}C\equiv C{-}R$$

The usual method of avoiding this last reaction is to ensure the presence of a large excess of acetic anhydride by slow addition *to* it of the Grignard reagent. Better results, however, were obtained by cooling the Grignard reagent to at least $-25°$ and then adding the acetic anhydride.

For purposes of comparison alkynylmagnesium chlorides, bromides and iodides were investigated and of the three the chlorides were found most suitable. While the bromides and iodides invariably gave considerable amounts of carbinol and higher boiling polymeric material, the reaction product from an alkynylmagnesium chloride and acetic anhydride usually contained only the desired ketone and a small amount of unreacted alkyne. Occasionally the iodide yielded some iodine-containing material which exploded violently on heating.

Acetylenemagnesium chlorides are apparently rather insoluble in ether. Within the concentration range used, that is, 0.5 to 1.0 mole per liter, the bromides and iodides were always completely soluble whereas the preparation of an acetylenemagnesium chloride always resulted in the formation of a heavy, white precipitate. This was found to be mainly undissolved Grignard reagent.

Acetylenic Grignard reagents apparently are much more stable as well as less reactive than the Grignard reagents from the corresponding saturated hydrocarbons. Arylacetylenemagnesium halides occupy an intermediate position. Indications of this stability may be found in the facts that no reaction was obtained with acetonitrile or acetamide under the ordinary conditions of refluxing the ether solution. In addition, oxygen reacts only to a negligible extent with alkynylmagnesium halides at $-25°$. In spite of this fact, however, the reactions described below were always performed in an atmosphere of nitrogen as recommended by Gilman and Hewlett.[6]

Experimental

Reagents.—The alkylacetylenes were prepared by a modified Picon synthesis.[7] Phenylacetylene was prepared from ethylbenzene as suggested by Friedel and Balsohn.[8] The acetyl chloride, acetic anhydride and methyl iodide were redistilled shortly before use. Ethyl bromide was obtained from the Eastman Kodak Company. The ethyl chloride was supplied through the kindness of E. I. du Pont de Nemours and Company. Anhydrous ether was stored over phosphorus pentoxide and small quantities were distilled off when needed.

Analysis of Grignard Reagents.—The acetylenemagnesium chlorides prepared as described below always con-

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[1] Paper XVII on the chemistry of alkylacetylenes and their addition compounds. Previous papers, in this series; XVI, THIS JOURNAL, **58**, 1609 (1936); XV, *ibid.*, **58**, 1806 (1936); XIV, *ibid.*, **58**, 1658 (1936).

[2] The major portion of the research herein reported was completed before the death of Dr. Nieuwland in June, 1936.

[3] Kroeger, Sowa and Nieuwland, *J. Org. Chem.*, **1**, 163 (1936).

[4] Nef, *Ann.*, **308**, 264 (1899); Moureu, *et al.*, *Bull. soc. chim.*, **25**, 302 (1901); *ibid.*, **31**, 343 (1904); *Ann. chim. phys.*, [7] **25**, 239 (1902); Andre, *ibid.*, [8] **29**, 540 (1913).

[5] Runge, "Chimie in Einzeldarstellungen," Vol. XVI, Part I, "Organomagnesiumverbindungen," Stuttgart, Wissenschaftliche Verlagsgesellschaft m. b. H., 1932, pp. 180–195.

[6] Gilman and Hewlett, *Rec. trav. chim.*, **48**, 1124 (1929).

[7] Picon, *Compt. rend.*, **158**, 1346 (1914); **169**, 32 (1919).

[8] Friedel and Balsohn, *Bull. soc. chim.*, **35**, 55 (1881).

tained considerable amounts of powdery, white, insoluble material which was analyzed as follows.

Three half-mole samples of ethylmagnesium chloride were prepared in ether, each having a volume of 250 ml. A 2-ml. sample of each was dropped into 50 ml. of ice cold, 0.1 *N* hydrochloric acid and back-titrated with 0.1 *N* sodium hydroxide. All three samples corresponded to 0.50 ± 0.02 mole of Grignard reagent.

One-half mole each of amyl-, butyl- and phenylacetylene, respectively, was dropped into the prepared Grignard reagents and the solutions were refluxed until no more ethane was evolved. The contents of each flask was then diluted with anhydrous ether to a volume of 500 ml. and 2-ml. samples were taken while the material in the flasks was being stirred vigorously. This last precaution was to ensure, as nearly as possible, representative samples. Titration of the samples showed that all three flasks contained 0.50 ± 0.01 mole of basic magnesium.

The solid material in each of the three samples was allowed to settle and the supernatant liquid was decanted under nitrogen. The solid was washed twice with 200-ml. portions of anhydrous ether which were then added to the original liquid. The three ether solutions were then diluted to 1000 ml. and 5-ml. samples were taken. They represented 0.20, 0.17 and 0.09 mole of amyl-, butyl-, and phenylacetylenylmagnesium chlorides, respectively.

Although these results give only a rough estimate of the solubilities of the acetylenemagnesium chlorides, they show definitely that the solid material is not magnesium chloride etherate, as it was first supposed, but that it consists largely, if not entirely, of active Grignard reagent.

At similar concentrations the acetylenemagnesium bromides and iodides were completely soluble.

Preparation of Acetylenic Grignard Reagents.—Methyl iodide, ethyl bromide or ethyl chloride was converted to the Grignard reagent in the usual manner. Ethyl chloride was diluted with twice its volume of ether and then added to the metallic magnesium. The preparations were carried out in nitrogen[6] and with mechanical stirring.

The calculated quantity of an acetylenic hydrocarbon was dissolved in ether and added to the prepared Grignard after which the solution was refluxed until no more ethane was evolved. In the case of quarter-mole runs, this required a half-hour for phenylacetylene and about two hours for the alkylacetylenes. Finally the apparatus was again flushed out with nitrogen. The volume of the solution at this point was about 500 ml.

Reaction of Hexynylmagnesium Bromide with Acetonitrile.—One-fourth mole of acetonitrile was added to 0.25 mole of hexynylmagnesium bromide, which was prepared from 21 g. of hexyne-1, and the solution was refluxed for eight hours. After hydrolysis with dilute acid in the usual way and drying, fractionation gave only hexyne-1, b. p. 70–71° (19.5 g.). Similarly, 20 g. of phenylacetylene was recovered from a quarter-mole run of phenylethynylmagnesium bromide.

Reaction of Heptynylmagnesium Bromide with Acetamide.—One mole of heptynylmagnesium bromide was prepared from 96 g. of heptyne-1. To this was added 0.33 mole of acetamide (20 g.) dissolved in warm ether. The acetamide had been previously fused to free it from water. A slight reaction was apparent and the solution was refluxed for four hours. Only heptyne-1 was recovered, b. p. 99–101° (90 g.).

Addition of Grignard Reagent to Acetic Anhydride.—One-half mole of hexynylmagnesium bromide in ether was slowly dropped into one mole of acetic anhydride cooled in an ice–salt mixture. The addition required three hours. Stirring was continued for two hours, then the product was hydrolyzed with ice water and steam distilled. From the steam distillate 20 g. of 3-octyne-2-one, b. p. 90–95° (30 mm.) was obtained. Fractionation of the tarry residue in the steam distillation flask gave 8 g. of *bis*-hexynylmethylcarbinol, b. p. 125–130° (5 mm.).

Phenylethynylmagnesium bromide (0.25 mole) when treated similarly gave 3 g. of 4-phenyl-3-butyne-2-one, b. p. 105–108° (5 mm.), and 30 g. of a yellow-brown powder, m. p. 108–111°. This material was extracted with hot alcohol and the extract diluted with an equal volume of water. The material so obtained was recrystallized six times from aqueous alcohol finally giving fine, white needles of *bis*-phenylethynylmethylcarbinol,[9] m. p. 111.5–112.0°.

Reaction of Hexynylmagnesium Chloride with Acetic Anhydride.—One-fourth mole of hexynylmagnesium chloride was prepared in the usual manner and cooled to −30° in a bath of liquid ammonia. One-half mole of acetic anhydride in ether was added at such a rate that the temperature of the mixture remained below −25°, vigorous stirring being maintained. The addition required two and one-half hours. Stirring was continued for two hours at −30° and then for two hours at −5° in an ice–salt bath. After hydrolysis with ice-water and drying, fractionation gave 8 g. of hexyne-1 and 18 g. of 3-octyne-2-one, b. p. 76–77° (15 mm.). This represents a 58% over-all yield or a 98% yield based on the amount of acetylene reacted.

Under similar conditions, 0.25 mole of heptynylmagnesium chloride gave 22 g. of 3-nonyne-2-one, b. p. 86–87° (13 mm.) and 10 g. of heptyne-1. In contrast to the practically quantitative yields from alkynes, only 40–45% yields of 4-phenyl-3-butyne-2-one were obtained. Considerable amounts of carbinol were always formed in this case.

Alkynylmagnesium bromides and iodides, when treated as outlined above, gave 10 to 20% yields of ketones.

Table I

Physical Properties of the Compounds

$R—C{\equiv}C—CO—CH_3$

R-	B. p., °C.	Mm.	n^{25}_D	d^{25}_4	MRD Calcd.	MRD Found
C_4H_9-	76–76.5	15	1.4446	0.8631	37.16	38.23
C_5H_{11}[4]-	89–89.5	15	1.4463	.8616	41.77	42.73
C_6H_5[4]-	101–102	3	1.5735	1.0239	42.79	46.40

Table II

Physical Properties of the Compounds

$(R—C{\equiv}C)_2(CH_3)C—OH$

R-	B. p., °C. (2 mm.)	n_D	d_4	MRD Calcd.	MRD Found
C_4H_9-	123–125	1.4660 (24°)	0.8840 (24°)	64.38	64.60
C_5H_{11}-	134–136	1.4678 (29°)	.8785 (29°)	73.62	74.09
C_6H_5[9]-	M. p. 111.5–112.0°				

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[9] Salkind, *J. Russ. Phys.-Chem. Soc.*, **50**, 24 (1917); *Chem. Zentr.*, **94**, 1391 (1923).

When acetyl chloride was substituted for acetic anhydride, the yields varied from 8 to 15% in the case of bromides and chlorides while the iodides gave nothing but a viscous tar which exploded on attempted vacuum distillation and gave off iodine vapor.

The Action of Oxygen on Hexynylmagnesium Bromide.—The inertness of acetylenic Grignard reagents is well illustrated by the following experiment.

During eight hours dry oxygen was bubbled rapidly through a solution of hexynylmagnesium bromide (0.25 mole) cooled to −30°. A 5-ml. sample was then hydrolyzed with dilute hydrochloric acid and the organic layer allowed to evaporate. A slight film of oil remained which had a faint odor of caproic acid.

While the Grignard reagent was still in the liquid ammonia bath, 0.25 mole of acetic anhydride was added and the product was worked up as usual. Fractionation gave 5 g. of 3-octyne-2-one and 16 g. of *bis*-hexynylmethylcarbinol, b. p. 123–125° (2 mm.).

Acknowledgment.—We are indebted to Mr. G. M. Wolf for carrying out several of these preparations.

Summary

1. Acetylenic ketones of the type R—C$\equiv$C—CO—CH_3 have been prepared from acetylenic Grignard reagents.

2. Alkynylmagnesium chlorides, when cooled to −25° and treated with acetic anhydride, gave almost quantitative yields of acetylenic ketones.

Notre Dame, Indiana Received July 14, 1936

[Contribution from the Laboratory of Physical Chemistry, University of Upsala]

Sedimentation and Electrophoresis of the Tobacco-Mosaic Virus Protein

By Inga-Britta Eriksson-Quensel and The Svedberg

The isolation by W. M. Stanley[1] of a crystalline protein showing the properties of the tobacco-mosaic virus has attracted much attention both in physiological and chemical circles. Stanley's substance is really the first example of a chemically well-defined virus, all previous preparations having been defined by means of biological tests only.

A quantity of the crystalline virus protein was kindly put at our disposal by Dr. Stanley for the purpose of an ultracentrifugal study. In view of the vivid discussion centering around the question whether a virus is a living being with the faculty of propagation or a high-molecular compound with the property of multiplication by autocatalysis a determination of the molecular weight and the degree of homogeneity of this virus protein seemed of great interest. Preliminary measurements by Dr. Stanley of the diffusion and osmotic pressure gave molecular weight values of the order of millions.

The object of our ultracentrifugal study was to determine by means of sedimentation velocity runs the sedimentation constant, and by sedimentation equilibrium runs the molecular weight as well as the dependence of the sedimentation constant on *p*H, *i. e.*, the *p*H stability region. Further we wanted to subject the material to a homogeneity test with regard to molecular weight by means of velocity scale runs and, should the virus protein prove inhomogeneous, to determine the distribution curve.

Previous work on proteins in this Laboratory has demonstrated the great sensitivity of the isoelectric point against chemical differences in the protein molecule. Thus the measurements carried out by K. O. Pedersen[2,3] on respiratory proteins have shown that the isoelectric point varies from species to species although the molecular weight is the same. For example the isoelectric point of the hemocyanin from Helix pomatia is 5.05 while that from Helix nemoralis is 4.63, both proteins possessing near the isoelectric point the molecular weight 6,400,000. On the other hand, the blood pigment of a certain species often contains several components all of which have the same isoelectric point and the same mobility in an electric field. For example, at *p*H 8.2 the hemocyanin of Helix pomatia has three well-defined components of molecular weight 6,400,000, 3,200,000, and 800,000, all of which are identical in electrophoretic respect. Subjected to a centrifugal field this particular protein system, therefore, is resolved into three components, while exposed to an electric field it moves with a single boundary. In view of this fact it was desirable to carry out a series of electrophoresis determinations on the virus protein.

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[1] W. M. Stanley, *Science*, **81**, 644 (1935).

[2] K. O. Pedersen, *Kolloid.-Z.*, **63**, 268 (1933).

[3] *Cf.* T. Svedberg, *J. Biol. Chem.*, **103**, 311 (1933).

Treatment of the Material. Specific Volume

Two grams of the protein was sent us in the form of crystals covered with half-saturated ammonium sulfate solution. It was recrystallized twice according to Stanley's method[1] taking care not to raise the *p*H above 8 when dissolving the crystals. The recrystallization was easy to perform.

The specific volume of the protein was determined pycnometrically at *p*H 6.8 and 8.5. The value 0.646 was obtained. It differs considerably from the ordinary value for proteins, this being 0.75.

Sedimentation Constant, *p*H Stability Range

Sedimentation velocity determinations were carried out before recrystallization, after one recrystallization, and after two recrystallizations. The light absorption method was generally used. The refractive index method was applied in some runs on the twice recrystallized material.

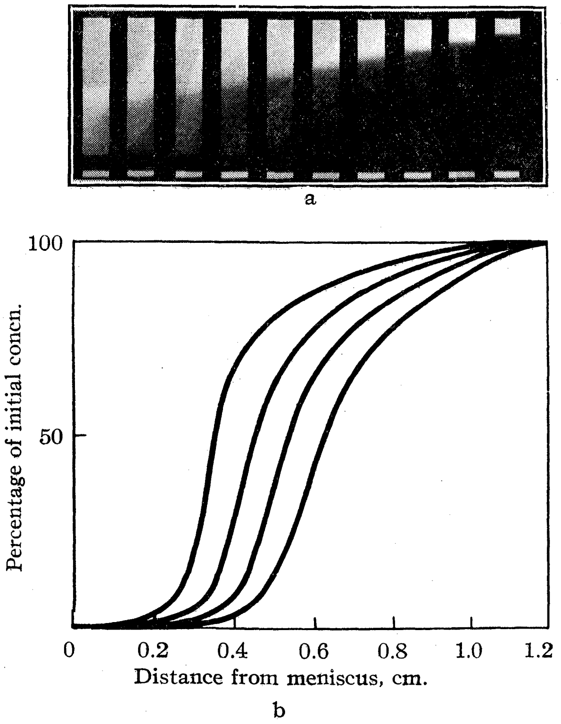


Fig. 1, a and b.—Sedimentation pictures (a), obtained by means of the light absorption method, and concentration curves (b) for the tobacco-mosaic virus protein at *p*H 6.8; centrifugal force 15,000 times gravity; time between the exposures 5 minutes. The blurring of the boundary and the change in shape of the curves with time of sedimentation indicate polydispersity.

Light Absorption Method.—In the ultracentrifuge the material appeared very polydisperse as compared with a well-defined high-molecular protein such as the hemocyanin from Helix pomatia (Figs. 1, 2, and 3). The recrystallizations seemed to have no effect on the degree of inhomogeneity. The sedimentation at different *p*H was studied. Below *p*H 3.8 the solubility was too small for determination. In the *p*H range 4.6–5.5 the particles were aggregated and went down to the bottom of the cell at very low speed. No change in sedimentation picture took place between *p*H 6 and 11.5. The sedimentation constant dropped slightly toward the alkaline side of the region, the mean value being 235 for the *p*H range 6–8 and 205 for the *p*H range 8–11.5. However, if a substance is inhomogeneous and does not consist of one or more well-defined components the sedimentation constant obtained with this method must be regarded as a mean value for all the different sized particles.

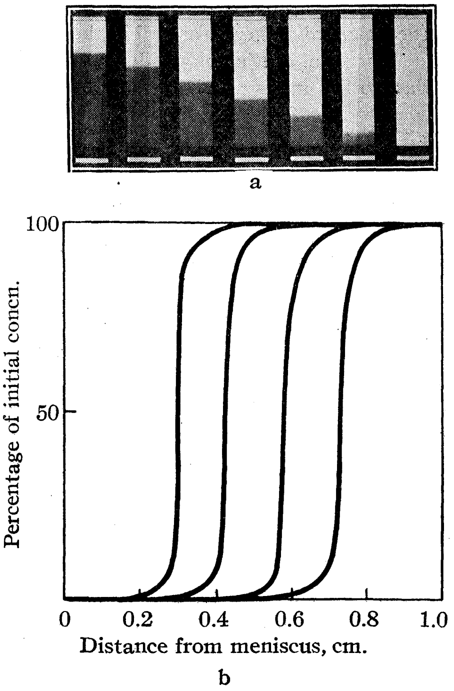
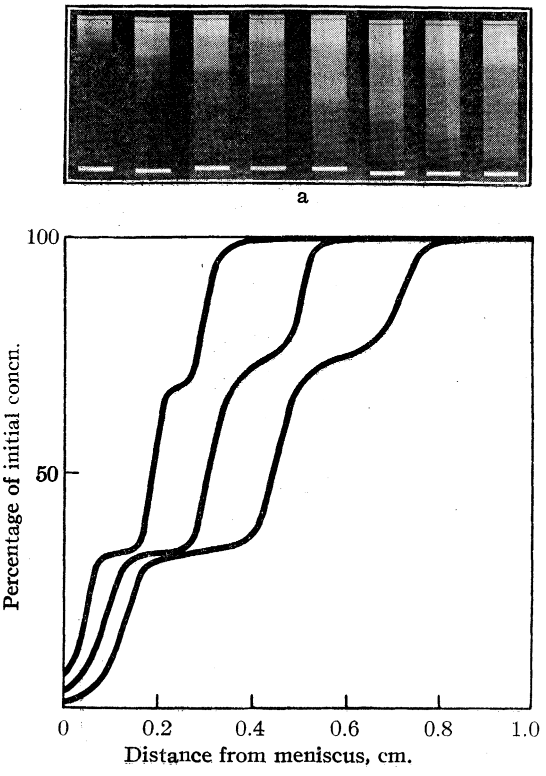


Fig. 2, a and b.—Sedimentation pictures (a) obtained by means of the absorption method, and concentration curves (b) for the hemocyanin from Helix pomatia at *p*H 5.5, ($M = 6{,}400{,}000$, $s = 98.9$); centrifugal force 45,000 times gravity, time between exposures 5 minutes. The sharpness of the boundary and steepness of the curves demonstrate the high degree of molecular homogeneity of this protein compared with that of the virus protein.

Refractive Index Method.—An example of a typical run on the virus protein with this method is given in Fig. 4. The concentration gradient curve has a rather sharp peak, due to a comparatively homogeneous part of the material. The sedimentation constants given refer to this homogeneous portion. The results of the measurements are summarized in Table I. The run at *p*H 9.5 shows a lower value than those at more neutral *p*H. The same is the case with the determination at *p*H 5.0 of the solution stored at 8.5, which means that the effect of a higher *p*H is not reversible.

Distribution Curve

The distribution of particle size[4-6] or molecular weight can be calculated easily from runs made by the refractive index method, provided the relation between rate of sedimentation and molecular weight is known. Because of the exceedingly low diffusion the spreading of the boundary is entirely due to molecular inhomogeneity. The scale runs give directly the concentration gradient as a function of distance from center of rotation. One of the most convenient types of distribution curve is the one where the percentage gradient dp/dM is given as a function of molecular weight. The area delimited by two ordinate lines, the abscissa axis and the distribution curve, represents the percentage of material having molecular weight in the interval in question. In the following we have assumed the dissymmetry constant to be independent of molecular weight and equal to 1.3, which is the value found for other high-molecular proteins.



a

b

Fig. 3, a and b.—Sedimentation pictures (a) obtained by means of the absorption method and concentration curves (b) for the hemocyanin from Helix pomatia at *p*H 8.2, molecular weight of components 6,400,000 ($s = 98.9$), 3,200,000 ($s = 62.0$) and 800,000 ($s = 16.0$); centrifugal force 60,000 times gravity; time between exposures 5 minutes. Each of these components is homogeneous with regard to molecular weight.

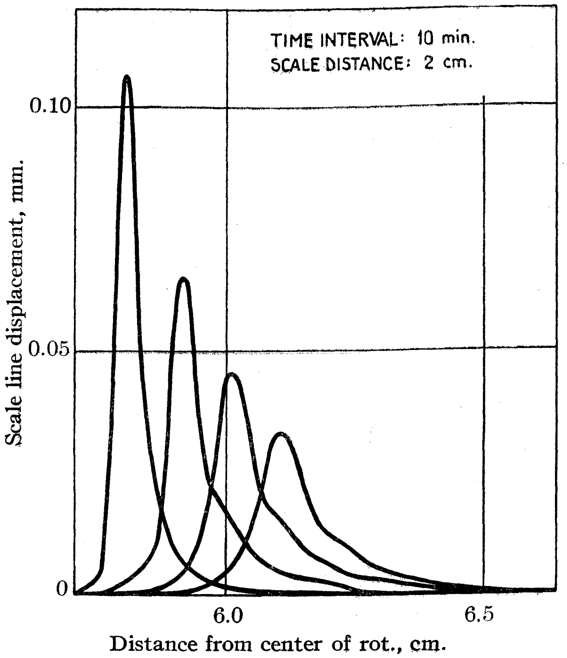


Fig. 4.—Sedimentation diagram, obtained by means of the refractive index method from the tobacco-mosaic virus at *p*H 9.5; centrifugal force 10,000 times gravity; time between exposures 10 minutes.

In Fig. 5 are given the distribution curves calculated from a run at *p*H 9.5. The agreement between the curves from different times of sedimentation is very good.

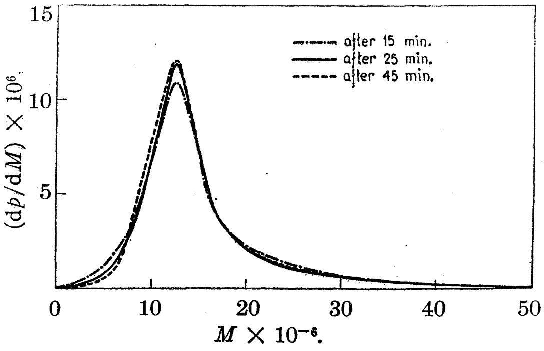


Fig. 5.—Molecular weight distribution curves calculated from the run shown in Fig. 4.

The result of runs at different *p*H is given in Fig. 6. A departure from neutrality (curve B, *p*H 6.8) causes a decrease in homogeneity both in the direction of higher alkalinity (curves C, *p*H 8.3 and D, *p*H 9.5) and higher acidity (curve A, *p*H 6.0). Not only the *p*H itself but also the time during which the solution is kept at a certain *p*H are of great importance. Thus curve E, *p*H 5.0 where the solution had been kept at *p*H 8.5 for two weeks represents a less homogeneous system than curve D, *p*H 9.5, where the solution was run immediately after the dissolution of the crystals. Recrystallization of material E did not bring it back to curve B, or thereabout, but on the contrary increased the inhomogeneity still more (curve F, *p*H 6.8).

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(4) R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 726 (1934).

(5) *Cf.* T. Svedberg and H. Rinde, THIS JOURNAL, **46**, 2677 (1924).

(6) *Cf.* O. Lamm, *Kolloid-Z.*, **69**, 44 (1934).

Molecular Weight by Sedimentation Equilibrium Measurements.—Two sedimentation equilibrium determinations were carried out in order to obtain the molecular weight of the protein. In one of the experiments the solution was run for seventeen days with a height of column of 1.5 millimeters, in the other twenty-three days with 3 mm. height of solution. On account of the extremely low diffusion and the inhomogeneity of material, the results are very uncertain. The value obtained is, however, of the same order of magnitude as that calculated from the sedimentation constant under the assumption of f/f_0 = 1.3 as found for other high molecular proteins.

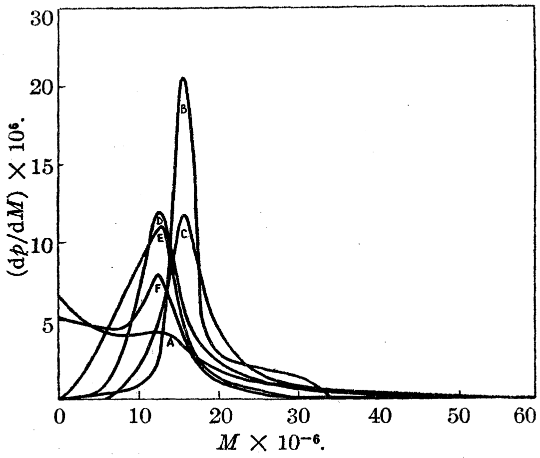


Fig. 6.—Molecular weight distribution curves for the tobacco-mosaic virus protein in solution of different *p*H.

Isoelectric Point and Mobility Gradient.—The isoelectric point was determined according to the very accurate method of Tiselius.[7,8]

In spite of its inhomogeneity with regard to molecular weight the protein shows a very uniform migration in the electrical field (Fig. 7). The results of the electrophoretic measurements are summarized in Table II. Figure 8 gives the *p*H–mobility curve. The isolectric point is situated at *p*H 3.49 and the slope of the *p*H–mobility curve (d*u*/d*p*H is 12.3 × 10^{-5}.

TABLE I

SEDIMENTATION VELOCITY MEASUREMENTS BY REFRACTIVE INDEX METHOD

Centrifugal force 15,000 times gravity; thickness of column of solution 1.2 cm.; scale distance 10–160 mm., source of light, mercury arc; light filter, methyl esculetin; plates Cramer

Solvent	*p*H of solvent	Total molar	$s_{20} \times 10^{13}$	
NaAc, HAc	5.0	0.20	191[a]	
Na_2HPO_4, KH_2PO_4	6.0	.20	201	93.4[b]
Na_2HPO_4, KH_2PO_4	6.8	.10	233	
Na_2HPO_4, KH_2PO_4, NaCl	6.8	.27	239	
$Na_2B_4O_7$, KH_2PO_4, NaCl	8.3	.24	244	
$Na_2B_4O_7$, Na_2CO_3, NaCl	9.5	.25	196	

[a] The solution was first stored for two weeks at *p*H 8.5. [b] A large part of the protein was aggregated and sedimented down at very low speed.

TABLE II

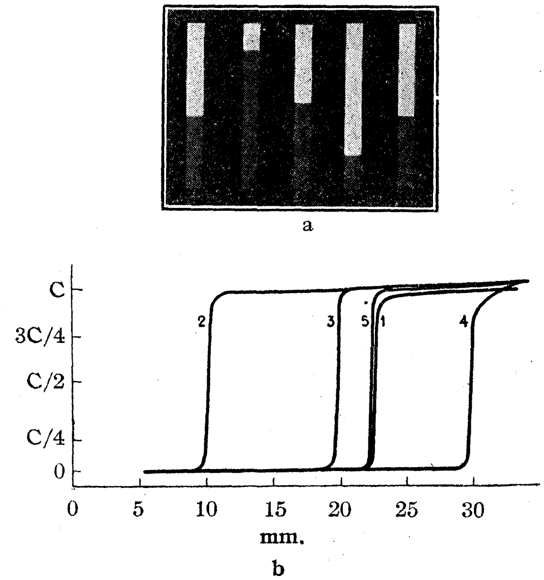
ELECTROPHORESIS MEASUREMENTS

Concentration of protein 0.06%. Solvent, acetate buffer, 0.02 *M* in NaAc. Light filters chlorine and bromine

*p*H	Migration	$u_{20°} \times 10^{15}$
3.63	Anodic	1.8[a]
3.83	Anodic	3.8[a]
4.01	Anodic	7.5
4.08	Anodic	7.2
4.16	Anodic	8.7
4.35	Anodic	10.5
4.65	Anodic	13.9
4.95	Anodic	18.9[b]

[a] Not in solution. [b] 0.04 *M* NaAc.

Isoelectric point 3.49. Slope of mobility *p*H curve (d*u*/d*p*H) 12.3 × 10^{-5}.



a

b

Fig. 7, a and b.—Electrophoresis pictures (a) and the corresponding concentration curves (b) for the tobacco-mosaic virus protein. The material is homogeneous in electrochemical respect.

Discussion of Results

The material of tobacco-mosaic virus protein studied by us has proved to be inhomogeneous with regard to molecular weight. Assuming the dissymmetry constant to be the same as for other high molecular proteins about 65% of the material falls in the molecular weight interval 15–20 millions at a *p*H of 6.8. Raising or lowering the *p*H increases the polydispersity. Even mere recrystallization may give rise to a more inhomogeneous system.

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(7) A. Tiselius, *Nova Acta Reg. Soc. Scient. Upsaliensis*, IV, 7, No. 4 (1930).

(8) Also described by K. O. Pedersen, *Kolloid-Z.*, **63**, 268 (1930).

It would seem, therefore, that any modifications in the process of isolation of the virus protein involving less drastic modes of operation (*p*H not higher than 7) than have hitherto been used, might render a product more homogeneous with regard to molecular weight. To judge from our data it is not impossible that the virus protein is quite homogeneous in its native state.

The fact that standing at *p*H 8.5 causes an irreversible change in the distribution curve not to be remedied by recrystallization, shows that a chemical change has taken place. The lack of homogeneity with regard to molecular weight, therefore, in all probability corresponds to a chemical inhomogeneity. On the other hand, this lack of chemical definition could not be very pronounced since the electrophoresis measurements did not reveal any inhomogeneity at all.

Our findings speak decidedly against the theory of the virus being a sort of bacteria. Even if we assume, for the sake of argument, that the particles of our distribution curves were living organisms in different stages of development and capable of orienting themselves and aggregating to "crystals," it would be extremely difficult to imagine these organisms to change their size with *p*H as found by us. The almost perfect homogeneity with regard to electrophoretic mobility indicates a chemical likeness hardly to be expected to obtain in the surface layer of organisms in different stages of development. The most likely interpretation of the facts revealed by us seems to be that the virus is a chemically well-defined protein, probably homogeneous with regard to molecular weight (17 millions) in the plant. It is very sensitive to deviations from neutral *p*H and is thus rendered inhomogeneous.

We are indebted to Dr. Stanley for his kindness in sending us this material and to The Rockefeller Foundation and the Foundation "Therese and Johan Anderssons Minne" for financial aid.

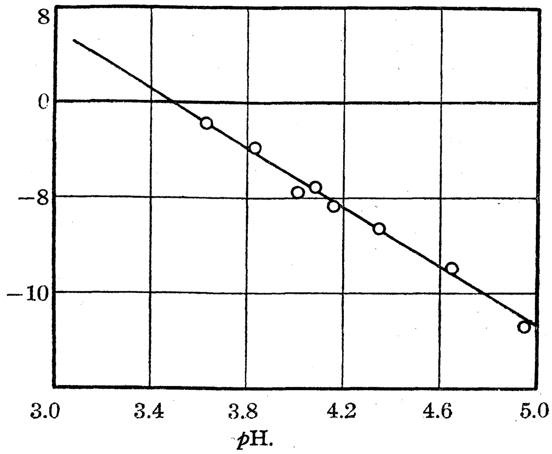

Fig. 8.—The *p*H–mobility curve for the tobacco-mosaic virus protein.

Summary

1. The tobacco-mosaic virus protein has been subjected to an ultracentrifugal and electrophoretic study.

2. Sedimentation velocity runs by the light absorption and the refractive index or scale method have revealed a considerable inhomogeneity with regard to molecular weight.

3. From the scale runs distribution curves were calculated. The position of the maxima and the dispersion changes with *p*H. At 6.8 about 65% of the material has molecular weight between 15 and 20 millions, provided the dissymmetry constant is the same as for other high molecular proteins.

4. It does not seem improbable that the virus protein might be homogeneous with regard to molecular weight in its native state.

5. Sedimentation equilibrium runs indicate a mean molecular weight of the same order.

6. Electrophoretic determinations showed the virus protein to be chemically well-defined and practically homogeneous.

UPSALA, SWEDEN RECEIVED JULY 1, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

The Solubility of Cobaltous Iodate in the Presence of Sodium Chloride, Sodium Iodate and Cobaltous Sulfate

BY H. M. TRIMBLE

The solubilities of the various hydrates of cobaltous iodate have been investigated carefully by Meusser.[1] The dihydrate is the stable form at and near room temperature; hence it was used in this study.

Preparation of Materials

Cobaltous iodate dihydrate is readily prepared by the reaction of any soluble cobaltous salt with any soluble iodate in aqueous solution. If the reagents are mixed in the cold this salt separates slowly, forming a close knit and hard mass of tiny crystals which can be removed from the precipitation vessel and purified only with difficulty. When the hot solutions are mixed with rapid stirring a more highly hydrated form, probably the tetrahydrate, separates along with the dihydrate, both forming larger crystals. Upon agitating the mixture with the mother liquor for some days, however, conversion to the dihydrate is complete, and good crystals are formed. Cementing together of the crystals is thus avoidable. This method was employed in preparing cobaltous iodate, using the best obtainable cobaltous nitrate and sodium iodate. The product was washed thoroughly and dried to constant weight at 50°. Repeated analyses established its exact composition and its purity.

The sodium chloride was a special product marked "for analysis" and was not further purified. Sodium iodate was prepared in this Laboratory, and several times recrystallized. Cobaltous sulfate was also recrystallized for use, starting with a commercial C. P. product. Redistilled water was used in the preparation of the salts and in preparing the solutions for saturation.

Experimental Methods and Results

Cobaltous iodate dihydrate dissolves very slowly; consequently saturated solutions are produced only after extended agitation. Contrary to the usual behavior of salts, too, saturation is approached from a condition of supersaturation much more slowly than from undersaturation. In three experiments in which solutions previously saturated at 60° were agitated with crystals of the dihydrate at 30° saturation had not yet been reached after a week. This persistence of metastable equilibrium was so great that solutions showed no separation of solute, even when allowed to stand for weeks at temperatures somewhat below that at which they had been saturated. Equilibrium was therefore always approached from below in these experiments, and times of seventy-five and one hundred and twenty hours were allowed in every case. A number of experiments with pure water and with solutions of various added salts showed that saturation was reached in the shorter time in every case.

All solutions were saturated at 30°. Their preparation and analysis were carried out in duplicate—many of them in triplicate. Solutions of sodium chloride, sodium iodate and cobaltous sulfate, respectively, were made up in suitable concentrations and analyzed and their densities were determined. Chloride concentrations were determined by the Volhard method. Sulfate was determined in the cobaltous sulfate solutions by the usual gravimetric method. Iodate was determined in all cases by iodometric titration. Potassium iodate was used in standardizing the thiosulfate solutions. After saturation, excess cobaltous iodate was filtered off, using a quantitative filter paper designed for the filtration of very fine precipitates. Then followed the iodometric titration of the iodate present in the saturated solutions. Carefully calibrated apparatus was used in all the determinations. The densities of the saturated solutions were determined in every case.

In the solutions in which sodium iodate was the added salt titration gave total iodate. Other samples of these solutions were treated with an excess of hydrochloric acid and boiled to destroy the iodate present and to remove the chlorine liberated by the reaction. Cobalt was then precipitated from the solutions as hydroxide by rendering them slightly alkaline with sodium hydroxide. After filtering and washing this precipitate, it was dissolved in hydrochloric acid and the cobalt was determined by the perborate method. From this determination the concentration of cobaltous iodate in each of the saturated solutions was calculated. The concentration of sodium iodate was found by difference. It was possible, also, to calculate the concentrations of these salts by the method, given below, which was used in those cases where sodium chloride and cobaltous sulfate were the added salts. This method of calculation gave results which agreed well with those from the direct analyses.

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[1] Meusser, *Ber.*, **34**, 2440 (1901).

For the solutions with sodium chloride and cobaltous sulfate as added salts, titration gave directly the concentration of cobaltous iodate. Subtracting the weight of this salt present in each liter of solution from the weight of that volume of solution gave the weight of the solution of the added salt which entered into it. It was then a simple matter to calculate the weight of added salt and of water per liter. Calculation of the molalities of the salts present gave the data of Table I.

TABLE I

SOLUBILITIES OF Co(IO$_3$)$_2$·2H$_2$O AT 30°

In NaCl Solutions

Molalities		
NaCl	Co(IO$_3$)$_2$	Densities
0.0	0.01165	1.0006
.0029	.0119	1.0007
.0052	.0120	1.0008
.0069	.0121	1.0009
.0111	.0124	1.0010
.0140	.0125	1.0011
.0267	.0131	1.0016
.0355	.0134	1.0020
.0532	.0139	1.0029
.0941	.0149	1.0054
.1449	.0158	1.0085
In NaIO$_3$ Solutions		
NaIO$_3$		
0.0	0.01165	1.0006
.0044	.0102	1.0006
.0076	.0093	1.0007
.0087	.0090	1.0008
.0127	.0080	1.0011
.0174	.0069	1.0014
.0202	.0063	1.0017
.0280	.0050	1.0026
.0360	.0040	1.0037
.0483	.0030	1.0056
.0999	.0010	1.0135
In CoSO$_4$ Solutions		
CoSO$_4$		
0.0	0.01165	1.0006
.0026	.0113	1.0008
.0052	.0111	1.0011
.0061	.0111	1.0012
.0123	.0107	1.0019
.0129	.0106	1.0020
.0235	.0102	1.0034
.0258	.0101	1.0037
.0516	.0095	1.0076
.0774	.0094	1.0117
.1032	.0093	1.0155

Summary

The solubility of cobaltous iodate dihydrate in solutions of sodium chloride, sodium iodate and cobaltous sulfate has been studied in the region of concentration 0 to approximately 0.1 molal for the added salt.

STILLWATER, OKLAHOMA RECEIVED FEBRUARY 28, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Allotropic Forms of Diphenylsulfone and the Determination of their Transition Point

BY VLADIMIR J. MIKESKA, NICHOLAS T. FARINACCI AND MARSTON TAYLOR BOGERT

In the course of an examination of certain still residues remaining from the preparation of phenol by the fusion of sodium benzene sulfonate with sodium hydroxide, we separated a crystalline solid, in a yield of over 30%, whose chemical properties and analysis coincided with those of diphenylsulfone. The formation of this compound as a by-product in the manufacture of phenol by the process stated has been known for years. The only puzzling thing about our product was its melting point. The literature on this subject is confusing, some investigators giving the figure as 124°, others as 128°.

It seemed of interest, therefore, to ascertain if possible the reason for this discrepancy, and our study of the problem disclosed the following facts. (1) Diphenylsulfone exists in two reciprocally convertible allotropic forms, one melting at 124° and the other at 128°. (2) The transition temperature for the two is in the neighborhood of 75°. When crystallization is induced (no matter how) above this temperature, the product always melts (if pure) at 128°; if induced below this, it melts at 124°.

Otto[1] obtained both forms, but concluded that the 124° form, because of its lower m. p., was probably impure.

Remsen and Saunders[2] gave 124° as the correct m. p. for the sulfone. Because they were unable by recrystallization to raise this m. p. to the

[1] Otto, *Ann.*, **136**, 160 (1865).

[2] Remsen and Saunders, *Am. Chem. J.*, **17**, 364 (1895).

128° reported by Otto, they at first doubted the identity of the two products, but analysis and comparison of other properties convinced them that their product was also the diphenylsulfone.

In the light of the results of our own experiments, it seems most likely that Otto carried out his final crystallization above 75°, and Remsen and Saunders carried out theirs below that temperature.

The sulfone can be supercooled to 72°. Hence crystallization can be induced at any temperature between 72 and 124°. If the sulfone is fused and then cooled rapidly, as is the usual case, it yields the 128° form, because under these conditions it solidifies above 75°. But when the fused sulfone is cooled slowly, it supercools below the transition point before it congeals, and the 124° form is produced. It is therefore possible to change the m. p. of the sulfone at will, by fusing and then inducing crystallization above or below the transition point.

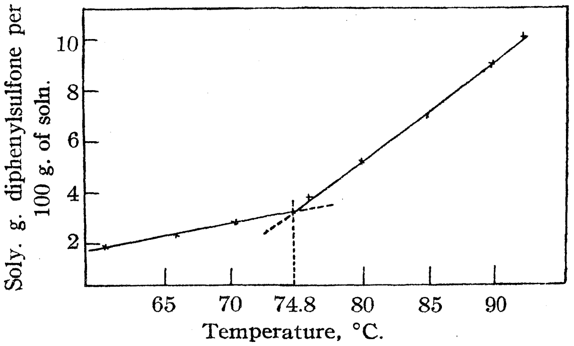

Fig. 1.—Allotropic forms of diphenylsulfone. The intersection of the three lines shows the transition point: α-form, m. p. 124°, stable below 74.8°, β-form, m. p. 128°, stable above 74.8°.

The method of inducing crystallization does not appear to make any difference. Cooling of the molten material was only one of several methods used. Seeding was another one. If the molten sulfone were seeded above 75° with either the 124 or the 128° form, it congealed immediately to the 128° form.

When the sulfone was crystallized from hot solvents under ordinary conditions, the 124° form generally resulted, because the crystals did not begin to separate until the solution had cooled below 75°. In these experiments, the solvents used were water, methyl and ethyl alcohols, ether, acetone, acetic acid, ligroin and chloroform. In every case, the 124° form was obtained, irrespective of whether the solute had been the 124 or the 128° form.

When the temperature of the solution was maintained above 75°, so that crystallization had to take place above this transition point, the 128° form resulted. Alcohol and acetic acid were the solvents employed. From the former, at 75 and at 78° the 128° type separated, at 66 and at 70° the 124° type. From acetic acid at 100°, the 128° type separated. When 50 g. of the 128° form, suspended in 600 cc. of 95% ethanol, was stirred for eight hours at 30°, it was transformed into the 124° form, a rearrangement which indicates that the lower-melting is the stabler form at the lower temperatures.

Another method used to induce crystallization at a desired temperature was to employ a mixture of two solvents, such as water and alcohol, in one of which (alcohol) it dissolved freely and in the other but slightly. An alcoholic solution of the sulfone saturated at the requisite temperature was treated with water heated to the same temperature. Crystallization ensued immediately at this temperature. When this mixing occurred above 75°, the 128° form was obtained, when below this the 124° form.

That the 124° form is not an impure 128° form was proved by the fact that no amount of purification enabled us to change the lower to the higher melting form.

The assumption that the 124° is a hydrated form of the 128° type is also untenable, for no water was evolved when the 124° form was heated, and the analysis of the two evidenced the identity of their composition, and both types could be obtained from water–alcohol mixtures. Further, as already noted, the 128° form could be changed to the 124° under strictly anhydrous conditions, *i. e.*, by fusing it and allowing it to crystallize slowly below 75°.

The transformation of the solid forms into each other seems to be slow. When the 128° form was kept at 66° for twenty-four hours, there was no evidence of its having changed; but when the 124° form was maintained at 100° for the same length of time it was partly converted into the 128° form. The higher velocity of transformation at the latter temperature may account for this partial transformation. The fact that the 124° type is obtained by metathesis in solution at low temperatures indicates that it is the stable form below the transition point.

A more precise determination of the transition point seemed to us desirable. The thermometric method was unsatisfactory, because of the slowness of the change of one solid form into the other, and also because there occurs appreciable sublimation of the sulfone above about 80°. We fell back, therefore, upon the solubility method, which was applied as follows.

A three-necked 500-cc. flask, containing a saturated solution of the sulfone in 45% aqueous acetic acid in contact with a large excess of the solid, was heated in a four-liter water-bath provided with a coil of perforated copper pipe. The water in the bath was kept in motion by air bubbles forced through pin-holes in this pipe, while the contents of the flask were agitated by a motor-driven glass stirrer. With the flask contents and bath liquid in vigorous agitation, the temperature of the solution in the flask was raised to 90°, and was then allowed to fall slowly, samples being removed at 76, 70.5, 66, and 60.5°. After this, the temperature was gradually raised again and samples taken at 80, 85, 90, and 92.5°. This procedure was adopted in order to ensure saturation and to facilitate the attainment of equilibrium. The samples were blown out of the flask by air pressure, through a preheated tube containing a plug of cotton wool to filter out any crystals, into tared bottles. The weights of liquid and solid were determined by evaporation to dryness, and the solubilities calculated on the basis of grams of solid per 100 g. of solvent. Eight determinations were made, with temperatures so chosen as to bring the transition point about halfway between the extremes. The graph shows these experimental results, with the transition point at 74.8°.

Summary

1. Diphenylsulfone exists in two reciprocally convertible allotropic forms, one melting at 128°, and the other at 124°.

2. The conditions are explained under which one form can be changed into the other, the transition temperature being about 74.8°.

3. Some of the confusion in the literature on this subject is thus explained.

NEW YORK, N. Y. RECEIVED JULY 17, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

The Condensation of 2-Butanone with Aldehydes of the Type RR'CHCHO[1,2]

BY S. G. POWELL AND MAYNARD M. BALDWIN

It has been shown that certain straight-chain aldehydes react with 2-butanone under the influence of alkaline condensing agents to form ketols of the type $RCHOHCH(CH_3)COCH_3$.[3] On the other hand, Thoms and Kahre found that with isobutyraldehyde the ketol $(CH_3)_2CHCHOHCH_2COC_2H_5$ was obtained.[4] It seemed therefore desirable to investigate the behavior of other aldehydes of the type RR'CHCHO.

2-Butanone was treated with methylethylacetaldehyde, diethylacetaldehyde, and ethyl-*n*-butylacetaldehyde in the presence of dilute potassium hydroxide. In each case the resulting ketol was dehydrated to the unsaturated ketone; this was reduced to the saturated secondary alcohol and this in turn oxidized to a mixture of acids as described in previous papers.[3c,3d,5] The water-insoluble acids obtained were then investigated and in each case the acid of the type RCH_2COOH (where the aldehyde in each instance is designated as RCHO) was found and in no case could the acid of the type RCOOH be identified, showing that the secondary alcohols were of the type $RCH_2CH_2CHOHC_2H_5$ and not $RCH_2CH(CH_3)COCH_3$, and that these aldehydes, like isobutyraldehyde, had reacted with the methyl group of the 2-butanone. The identity of the acids was established by a comparison of their piperazonium salts with those prepared from known samples of the acids which might be formed. Of the acids required for purposes of comparison β-ethylenanthic and γ-ethylcaprylic acids could not be found described in the literature and their preparation is given in detail. The other acids were

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[1] Presented before the Division of Organic Chemistry at the San Francisco meeting of the American Chemical Society, August, 1935.

[2] Based upon a thesis submitted by Maynard M. Baldwin in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Washington.

[3] (a) U. S. Patent 981,668; (b) Salkind, *J. Russ. Phys.-Chem. Soc.*, **37**, 484 (1905); (c) Powell, THIS JOURNAL, **46**, 2514 (1924); (d) Powell, Murray and Baldwin, *ibid.*, **55**, 1153 (1933).

[4] Thoms and Kahre, *Arch. Pharm.*, **263**, 241–252 (1925).

[5] Powell and Secoy, THIS JOURNAL, **53**, 765 (1931).

either purchased or prepared by standard methods.

Experimental Part

Methylethylacetaldehyde.—This was prepared by the dehydrogenation of *s*-butylcarbinol with a copper–chromium–barium oxide catalyst.[6] The *s*-butylcarbinol was made by the fractionation of the technical product obtained from the Eastman Kodak Company. The fraction boiling at 127–128° was used and its purity was tested by preparing the 3,5-dinitrobenzoate and comparing it with that of pure *s*-butylcarbinol and with that of isoamyl alcohol, the most likely impurity.

Diethylacetaldehyde.—One portion of this was prepared by the method of Darzens[7] from diethyl ketone and ethyl chloroacetate. The other portion was prepared from ethylmagnesium bromide and ethyl ethoxyacetate.[8]

Ethyl-*n*-butylacetaldehyde.—This was purchased from the Carbide and Carbon Chemicals Corporation under the name of "octyl aldehyde." The material was dried and distilled and the fraction boiling at 161–162° retained for use.

The Saturated Alcohols.—In Table I are listed some of the properties of the saturated secondary alcohols obtained by reducing the unsaturated ketones formed when the ketols were dehydrated.

Table I

	Alcohol	B. p., °C.	Mm.	n_D	d_4
1	6-Methyl-3-octanol	81–83	15	1.4372 (28°)	0.8320 (28°)
2	6-Ethyl-3-octanol	90–92	20	1.4371 (24°)	.8396 (24.5°)
3	6-Ethyl-3-decanol	119–120	18	1.4435 (28°)	.8364 (28°)

	Analyses			
	Calcd.		Found	
	C	H	C	H
1	74.92	13.98	75.02	13.55
2	75.87	14.02	75.37	13.76
3	77.33	14.07	76.99	13.67

β-Ethylenanthic Acid.—Ethyl-*n*-butylacetaldehyde was reduced to 2-ethyl-1-hexanol and this was converted into the bromide by treatment with phosphorus tribromide. The crude bromide was treated with sodium cyanide and the nitrile hydrolyzed in the usual manner with sodium hydroxide. The acid boiled at 135° (25 mm.) and at 236° (760 mm.).

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.29; H, 11.47. Found: C, 68.41; H, 11.79.

2-Ethyl-1-hexanol.—The reduction of the ethyl-*n*-butylacetaldehyde was carried according to the method described for the preparation of 1-heptanol[9] using iron and acetic acid, and also by the use of sodium and moist ether. While the second method was inferior to the first in the matter of yield it was superior to it from the standpoint of convenience and time consumption. A solution of 5 g. of magnesium sulfate in 600 cc. of water, 500 cc. of ether, and 64 g. (0.5 mole) of the aldehyde were placed in a two-liter flask fitted with a condenser and dropping funnel. Sixty grams of sodium was then added in small portions through the condenser and at the same time acetic acid was added from the dropping funnel at such a rate that a slight precipitate of magnesium hydroxide was always present; yield 45%.

γ-Ethylcaprylic Acid.—This was prepared in the usual manner from 2-ethyl-1-bromohexane and ethyl malonate. The acid boiled at 253–256° (760 mm.).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.70; H, 11.71. Found: C, 69.67; H, 11.66.

The Piperazonium Salts.—The method of Pollard, Adelson, and Bain[10] was used for the preparation of these salts. Table II gives the properties of the piperazonium salts of the acids actually found among the water-insoluble oxidation products of the saturated alcohols. Although γ-ethylcaprylic acid was not among these, it is included in the table because it is a hitherto unknown acid.

Table II

Piperazonium salt of	M. p., °C.	Neut. equiv. Calcd.	Neut. equiv. Found	Nitrogen, % Calcd.	Nitrogen, % Found
β-Methylvaleric acid	129	318.2	316.2	8.79	8.85
γ-Methylcaproic acid	109	346.3	343.8	[a]	
β-Ethylvaleric acid	134	346.3	343.6	8.08	7.78
β-Ethylenanthic acid	100	402.2	398.4	6.96	7.14
γ-Ethylcaprylic acid	110	430.4	433.6	6.51	6.56

[a] Not enough of the salt was available to carry out both determinations.

Summary

Methylethylacetaldehyde, diethylacetaldehyde, and ethyl-*n*-butylacetaldehyde react with the methyl group of 2-butanone under the influence of alkaline condensing agents.

Seattle, Washington

Received July 14, 1936

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[6] Connor, Folkers, and Adkins, This Journal, **54,** 1139 (1932).

[7] Darzens, *Compt. rend.*, **139,** 1214 (1904).

[8] Béhal and Sommelet, *Bull. soc. chim.*, [3] **31,** 300 (1904).

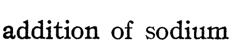
[9] Clarke and Dreger, "Organic Syntheses," Coll. Vol. I, p. 298.

[10] Pollard, Adelson and Bain, This Journal, **56,** 1759 (1934).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Addition of Sodium Bisulfite to Alkylene Oxides

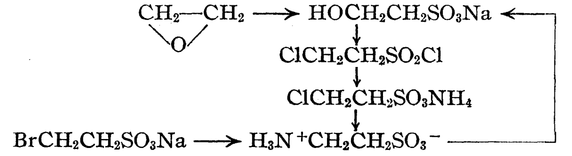
BY WALTER M. LAUER AND ARCHIE HILL

The addition of sodium or potassium bisulfite to an alkylene oxide has generally been assumed[1-5] to yield the corresponding salt of a β-hydroxysulfonic acid, even though the structure of addition compounds of this type has not been rigorously established. The work of Fromm, Kapeller and Taubmann[6] has introduced an element of doubt, however, since they have reported that the sodium bisulfite addition product obtained from epichlorhydrin,  $ClCH_2CH{-}CH_2$ (O bridging), after boiling with aqueous sodium hydroxide and subsequent treatment with hydrochloric acid, gave a positive test for sulfur dioxide. They regarded this as evidence for a C–O–S linkage and it therefore became of interest to attempt to decide between the two structures

$RCH(OH)CH_2SO_3Na$ (I) $RCH(OH)CH_2OSO_2Na$ (II)

for the product obtained by the action of sodium bisulfite on an alkylene oxide.

The following series of reactions, which demonstrates the correctness of the β-hydroxysulfonic acid structure (I), was carried out.



The taurine obtained in this manner from the bisulfite addition compound of ethylene oxide was identical with that obtained from sodium β-bromoethanesulfonate by the method of Marvel, Bailey and Sparberg[7] and the completion of the cycle of transformations by conversion of the taurine to the original addition compound makes a structural rearrangement improbable.

Since the alkali metal salts of β-hydroxysulfonates are water soluble and not infrequently difficult to free of inorganic sulfites, it is conceivable that the presence of sulfur dioxide upon acid treatment of the addition compound of Fromm, Kapeller and Taubmann can be accounted for in this way.

Experimental

Sodium β-Hydroxyethanesulfonate.—Ethylene oxide was passed into a concentrated solution of sodium bisulfite contained in a 500-cc. three-necked round-bottomed flask fitted with a mechanical stirrer and a reflux condenser. The ethylene oxide was absorbed rapidly with the evolution of heat. The bisulfite addition compound was obtained by evaporating the solution to dryness and extracting the solid residue repeatedly with 95% alcohol. Colorless crystalline sodium β-hydroxyethanesulfonate (m. p. 192–194°) separated from the alcoholic extract in approximately 60% yield.

Anal. Calcd. for $C_2H_5O_4SNa$: Na, 15.52. Found: Na, 15.68, 15.53.

Acetylation in a manner similar to that used in the case of the bisulfite addition compound of formaldehyde,[8] followed by crystallization from alcohol, yielded the acetyl derivative.

Anal. Calcd. for $C_4H_7O_5SNa$: Na, 12.10. Found: Na, 11.82, 11.98.

Potassium β-hydroxyethanesulfonate (m. p. 191–193°) was prepared in a manner similar to that described for the sodium compound. It was easier to obtain in pure form than the sodium salt.

Anal. Calcd. for $C_2H_5O_4SK$: K, 23.80. Found: K, 23.82, 23.94.

The acetylated product melted at 258–260°.

Anal. Calcd. for $C_4H_7O_5SK$: K, 18.95. Found: K, 19.08, 18.75.

The myristoyl derivative of the sodium β-hydroxyethanesulfonate, prepared by means of myristoyl chloride, was obtained in the form of a white powder which was rather difficult to purify. A mixture of benzene and water formed an emulsion when shaken with some of this material.

Anal. Calcd. for $C_{16}H_{31}O_5SNa$: Na, 6.44. Found: Na, 6.76.

β-Chloroethanesulfonyl Chloride.—The directions of Kolbe,[9] with slight modifications, served for the conversion of either the sodium or potassium β-hydroxysulfonate to β-chloroethanesulfonyl chloride. After the initial vigorous reaction with excess phosphorus pentachloride, the reaction mixture was refluxed gently for two to three hours. The reaction mixture was then poured onto ice. The oily layer was next fractionated; b. p. 13 mm. 86–88° (198–204° at 760 mm.). Twenty grams of the sodium bisulfite addition product and 57 g. of phosphorus pentachloride

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(1) Erlenmeyer and Darmstaedter, *Z. Chem.*, 342 (1868).

(2) Darmstaedter, *Ann.*, **148**, 125 (1868).

(3) Pazschke, *J. prakt. Chem.*, [2] **1**, 86 (1870).

(4) Brunel, *Compt. rend.*, **137**, 63 (1903).

(5) German Patent 569,148 (1931).

(6) Fromm, Kapeller and Taubmann, *Ber.*, **61**, 1353 (1928).

(7) Marvel, Bailey and Sparberg, THIS JOURNAL, **49**, 1833 (1927).

(8) Lauer and Langkammerer, *ibid.*, **57**, 2361 (1935).

(9) Kolbe, *Ann.*, **122**, 42 (1862); see also ref. 7.

yielded 14 g. of β-chloroethanesulfonyl chloride. Hydrolysis yielded β-chloroethanesulfonic acid.[10]

Ammonium β-Chloroethanesulfonate.—The viscous β-chloroethanesulfonic acid was treated with concd. ammonium hydroxide and the solution evaporated to dryness under reduced pressure. The residue was crystallized from alcohol.

Anal. Calcd. for $C_2H_8O_3ClNS$: C, 14.86; H, 4.99. Found: C, 15.18; H, 5.25.

Taurine was prepared by heating ammonium β-chloroethanesulfonate for twelve hours in a sealed tube at 105° with an excess of concd. ammonium hydroxide. Upon cooling, taurine separated out. It was recrystallized several times from water and was identical with a sample of taurine prepared by the method of Marvel, Bailey and Sparberg.[7] Identity was established by means of crystallographic examination.[11]

Potassium β-Hydroxyethanesulfonate from Taurine.—Acetic acid was added slowly to a hot aqueous solution containing taurine and potassium nitrite. After no further gas evolution, addition of acetic acid was discontinued and the solution was evaporated to dryness. The solid residue was extracted with hot alcohol. The alcohol extract yielded crystalline potassium β-hydroxyethanesulfonate; m. p. 189–191°.

Anal. Calcd. for $C_2H_5O_4SK$: K, 23.80. Found: K, 23.84.

A crystallographic examination showed this product to be identical with the one obtained by the addition of potassium bisulfite to ethylene oxide. Attempts to convert sodium β-bromoethanesulfonate to sodium β-hydroxyethanesulfonate by means of silver oxide led to products which were unsuited for crystallographic comparison.

Summary

The addition compound obtained by the action of sodium or potassium bisulfite on ethylene oxide has been shown to possess the β-hydroxysulfonic acid structure, a result which was generally accepted, but not demonstrated previously.

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(10) Kohler, *Am. Chem. J.*, **20**, 683 (1898).

(11) We are indebted to Dr. E. B. Sandell of the Division of Analytical Chemistry for the crystallographic comparisons reported in this paper.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Reaction of Haloamines with Ketenes

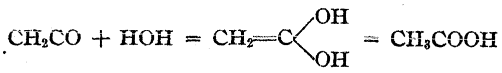
BY GEORGE H. COLEMAN, ROLF L. PETERSON AND GILBERT E. GOHEEN

Previous work in this Laboratory has shown that in the addition of nitrogen trichloride to unsaturated compounds[1] a chlorine atom in nitrogen trichloride behaves as though it were electropositive with respect to the NCl_2 group. By analogy it might be assumed that the halogens in other haloamines such as monochloroamine, monobromoamine, dibromoamine and the alkylchloroamines would show a similar behavior. The reactions of these compounds with reducing agents support this assumption. Attempts to bring about addition reactions of some of the haloamines other than nitrogen trichloride with unsaturated hydrocarbons have not been thus far successful. Monochloroamine reacts with Grignard reagents[2] to form primary amines and ammonia. With many of these reagents the percentage of amine formed is much greater than the percentage of ammonia. Such a result does not seem to be consistent with the assumption that in all reactions the NH_2 group in monochloroamine is electronegative with respect to the chlorine.

In the present work a study was made of the reactions of monochloroamine, dibromoamine, nitrogen trichloride and dimethylchloroamine with ketene and diphenylketene. The suitability of ketenes for this work depends on the fact that they are very reactive substances which add diverse molecules in a definite manner, as illustrated in the following well-known examples

$$CH_2CO + HOH = CH_3COOH$$
$$CH_2CO + RNH_2 = CH_3CONHR$$
$$CH_2CO + HCl = CH_3COCl$$

The activity of this class of compounds may be due to addition to the carbonyl group first and then rearrangement of the resulting enol form as postulated by Staudinger,[3] *e. g.*



$$CH_2CO + HOH = CH_2{=}C\begin{matrix}\diagup OH \\ \diagdown OH\end{matrix} = CH_3COOH$$

Regardless of the mechanism, however, by which the addition takes place, the final product is such that the electropositive portion of the adding molecule is found attached to the carbon farthest

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(1) Coleman and co-workers, THIS JOURNAL, **45**, 3084 (1923); **49**, 2593 (1927); **50**, 1816 (1928); **50**, 2739 (1928); **50**, 2754 (1928); **51**, 937 (1929).

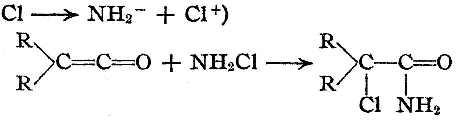
(2) (a) Coleman and Hauser, *ibid.*, **50**, 1193 (1928); (b) Coleman and Yager, *ibid.*, **51**, 567 (1929); (c) Coleman and Forrester, *ibid.*, **58**, 27 (1936).

(3) Schlenk and Bergmann, "Ausführliches Lehrbuch der organischen Chemie," Franz Deuticke, Vienna, 1932, Vol. I, p. 374.

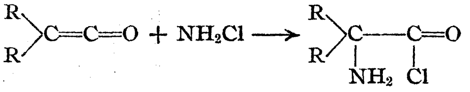
from the oxygen and the electronegative portion to the carbon to which the oxygen is united.

Applying these considerations to the question of the character of the halogen atoms in haloamines the following possibilities can be formulated for the reaction of monochloroamine with ketenes

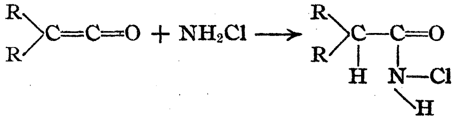
($NH_2Cl \longrightarrow NH_2^- + Cl^+$)


(1)

($NH_2Cl \longrightarrow NH_2^+ + Cl^-$)


(2)

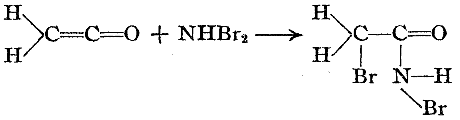
($NH_2Cl \longrightarrow NHCl^- + H^+$)


(3)

Diphenylketene was found to react with monochloroamine to form diphenylchloroacetamide according to equation (1). No evidence of the formation of other addition products was observed although the yield of diphenylchloroacetamide isolated was only 51% of the theoretical. With unsubstituted ketene (CH_2CO) N-chloroacetamide was formed in 70–75% yields, the reaction apparently occurring according to equation (3). The fact that the reaction with diphenylketene proceeds differently than that with ketene is not necessarily surprising, considering the electronegative character of the phenyl groups relative to hydrogen (Kharasch).[4]

Dibromoamine and ketene formed monobromoacetamide, a result most readily explained by assuming the reaction

($NHBr_2 \longrightarrow NHBr^- + Br^+$)


(4)

The replacement of the bromine on nitrogen by hydrogen is probably due to the presence of hydrobromic acid in the reaction mixture. If dibromoamine added to ketene in any other manner, acetamide or glycine would be the final product under the experimental conditions. It also seems quite improbable that the bromine on carbon could be due to direct bromination.

A nearly quantitative yield of N,N-dimethyldiphenylchloroacetamide was formed in the reaction of dimethylchloroamine with diphenylketene. In the light of previous work this product was to be expected.

With ketene and dimethylchloroamine a liquid product was obtained which after distillation had a chlorine and nitrogen content corresponding to that of N,N-dimethylchloroacetamide.

Nitrogen trichloride reacted with ketene to give as a final product monochloroacetamide in about 14% yields. This is in agreement with the assumption of relatively electropositive chlorine atoms in nitrogen trichloride. Boismenu[5] states that N,N-dichloroacetamide is unstable above 0°, decomposing with the liberation of chlorine. This instability may account in part for the low yield. The substitution of hydrogen for the chlorine on nitrogen is again doubtless due to the formation of hydrochloric acid in the reaction mixture.

The reaction of nitrogen trichloride with diphenylketene has been reported previously.[6] The results were interpreted as indicating the formation of N,N-dichlorodiphenylchloroacetamide which was transformed to benzophenoneimide hydrochloride. This reaction was repeated under different experimental conditions and a product isolated which was unstable at room temperature and contained chlorine attached to nitrogen. Its chlorine content corresponded to that of N,N-dichlorodiphenylchloroacetamide.

Experimental

Preparation of Haloamines.—The methods used in the preparation and analysis of monochloroamine,[2c,7] dibromoamine,[7] dimethylchloroamine[8] and nitrogen trichloride[9] were essentially those which have been described previously.

Preparation of Diphenylketene.—Diphenylketene was prepared as described by Schroeter.[10] The method has been investigated more recently by Ritter and Wiedeman.[11] It consists in the oxidation of benzil monohydrazone in benzene solution with yellow mercuric oxide. The azibenzil which is formed loses nitrogen on heating and rearranges to the ketene. The observations of Ritter and Wiedeman with respect to the freshness and character of the mercuric oxide to be used were substantiated. It was noticed that the tendency to form the side product bisbenzalketazine increased whenever the concentration of

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[4] (a) Kharasch and Flenner, THIS JOURNAL, **54**, 674 (1932); (b) Kharasch, *J. Chem. Education*, **8**, 1703 (1931).

[5] Boismenu, *Ann. chim.*, [9] **9**, 166 (1918).

[6] Coleman and Campbell, THIS JOURNAL, **50**, 2754 (1928).

[7] Coleman, Yager and Soroos, *ibid.*, **56**, 965 (1934).

[8] Coleman, *ibid.*, **55**, 3001 (1933).

[9] Coleman, Buchanan and Paxson, *ibid.*, **55**, 3669 (1933).

[10] Schroeter, *Ber.*, **42**, 2346 (1909).

[11] Ritter and Wiedeman, THIS JOURNAL, **51**, 3583 (1929).

TABLE I

Reactants	Yield, %	M. p., °C.	Formula of product	Analyses, % Calcd. N	Cl	Found N	Cl
$CH_2CO + NH_2Cl$	73	111–112	$CH_3CONHCl$	14.96	37.96	14.85	37.86
$CH_2CO + NHBr_2$	18	88–89	$CH_2BrCONH_2$		Br, 57.93		Br, 57.99
$CH_2CO + NCl_3$	14	114–115	$CH_2ClCONH_2$				
$CH_2CO + (CH_3)_2NCl$		B. p. 98–100° (11 mm.)	$CH_2ClCON(CH_3)_2$[a]	11.53	29.20	11.57	29.05
$(C_6H_5)_2CCO + NH_2Cl$	51	116–117	$(C_6H_5)_2CClCONH_2$		14.44		14.41
$(C_6H_5)_2CCO + NCl_3$		112[b]	$(C_6H_5)_2CClCONCl_2$[a]		33.9		35.08
$(C_6H_5)_2CCO + (CH_3)_2NCl$	95	122–123	$(C_6H_5)_2CClCON(CH_3)_2$				

[a] Not completely identified. [b] Copper block method.

the azibenzil solution was too great or whenever the solution was allowed to stand for some time. This was accompanied by premature slow evolution of nitrogen. The formation of the side product was avoided by using 8–9 cc. of dry benzene per gram of benzil monohydrazone, keeping the temperature at 23–24° during the oxidation and working up the reaction mixture without extended delay. In a typical run using 90 g. of powdered benzil monohydrazone there was obtained 44 g. of diphenylketene, b. p. 120–124° (1 mm.). This was 56% of the theoretical yield.

Preparation of Ketene.—Ketene was prepared by the method described by Hurd.[12] It was collected by bubbling the gases from the condenser into anhydrous ether cooled to −60°. The concentration was determined by adding aliquot portions to 3.5 *N* alkali and titrating the excess alkali with standard acid. The ethereal solutions were used at once.

The general method of carrying out the reactions with the haloamines is typified in the procedures described for the reactions of monochloroamine with ketene and diphenylketene. The essential results of the seven reactions studied are given in Table I. The products, with the exception of the two noted in the table, were identified by comparison with authentic samples.

Monochloroamine with Ketene.—Two hundred and twenty cubic centimeters of an ethereal solution containing 0.12 mole of monochloroamine was cooled to −60° and added to 225 cc. of an ethereal solution containing 0.162 mole of ketene also at −60°. The solutions were not exposed to moist air, the addition of the monochloroamine solution being effected through a vacuum jacketed glass tube. A white turbidity appeared at once. The reaction mixture was kept at −60° for three hours and then allowed to warm to room temperature and filtered. The white precipitate weighed 2.60 g. The filtrate was partially evaporated and a second crop of white crystals weighing 4.56 g. obtained. By complete evaporation of the solvent a third portion was obtained which after purification weighed 1.06 g. The total product weighed 8.22 g. It was recrystallized by dissolving in warm ether and cooling the solution to about −60°. Shiny white plates were formed, m. p. 111–112°.

Monochloroamine with Diphenylketene.—This reaction was carried out in a manner similar to that used with ketene. An ethereal solution of 0.13 mole of monochloroamine was added at −65° to an ethereal solution of 0.106 mole of diphenylketene. As the monochloroamine was added the orange color of the ketene solution faded and a white precipitate formed which proved to be ammonium chloride. The mixture was kept at −60° for thirty minutes, then allowed to warm to room temperature and kept at this temperature for eight hours. It was then filtered and the solvent evaporated at room temperature or below under reduced pressure. The residue was recrystallized from toluene. The total weight of material obtained melting above 105° was 13.4 g. (51% of the theoretical yield). After further recrystallization the product melted at 116.5–117°.

Summary

The haloamines monochloroamine, dibromoamine, nitrogen trichloride, and dimethylchloroamine react with ketene and diphenylketene to form amides or halogen substituted amides.

IOWA CITY, IOWA RECEIVED JULY 17, 1936

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[12] Hurd, "Organic Syntheses," Coll. Vol. I, 1932, p. 324.

[CONTRIBUTION NO. 164 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Molecular Size Distribution in Linear Condensation Polymers[1]

BY PAUL J. FLORY

Introduction

All synthetic polymers and most natural ones are recognized to be non-homogeneous substances consisting of mixtures of chemically similar molecules which are distributed in size about an average, some of them being much smaller and some much larger than this average. By various methods, more or less approximate estimates of the average molecular weights of such materials can be made, but as yet information concerning the distribution of molecules amongst the various sizes is exceedingly meager. An adequate understanding of the fundamental nature of polymeric substances requires comprehension of the molecular size distributions as well as the empirical compositions and average molecular weights.

Methods have been developed for the experimental determination of molecular size distributions in polymers by using the Svedberg ultracentrifuge,[2] but they have so far been applied only to a limited extent. Theoretical calculation of the molecular size distribution is possible if the kinetic mechanism of the polymerization process is sufficiently well understood. Such calculations have been attempted for vinyl polymerizations by Chalmers,[3] by Dostal and Mark,[4] and more recently by Schulz.[5]

The present paper offers a theoretical analysis of the molecular size distribution in linear condensation polymers formed by the inter-molecular reaction of bifunctional compounds. The polyesters prepared by Carothers and co-workers[6] provide excellent examples of this type of polymer. They are of two kinds, those formed from hydroxy acids

$$\text{HO—R—COOH} \xrightarrow{-\text{H}_2\text{O}} \text{H(O—R—CO)}_x\text{OH}$$

and those formed from glycols and dibasic acids

$$\text{HO—R—OH} + \text{HOCO—R}'\text{—COOH} \xrightarrow{-\text{H}_2\text{O}} \text{H(O—R—O—CO—R}'\text{—CO)}_x\text{OH}$$

In general, polymerizations[7] of the first type above may be formulated as

$$\text{(i)} \qquad x\ \text{A—B} \longrightarrow \text{A—B (A—B)}_{x-2}\text{A—B}$$

where A and B represent functional groups and AB, or BA, the product of their reaction with one another. A simple molecule such as water may or may not be released in this process. If, as in the second example above, there are two kinds of reactants, A—A and B—B, three varieties of molecules may be formed in the polymeric mixture, *viz.*,

(iia) If x, the total number of reactant molecules combined in the polymer molecule, is an even integer

$$x/2\ \text{A—A} + x/2\ \text{B—B} \longrightarrow \text{A—A (B—BA—A)}_{(x-2)/2}\text{B—B}$$

(iib) If x is odd, either

$$\left(\frac{x+1}{2}\right)\text{A—A} + \left(\frac{x-1}{2}\right)\text{B—B} \longrightarrow \text{A—A(B—BA—A)}_{(x-3)/2}\text{B—BA—A}$$

or

$$\left(\frac{x-1}{2}\right)\text{A—A} + \left(\frac{x+1}{2}\right)\text{B—B} \longrightarrow \text{B—BA—A(B—BA—A)}_{(x-3)/2}\text{B—B}$$

Another case which might be considered is that in which the functional groups are all alike, but this may be taken as a special case of (i) in which A = B.

It is characteristic of all of these polymerizations that they involve the coupling of two bifunctional compounds to form a bifunctional compound of higher molecular weight, which in turn is capable of polymerizing with other molecules. Here the reactions: monomer with monomer, monomer with polymer, and polymer with polymer all involve the same chemical process. These condensation polymerizations are not to be confused with polymerizations proceeding by a chain mechanism, for example, vinyl polymerizations,[8] or

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[1] A preliminary account of part of this work was included in a paper presented by Dr. Wallace H. Carothers before the Faraday Society Symposium, September, 1935 [*Trans. Faraday Soc.*, **32**, 39 (1936)].

[2] (a) Svedberg, *Chem. Rev.*, **14**, 1 (1934). (b) Signer and Gross, *Helv. Chim. Acta*, **17**, 726 (1934), and Signer, *Kolloid Z.*, **70**, 24 (1935), have calculated size distributions for polystyrenes from sedimentation velocities in the ultracentrifuge. (c) Lansing and Kraemer [THIS JOURNAL, **57**, 1369 (1935)] have derived methods for calculating a "non-uniformity coefficient" from determination of the sedimentation equilibrium distribution of a polymeric material in the ultracentrifuge.

[3] Chalmers, *ibid.*, **56**, 912 (1934).

[4] Dostal and Mark, *Z. physik. Chem.*, **B29**, 299 (1935).

[5] Schulz, *ibid.*, **B30**, 379 (1935).

[6] Carothers, *Chem. Rev.*, **8**, 359–68 (1931).

[7] The reasons for classing bifunctional condensations such as these as true polymerizations have been set forth by Carothers.[1]

[8] Semenoff, "Chemical Kinetics and Chain Reactions," Oxford Univ. Press, Oxford, England, 1935, p. 444.

the polymerization of formaldehyde catalyzed by formic acid.[9]

The treatment which follows rests upon the fundamental assumption that the reactivity of a functional group, A or B, is independent of the size of the molecule to which it is attached. If the functional groups are separated by more than three atoms in the chain, this assumption is probably not seriously in error; if only one or two atoms separate the functional groups in the monomer, then the reactivities of monomer and dimer may differ greatly although the difference between dimer and trimer will be much less, between trimer and tetramer still less, etc.[10] If the reverse reaction, polymer degradation, occurs appreciably, it is necessary to append the assumption of equal reactivity of all links, AB, with respect to the reverse reaction, *e. g.*, hydrolysis in the case of polyesters. It is also assumed that the formation of cyclic compounds (as well as other side reactions) does not occur to an appreciable extent.[11] The errors arising from the assumptions will in general be most significant in the range of low molecular weights; for polymers of high average molecular weight, where the distribution is broad and the low molecular weight portion is small, deviation from the calculated results should not be large.

Theoretical Treatment and Discussion

Type (i) polymers and type (ii) polymers formed from equivalents of A—A and B—B molecules can be subjected to the same treatment and so will be considered simultaneously. The special and more complicated problem of the size distribution relations in type (ii) polymers formed from non-equivalents of A—A and B—B molecules will be relegated to a separate later section.

Definitions.—A reactant molecule or its radical will be defined as a "segment" and the term "x-mer" will denote a polymer composed of x segments, *e. g.*, a hexamer is a polymer composed of six segments.[12]

The following notation will be used:

n_0 = total number of segments = total number of A (or B) groups.

N = number of unreacted A (or B) groups which remain after the reaction has been in progress for a time, t.

$N_0 - N$ = number of reacted A (or B) groups.

(If desired, the N's may be expressed in moles without altering any of the equations which follow.)

p, the extent of reaction, = fraction of the total number of A (or B) groups which have reacted at time t

$$p = (N_0 - N)/N_0 \qquad (1)$$

Fundamental Distribution Functions.—In order to derive the distribution functions, let us determine the probability, Π_x, that a particular segment selected at random is part of an x-mer. Picture a large group of partially polymerized segments laid end to end, thus

$$\text{etc.}\ \underset{b_{-3}}{\underline{\qquad}}\ \ \underset{b_{-2}}{\underline{\qquad}}\ \ \underset{b_{-1}}{\overset{\text{S}}{\underline{\qquad}}}\ \ \underset{b_{1}}{\underline{\qquad}}\ \ \underset{b_{2}}{\underline{\qquad}}\ \ \underset{b_{3}}{\underline{\qquad}}\ \text{etc.}$$

the b's designating the linkages, or potential linkages, between the segments. Since all unreacted functional groups are assumed to be equally reactive, the probability that reaction has occurred to link the segments at any particular b is p and the probability that no linkage exists is $1-p$. There are x possible configurations, such as for example that consisting of linkages at $b_1, b_2 \ldots b_{x-1}$ and unreacted functional groups at b_{-1} and b_x, which fulfill the condition that the segment S be part of an x-mer. Since each of these consists of $x-1$ linkages and two unreacted potential linkages, the probability of the existence of each particular configuration is $p^{x-1}(1-p)^2$. The probability that any of the x configurations exists is[13]

$$\Pi_x = xp^{x-1}(1-p)^2 \qquad (2)$$

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[9] Carruthers and Norrish, *Trans. Faraday Soc.*, **32**, 195 (1936).

[10] Factors which cause change in reaction rate during the course of the reaction do not invalidate this assumption if the rates of reaction of a monomer, a dimer, etc., are all affected equally. Thus, the increase in viscosity of the medium as the reaction progresses might slow down the reaction, but if the rate of reaction of each molecular species is slowed down proportionately the equality of the reactivities of all functional groups at any one time remains undisturbed.

[11] That the extent of ring formation in bifunctional esterifications involving unit lengths beyond 7 is exceedingly small has been shown experimentally in many papers published from this Laboratory—*e. g.*, Carothers and Hill, THIS JOURNAL, **54**, 1561 (1932). More recently something in the nature of quantitative data on this point has become available in a paper by Stoll and Rouve [*Helv. Chim. Acta*, **18**, 1087 (1935)]. By a long (and somewhat doubtful) extrapolation one can, for example, calculate that pure hydroxydecanoic acid would furnish only 0.0005% of monomeric lactone at complete esterification, while higher hydroxy acids might give as much as 0.2% of lactone.

[12] In condensations of type (i) a segment is identical with a "structural unit" as previously defined by Carothers [THIS JOURNAL, **51**, 2548 (1929); *ibid.*, **55**, 5023 (1933)], but in type (ii) condensations a segment is one A—A or one B—B group whereas the structural unit is A—AB—B. For type (ii) polymers the above definition of an x-mer does not agree with the previous definition according to which an x-mer contains x *structural units*. The above definitions have been adopted for the sake of simplifying the following analysis.

[13] Kuhn, *Ber.*, **63**, 1503 (1930), has derived the same equation for the molecular size distribution in a degraded cellulose formed by the hydrolysis of infinitely large cellulose molecules, assuming that all linkages are equally hydrolyzable. That the two distributions should be identical is obvious when one considers the equivalence of the formation of polymer molecules through random formation of linkages and through random breaking of linkages already formed. In a further study of the problem of cellulose degradation, Klages, *Z. physik. Chem.*, **A159**, 357 (1932), and Kuhn, *ibid.*, **A159**, 368 (1932), have taken into account the finite size of the cellulose molecule prior to its degradation, and they have deemed it necessary to consider different rates for mid-chain hydrolysis and for hydrolysis of the terminal unit. These added complications lead to results which differ from those for bifunctional condensations.

Schulz's[5] equation for the weight fraction distribution in vinyl

As a consequence of the definition of Π_x

$$\Pi_x = \frac{\text{Total number of segments which exist as components of } x\text{-mers}}{\text{Total number of segments } (= N_0)}$$

If in the condensation process no molecule such as water is eliminated, the molecular weight will be exactly proportional to the number of segments in the molecule, and Π_x will be exactly equal to the weight fraction of x-mers. If a molecule is eliminated in the condensation, the deviation from this proportionality (due to the excess weight of the unreacted terminal functional groups) will be negligible except for the very low molecular weight polymers. Hence, Π_x will be regarded hereinafter as the weight fraction.[14]

The number of x-mer molecules is given by

$$N_x = \frac{N_0\Pi_x}{x} = N_0p^{x-1}(1-p)^2 \qquad (3)$$

Since there is an average of one A (or B) group per molecule, the total number of molecules $N = N_0(1-p)$ (see (1)). Therefore, letting P_x be the mole fraction of x-mers

$$P_x = N_x/N = p^{x-1}(1-p) \qquad (4)$$

In order to locate the x value which gives a maximum in Π_x, let

$$\partial\Pi_x/\partial x = (1-p)^2\,(p^{x-1} + xp^{x-1}\ln p) = 0$$

Solutions are, $x = \infty$ (minimum), and

$$x_{\text{max.}} = -1/\ln p \qquad (5)$$

which for values of p near unity becomes

$$x_{\text{max.}} \cong 1/(1-p) = N_0/N = \text{average value of } x \qquad (5b)$$

At the maximum

$$\Pi_{\text{max.}} = -\frac{(1-p)^2}{\ln p}\,e^{-(1+\ln p)} \qquad (6)$$

which, on introducing approximations valid when p is near unity, becomes

$$\Pi_{\text{max.}} = (1-p)/e \qquad (6b)$$

Differentiating P_x with respect to x and equating to zero

$$\frac{\partial P_x}{\partial x} = p^{x-1}(1-p)\ln p = 0$$

Since $x = \infty$ is the only solution, P_x possesses no maximum with respect to x.

The values of p which will give respectively the maximum amount and the maximum number of a particular x-mer may be obtained as follows

$$\partial\Pi_x/\partial p = xp^{x-2}(1-p)(x-1-px-p) = 0$$

for which solutions are $p = 0$, 1 or

$$p_{\text{max.}} = (x-1)/(x+1) \qquad (7)$$

Similarly

$$\frac{\partial P_x}{\partial p} = p^{x-2}(x-px-1) = 0$$

$$p_{\text{max.}} = (x-1)/x \qquad (8)$$

Discussion and Graphs.—The weight fraction distribution function (2) and the mole fraction distribution function (4) are represented graphically in Figs. 1 and 2 and in Figs. 3 and 4, respectively, for the several values of p indicated above each curve. From the curves in Figs. 1 and 2 one can determine the relative quantities (by weight) of each molecular species; the curves in Figs. 3 and 4 give the relative numbers of molecules of each species. For the smaller values of p the weight fraction curve possesses a sharp maximum, but as p approaches unity, this maximum becomes lower, shifted to larger values of x, and broader in the sense that there are more species present in approximately the maximum amount.[15]

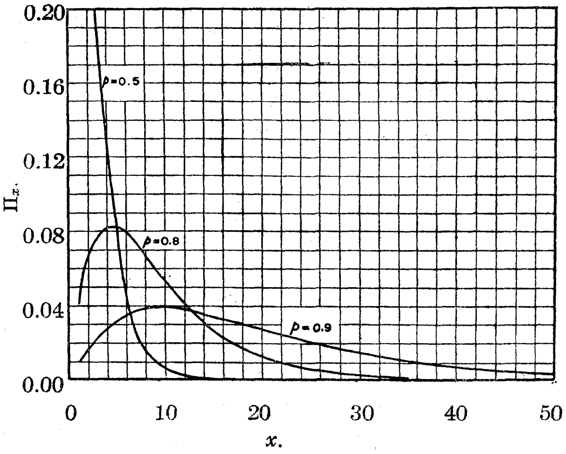

Fig. 1.—Weight fraction distributions for moderate extents of reaction (p). One square = 0.02 weight fraction.

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polymers is essentially the same as (2) also, although it is based on an entirely different set of conditions. His equation for the weight fraction of x-mer expressed in the symbols used in this paper is $xp^x\,(\ln p)^2$ where $1-p$ $(1-\alpha$ in Schulz's terminology) is the ratio of the velocity of chain termination to the velocity of chain propagation. Inasmuch as Schulz was interested only in large x values, he replaced $1-x$ with x in the exponential. The constant term, $(\ln p)^2$, was evaluated by integration, a method which is approximate when applied to a mixture of molecules which vary in size in a stepwise manner. Had direct summation been used, this term would have been $(1-p)^2$ as in (2). However, for values of p near unity $(1-p)^2 = (\ln p)^2$.

(14) In type (ii) polymers it will be recalled that we have one type of x-mer when x is even and two when x is odd. When x is even the considerations of the preceding paragraph apply at once. When x is odd the numbers of the two types of x-mers are equal as a consequence of the assumption of equal reactivity of all A and of all B groups. It follows from this that if we take Π_x when x is odd to include both kinds of x-mers combined, then Π_x can be taken as the approximate weight fraction of x-mers in type (ii) as well as in (i) without further assumptions.

(15) It can be shown that the curves in Figs. 2 and 4 may be used for larger values of p by altering the coördinate scale according to the following rule: if p be increased so that $1-p$ is decreased n-fold, then the ordinate must be divided by n and the abscissa multiplied by n. Thus, the $p = 0.98$ curve may be used for $p = 0.998$ if the Π_x, or P_x values be divided by ten and the x values multiplied by ten. This procedure is approximate, but the error is insignificant if p is $\geqq 0.95$ and $x \geqq 20$.

The x-mer which is present in greater amount than any other, specified by the maximum in the Π_x curve, is given by (5) or (5b), and the quantity of this species is given by (6) or (6b). $x_{\text{max.}}$ coincides approximately with the average value of x (number-average, *cf. seq.*). It can be shown that for values of $p < 0.5$, monomer is in excess (by weight) of any other species; for $p > 0.5$, $x_{\text{max.}} \geqq 2$. As is shown by the above analysis, there is no maximum in the P_x curve for any value of p (see Figs. 3 and 4), and so *there are always more molecules of monomer than of any other single species.*

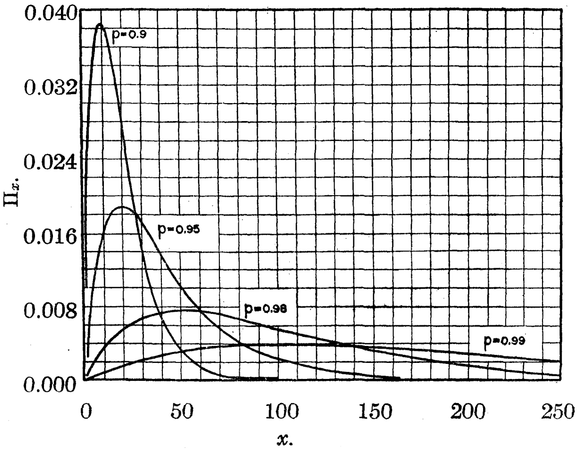

Fig. 2.—Weight fraction distributions for large extents of reaction. One square = 0.02 weight fraction.

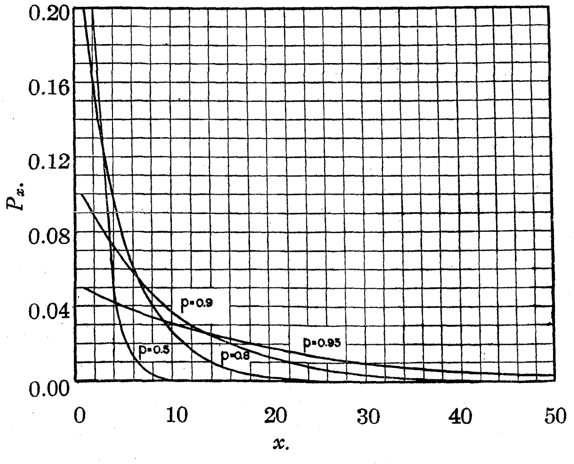

Fig. 3.—Mole fraction distributions for moderate extents of reaction (p). One square = 0.02 mole fraction.

In Fig. 5 the weight fraction is plotted against p for several values of x. As the reaction progresses, the amount of a particular x-mer builds up to a maximum located according to (7) at $p = (x - 1)/(x + 1)$ and then falls away to approach zero as p approaches unity. As x is increased, the maximum is lowered and shifted to higher p values. The mole fraction of a particular x-mer increases in a similar (but not identical) way as the reaction progresses, reaches a maximum (equation (8)) and then decreases to zero as p approaches unity.

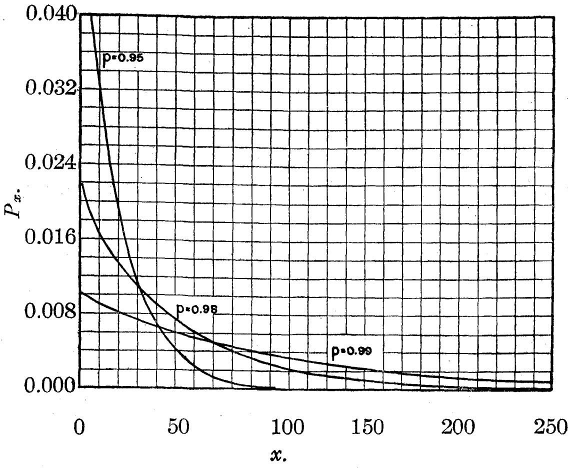

Fig. 4.—Mole fraction distributions for large extents of reaction. One square = 0.02 mole fraction.

The sum of the weight fractions of all constituents, of necessity always equal to unity, is approximately equal to the area under one of the curves in Figs. 1 and 2 from $x = 1$ to $x = \infty$, since[16]

$$\sum_{x=1}^{x=\infty} \Pi_x \cong \int \Pi_x \, dx$$

Similarly, the weight fraction of all constituents between $x = x_1$ and $x = x_2$ is approximately equal to the area under the curve from $x = x_1$ to

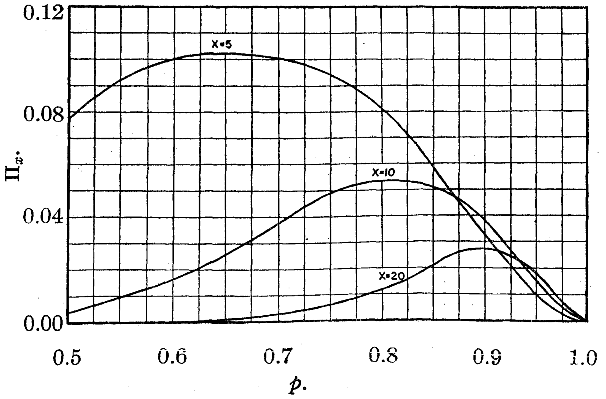

Fig. 5.—Weight fraction of x-mer *vs.* extent of reaction.

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(16) The failure of this area to equal unity exactly arises because of the treatment of a discontinuous phenomenon as a continuous one; that is, only integral values of x have physical meaning, whereas the integration is carried out continuously over all values of x. When p is sufficiently large, however, the integral (or the area under the curve) differs inappreciably from unity.

$x = x_2$, and so the total weight fraction of these constituents can be evaluated graphically. This may be done in Figs. 1 and 2 by counting the squares under the curve between these limits and multiplying by 0.02. Similar considerations apply to the mole fraction graphs. This procedure is approximate, but for broad distributions ($p \geqq 0.90$) it may be used without significant error. For such distributions nearly three-fourths of the material (by weight) consists of molecules for which $x > x_{\text{max.}} \cong$ average x.

Molecular Weight Averages.—Lansing and Kraemer[2c] have discussed three different kinds of average molecular weights which are amenable to physical measurement. These are defined by the equations

$$M_n = \Sigma M_x N_x / \Sigma N_x \qquad (9)$$
$$M_w = \Sigma M_x^2 N_x / \Sigma M_x N_x \qquad (10)$$
$$M_z = \Sigma M_x^3 N_x / \Sigma M_x^2 N_x \qquad (11)$$

where M_x is the molecular weight of an x-mer molecule and N_x is the number of x-mers. The "number-average" molecular weight, M_n, may be obtained by ordinary physical or chemical methods (end group determination, osmotic pressure measurement, etc.); the "weight-average" molecular weight, M_w, and the "Z-average" molecular weight, M_z, can be evaluated from sedimentation equilibrium measurements in the ultracentrifuge. M_w may also be determined by means of Staudinger's[17] viscosity method (*cf. seq.*) in cases where this method is capable of yielding valid results.

These molecular weight averages may be evaluated in terms of p by substituting equation (3) for N_x, and xM_0 for M_x, the molecular weight of an x-mer molecule, where M_0 is the molecular weight of one segment.[18] These substitutions lead to the equations

$$M_n = M_0 \Sigma x p^{x-1}(1 - p)^2 / \Sigma p^{x-1}(1 - p)^2$$
$$M_w = M_0 \Sigma x^2 p^{x-1}(1 - p)^2 / \Sigma x p^{x-1}(1 - p)^2$$
$$M_z = M_0 \Sigma x^3 p^{x-1}(1 - p)^2 / \Sigma x^2 p^{x-1}(1 - p)^2$$

It can be shown that the values of the summations are as follows

$$\Sigma p^{x-1}(1 - p)^2 = 1 - p$$
$$\Sigma x p^{x-1}(1 - p)^2 = 1$$
$$\Sigma x^2 p^{x-1}(1 - p)^2 = (1 + p)/(1 - p)$$
$$\Sigma x^3 p^{x-1}(1 - p)^2 = (1 + 4p + p^2)/(1 - p)^2$$

Substituting these values in the equations for M_n, M_w and M_z

$$M_n = M_0/(1 - p) \qquad (12)$$
$$M_w = M_0(1 + p)/(1 - p) \qquad (13)$$
$$M_z = M_0(1 + 4p + p^2)/(1 - p^2) \qquad (14)$$

Also

$$M_n{:}M_w{:}M_z = 1{:}(1 + p){:}(1 + 4p + p^2)/(1 + p) \qquad (15)$$

The divergence among the three average molecular weights is a measure of the non-homogeneity of the polymer, and from it Lansing and Kraemer[2c] derive their "non-uniformity coefficient." The three averages are all equal when $p = 0$. As the polymerization proceeds and p increases, M_w becomes progressively greater than M_n, and M_z becomes greater than M_w. When p is close to unity, *i. e.*, when the average molecular weight is high, the ratio (15) becomes approximately

$$M_n{:}\,M_w{:}\,M_z = 1{:}2{:}3 \qquad (15b)$$

It will be well to emphasize the bearing of these results on Staudinger's method for determining molecular weights of linear polymers from the viscosities of their dilute solutions. He has advocated the use of the following relation for the determination of the average molecular weight of linear polymeric substances

$$KM_n = \left(\frac{\eta_r - 1}{c}\right)_{(c \rightarrow 0)}$$

where η_r is the relative viscosity, c is the concentration, and K is the Staudinger constant. Without taking into account different averages, Staudinger has used the common number-average molecular weight in the above equation. Kraemer and Lansing[19] have shown that the weight-average molecular weight, M_w, should be used in this equation instead of M_n. Therefore, only in cases where the ratio M_w/M_n is constant can it also be presumed that $[(1 - \eta_r)/c]_{(c \to 0)}$ will be proportional to M_n. As shown above, this ratio does become very nearly constant (equal to two) for high molecular weight polymers of the type considered here. Hence, though the Staudinger equation may be applicable to high molecular weight polymers of this type, when the molecular weight is low (when $p < 0.9$ and $M_n/M_0 < 10$), the use of this equation is no longer permissible. In its stead, one should use the equation

$$\left(\frac{\eta_r - 1}{c}\right)_{(c \rightarrow 0)} = K'M_w = K'(1 + p)M_n$$

where $K' = {}^1\!/_2K$. It would be interesting to trace experimentally the deviation from the

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[17] Staudinger, "Die hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932.

[18] M_x may not equal xM_0 exactly inasmuch as the molecular weight of terminal groups (H and —OH in the case of polyesters) is neglected. However, for large molecules the discrepancy will be very small. If two kinds of segments are present (case (ii)), then M_0 must be taken as the mean molecular weight of the segments.

[19] Kraemer and Lansing, *J. Phys. Chem.*, **39**, 153 (1935); see also Kern, *Ber.*, **68**, 1439 (1935), and the work of Schulz[5] on vinyl polymers.

Staudinger equation in the range of low molecular weights.

Type (ii) Polymers Prepared from Nonequivalent Amounts of the Reactants.—As was described in the introduction, three kinds of molecules may be formed in type (ii) polymerizations: molecules composed of an even number of segments ("*even*" x-mers), molecules composed of an odd number of segments and terminated by A groups ("*odd*-A" x-mers), and molecules containing an odd number of segments and terminated by B groups ("*odd*-B" x-mers). When an excess of one reactant, arbitrarily chosen here as the reactant designated by B—B, is used, separate functions must be derived for each of the three kinds of molecules. The following modified terminology will be used.

N'_0 = number of A groups = twice number of A—A segments.

N''_0 = number of B groups = twice number of B—B segments.

N' and N'' are the numbers of the respective unreacted functional groups.

$N''_0 - N'_0 = N'' - N' = n$ = excess of B—B segments.

p = probability that an A group has reacted = $(N'_0 - N')/N'_0$

q = probability that a B group has reacted

$$= \frac{N''_0 - N''}{N''_0} = \frac{N'_0 - N'}{N''_0} = rp$$

where $r = N'_0/N''_0$.

In analogy to the method of derivation used formerly, a single segment S is selected at random from the sequence of segments

$$\begin{array}{c} \mathrm{S} \\ \text{—BA—AB—BA—AB—BA—AB—etc.} \\ b_3 \quad b_2 \quad b_1 \quad b_1 \quad b_2 \quad b_3 \end{array}$$

and the probability that it is a component of an x-mer is determined by adding the probabilities of each configuration which will meet this requirement. Because of the different varieties of polymers (see (iia) and (iib)) and the non-interchangeability of A—A and B—B when the latter are in excess, it will be necessary to use superscripts and subscripts to designate the various Π_x's, N_x's and P_x's which arise.

First, molecules for which x is an even integer will be considered. If the segment S selected at random happens to be an A—A, the probability that there is linkage at b_1 is p, at b_2 it is q, at b_3 it is p, etc., alternately. A similar rule applies to b_{-n}, and so we have p for the probability of linkage where n is odd (either + or −) and q where n is even. For each of the x configurations which will include S in the *even* x-mer, there will be $x/2$ links where n is odd, $(x/2)-1$ links where n is even, and one of the terminal groups will be A and the other B. The probability that any given A—A segment is a component of an *even* x-mer is, therefore

$$\begin{aligned} \Pi_x(even) &= xp^{x/2}q^{(x/2)-1}(1-p)(1-q) \\ &= xp^{x-1}\,r^{(x/2)-1}(1-p)(1-rp) \quad (16) \end{aligned}$$

If a B—B group had been selected as the segment S, the same considerations would apply with p and q interchanged. That is, if A's and B's were interchanged in the chain of segments pictured above then S would become a B—B segment, q would be the probability of linkage at b_n when n is odd, and p would be the probability when n is even. By interchanging p and q in (16) the probability, $\Pi''_x(even)$, that any given B—B segment is a part of an *even* x-mer is obtained.

$$\Pi''_0(even) = xp^{x-1}\,r^{x/2}(1-p)(1-rp) = r\Pi'_x(even) \quad (17)$$

The total number of segments in *even* x-mers = $xN_x(even)$ =

$$(N'_0/2)\Pi'_x(even) + (N''_0/2)\,\Pi''_x(even)$$

Substituting (16) and (17) and recalling that $rN''_0 = N'_0$

$$N_x(even) = \frac{N'_0\Pi'_x(even)}{x} = N'p^{x-1}\,r^{x/2}\,[(1-p)(1-rp)r^{-1}] \quad (18)$$

For the fraction of the total number of *both* kinds of segments which are contained in *even* x-mers

$$\Pi_x(even) = \frac{xN_x(even)}{1/2\,(N'_0 + N''_0)}$$

Substituting $N'_0 + N''_0 = N'_0(1+r)/r$ and (18) in the above

$$\Pi_x(even) = xp^{x-1}\,r^{x/2}\,\frac{2(1-p)(1-rp)}{1+r} \quad (19)$$

$\Pi_x(even)$ is the approximate weight fraction of an *even* x-mer (21).

For the mole fraction of *even* x-mer

$$P_x(even) = \frac{N_x}{\text{Total no. of molecules}} = \frac{N_x}{1/2(N' + N'')}$$

$$N' = (1-p)N'_0$$

$$N'' = (1/r - p)N'_0$$

From (18), therefore

$$P_x(even) = p^{x-1}\,r^{x/2}\left[\frac{2(1-p)(1-rp)}{(1+1/r-2p)r}\right] \quad (20)$$

When x is odd the number of links is even and the two terminal groups are either both A's or both B's (see (iib)). First, let us find the probability, $\Pi'_x(odd\text{-A})$, that an A—A segment such as S is a component of an *odd* x-mer having A groups at its ends. Each of the $(x+1)/2$ configurations fulfilling this requirement contains

$(x - 1)/2$ links at b_n's where n is odd and $(x - 1)/2$ links where n is even. Therefore

$$\Pi_x'(odd\text{-A}) = \left(\frac{x+1}{2}\right)(pq)^{(x-1)/2}(1-p)^2$$
$$= \left(\frac{x+1}{2}\right)p^{x-1}\,r^{(x-1)/2}(1-p)^2 \qquad (21)$$

There are $(x - 1)/2$ configurations containing the A—A segment, S, which give *odd* x-mers having B end groups. For each of these there are $(x + 1)/2$ links where n is odd and $(x - 3)/2$ where n is even. Consequently

$$\Pi_x'(odd\text{-B}) = \frac{x-1}{2}\,p^{x-1}\,r^{(x-3)/2}(1-rp)^2 \qquad (22)$$

To find the corresponding probabilities that a B—B segment is a component of an *odd* x-mer, A is interchanged with B and p with q, as was done above. When A and B are interchanged in configurations giving *odd*-A terminated x-mers, *odd*-B terminated x-mers result. By interchanging p and q in (21) one gets the probability, Π_x'' (*odd*-B), that any given B—B segment is contained in an *odd* x-mer terminated with B groups.

$$\Pi_x''(odd\text{-B}) = \frac{x+1}{2}\,p^{x-1}\,r^{(x-1)/2}(1-rp)^2 \qquad (23)$$

Similarly by interchanging p and q in $\Pi_x'(odd\text{-B})$ one gets

$$\Pi_x''(odd\text{-A}) = \frac{(x-1)}{2}\,p^{x-1}\,r^{(x+1)/2}(1-p)^2 \qquad (24)$$

The total number of segments contained in *odd* x-mers terminated with A groups is given by $xN_x(odd\text{-A}) = {}^1/_2\ N_0'\ \Pi_x'(odd\text{-A}) + {}^1/_2\ N_0''\ \Pi''$ (*odd*-A). Replacing N_0'' by N_0'/r and introducing (21) and (24)

$$N_x(odd\text{-A}) = N'\,p^{x-1}\,r^{x/2}\,[1/2(1-p)^2\,r^{-1/2}] \qquad (25)$$

Similarly

$$N_x(odd\text{-B}) = N'\,p^{x-1}\,r^{x/2}\,[1/2\,(1-rp)^2\,r^{-3/2}] \qquad (26)$$

The corresponding Π_x's are

$$\Pi_x(odd\text{-A}) = \frac{xN_x(odd\text{-A})}{1/2(N' + N'')}$$
$$= xp^{x-1}\,r^{x/2}\left[\frac{(1-p)^2\,r^{-1/2}}{1+r}\right] \qquad (27)$$

and

$$\Pi_x(odd\text{-B}) = xp^{x-1}\,r^{x/2}\left[\frac{(1-rp)^2}{1+r}\,r^{-1/2}\right] \qquad (28)$$

The mole fractions $P_x(odd\text{-A})$ and $P_x(odd\text{-B})$ can be derived from (25) and (26) in the same way that (20) was obtained from (18).

$$P_x(odd\text{-A}) = p^{x-1}\,r^{x/2}\left[\frac{(1-p)^2\,r^{-1/2}}{1+1/r-2p}\right] \qquad (29)$$

and

$$P_x(odd\text{-B}) = p^{x-1}\,r^{x/2}\left[\frac{(1-rp)^2\,r^{-3/2}}{1+1/r-2p}\right] \qquad (30)$$

Overlooking for the moment that x cannot assume the same integers in both *even* and *odd* functions, (19), (27) and (28) lead to the ratio

$$\Pi_x(even):\Pi_x(odd\text{-A}):\Pi_x(odd\text{-B}) =$$
$$2(1-p)(1-rp):(1-p)^2r^{1/2}:(1-rp)^2\,r^{-1/2} \qquad (31)$$

which is independent of x. The corresponding ratios for the N_x's and P_x's are identical with the above ratio.

Substituting $p = 1$ in the above equations to obtain distributions at completion of the reaction

$$\Pi_x(even) = \Pi_x(odd\text{-A}) = 0$$
$$P_x(even) = P_x(odd\text{-A}) = 0$$
$$\Pi_x(odd\text{-B}) = xr^{x/2}(1-r^2)r^{-1/2}/(1+r) \qquad (28b)$$
$$P_x(odd\text{-B}) = r^{x/2}(1-r)r^{-1/2} \qquad (30b)$$

The complete absence of *even* and *odd*-A molecules is a consequence of the reaction of all A groups.

To summarize the above equations, (18), (19) and (20) give, respectively, the numbers, the weight fractions and the mole fractions of *even* molecules. The corresponding quantities for *odd*-A molecules are given by (25), (27) and (29), and for *odd*-B molecules by (26), (28) and (30). The distributions at completion of the reaction ($p = 1$) are given by (28b) and (30b).

The weight fraction distribution functions are plotted in Fig. 6 for $r = 0.80$ (25% excess of B—B molecules) at the three stages of the reaction, $p = 0.85$, 0.95 and 1.00. All three curves for a given pair of r and p values are similar in the sense that, as shown by (30), for all x values the ratio of the three Π_x's is the same. Consequently, all three maxima come at the same molecular size (x value). In Fig. 7 the weight-fraction of x-mer (*odd*-B only, since all other types are absent) is plotted against x at complete reaction (equation (28b)) for several values of r. The method of area summation given above can be applied in these figures also.

For any value of r there are present initially ($p = 0$) only *odd*-A (A—A) and *odd*-B (B—B) molecules, and even molecules are absent entirely. If the numbers of the two kinds of segments are equal ($r = 1$), the amount of *even* polymer will increase steadily (starting from zero) as the reaction progresses, until the amounts of *even* and *odd* (*odd*-A plus *odd*-B) molecules become practically equal. With an excess of B—B segments present, the amount of *even* polymer increases until a maximum is reached and then decreases steadily, returning to zero when $p = 1$. At this maximum the amount of *even* polymer may or may not be greater than the amount of *odd*-B polymer, but for all values of p the amount of *even* polymer is less than the amount of BOTH kinds of *odd* polymer. The amount of *odd*-A polymer is always less than the amount of *odd*-B polymer and the ratio of the former to the latter becomes less as p increases. These characteristics are illustrated in Fig. 6.

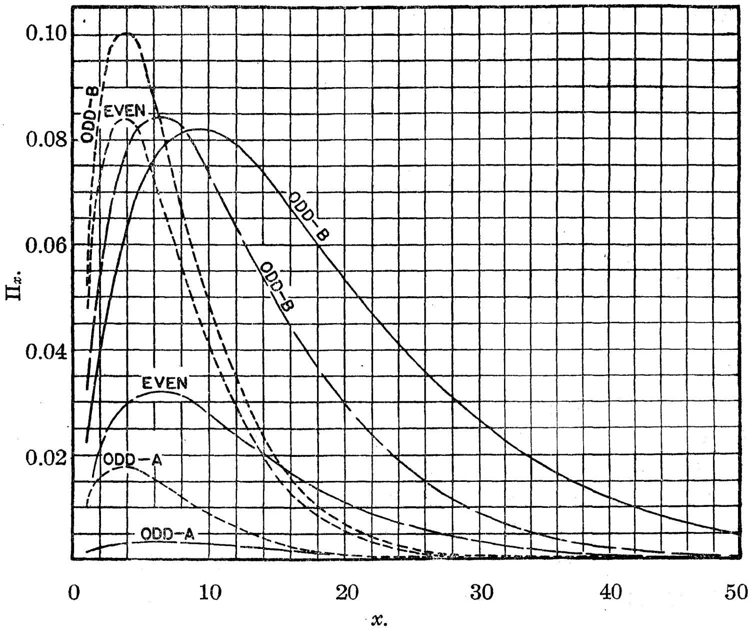

Fig. 6.—Weight fraction distribution curves for a 25% excess of B groups (r = 0.80). When p = 0.85 - - - -, p = 0.95 ——— and p = 1.00 ———. Curves labeled "even" are for *even* molecules, *i. e.*, those having an even number of segments; those labeled "odd-A" are for *odd* molecules having A groups as termini, and those labeled "odd-B" are for *odd*, B terminated molecules. The even curves apply for even integers only, the odd curves for odd integers only. One square = 0.005 weight fraction.

When equivalents of the reactants are used, the number-average molecular weight is

$$M_n = \frac{M_0(N_0' + N_0'')}{N' + N''} = M_0(1 + r)/(1 + r - 2rp) \quad (32)$$

where M_0[20] is the average molecular weight of one segment. When $r = 1$ this equation reduces to (12). At completion of the reaction when $p = 1$

$$M_n = M_0\,(1 + r)/(1 - r) \quad (32b)$$

This equation shows the effect of an excess of one reactant in limiting the maximum molecular weight which can be reached.

The type of distribution of molecules obtained when an excess of one reactant is used closely simulates the distribution in polymers formed from exact equivalents. (Compare curves in Figs. 6 and 7 with those in Figs. 1 and 2.) The dependence of weight fraction, or mole fraction, on x is of the same type; the principal difference lies in the replacement of p by $r^{1/2}p$. It can be shown that if $r^{1/2}p$ for one polymer equals $r^{1/2}p$ for another polymer, then their average molecular weights will be nearly the same (except when $r^{1/2}p$ is much less than unity), the maxima in their Π_x *vs.* x curves will occur at the same x value, and the distribution curves will vary with x in a similar way. The two distributions will differ only in the ratio of the quantities of the three kinds of molecules, *even*, *odd*-A and *odd*-B (2:1:1 for r = 1). Thus, for example, for a particular even value of x there will be fewer *even* x-mers contained in a polymer for which $r = r_1$ than in another polymer of the same average molecular weight (*i. e.*, the same $r^{1/2}p$ value) but for which $r = r_2 > r_1$; but the amount of *odd* (x + 1)-mers in the former polymer will be greater by a corresponding amount (unless M_n is very low). Unless the method of examination of the two polymers is sufficiently precise to differentiate consecutive members in the sequence of sizes, the two distributions will appear to be identical if $r^{1/2}p$ of one equals $r^{1/2}p$ for the other.

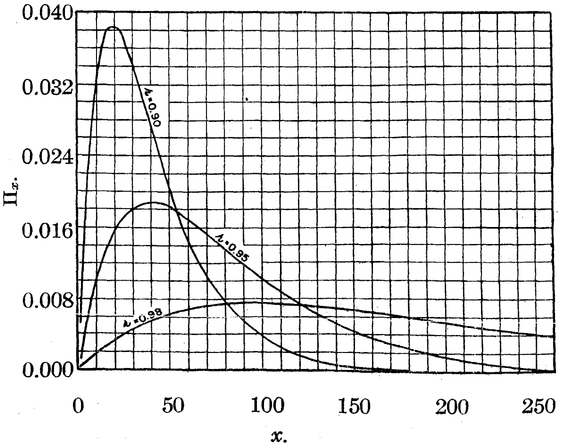

Fig. 7.—Weight fractions at completion of the reaction (p=1) for several values of r. Only odd integral values of x are significant. One square = 0.01 weight fraction.

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[20] In this case, $M_0 = \dfrac{M_0'N_0' + M_0''N_0''}{N_0' + N_0''}$ where M_0' and M_0'' are the respective molecular weights of the two segments as contained within a polymer molecule.

The distribution functions possess maxima characteristics similar to those previously discussed for "$r = 1$" polymers. In fact, the same equations may be used for locating the $x_{\text{max.}}$ value for Π_x by replacing p with $r^{1/2}p$. Exact equations for M_w and M_z, corresponding to equations (13) and (14), are cumbersome; for all practical purposes it is permissible merely to replace p with $r^{1/2}p$ in (13) and (14), respectively. It follows that here also the ratio of $M_n:M_w:M_z$ approaches 1:2:3 for high molecular weights. Thus, sedimentation equilibrium measurements in the ultracentrifuge would not distinguish the two types of polymers.

The author wishes to acknowledge his gratitude to Dr. Wallace H. Carothers for his valuable advice and keen interest in this work. The author is also indebted to Dr. E. O. Kraemer for reading and criticizing the manuscript.

Summary

1. Equations expressing the weight fraction, number, and mole fraction of each molecular species in a linear condensation polymer have been derived on the basis of simple and not improbable assumptions. The characteristics of these functions have been demonstrated and discussed.

2. The number-average, weight-average and Z-average molecular weights of Lansing and Kraemer are shown to be in the ratio 1:2:3 for the high molecular weight polymers. The bearing of this result on Staudinger's method for determining molecular weights has been discussed.

3. The special case of polymers prepared by the condensation of non-equivalents of two bifunctional reactants (A—A + B—B) has been analyzed and shown to conform to a distribution similar to the above. Other special cases can be subjected to a similar analysis.

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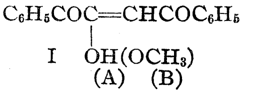
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

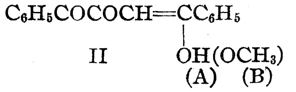
Further Studies on 1,4-Diphenyl-1,2,4-butanetrione Enol, Including Alkylation and Benzoylation

BY ROBERT E. LUTZ AND ALFRED H. STUART

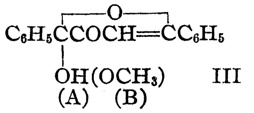
Two methyl ethers have been obtained from the enol. One of these, dibenzoylmethoxyethylene I(B), the structure of which is certain, was made directly by the action of diazomethane.[1b] The other, a structural isomer II(B) or III(B), was obtained by the action of methanol and acid on the enol or various of its derivatives and was believed to have the open chain structure II(B) because it gave methyl benzoate on ozonization;[1b] however, the alternative cyclic structure III(B),[2] which was not considered at that time, also would account for this result.


I

$C_6H_5COC(OH(OCH_3))=CHCOC_6H_5$ (A) (B)


II

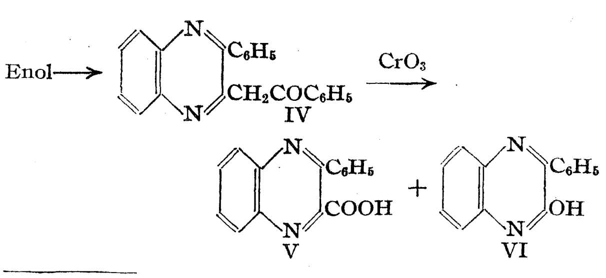
$C_6H_5COCOCH=CC_6H_5(OH(OCH_3))$ (A) (B)


III

$C_6H_5C(OH(OCH_3))COCH=CC_6H_5$ (A) (B)

The ease of formation of the isomeric ether by catalytic etherification does not distinguish between the two formulations II(B) and III(B) since there is analogy for the reaction in both open chain and cyclic types (*cf.* hydroxynaphthoquinone[3] and the sugars). The quinoxaline reaction, however, which is specific for α-diketones, has been used.[2a]

o-Phenylenediamine reacts readily with the enol to give a quinoxaline (IV) which is bright orange in color in contrast with other quinoxalines of this series. Oxidation of this product by means of chromic acid gives the carboxy and



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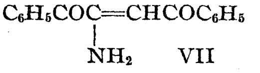
(1) *Cf.* (a) Lutz, THIS JOURNAL, **56**, 1590 (1934); (b) Lutz, Wilder and Parrish, *ibid.*, **56**, 1980 (1934); Lutz and Wilder, *ibid.*, **56**, (c) 1987, (d) 2065, (e) 2145 (1934).

(2) *Cf.* (a) Blatt, *ibid.*, **57**, 1103 (1935); (b) Kohler, Westheimer and Tishler, *ibid.*, **58**, 264 (1936).

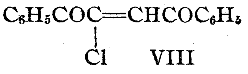
(3) Fieser, *ibid.*, **48**, 2922, 3201 (1926).

hydroxy quinoxalines V and VI.[4] The structure of IV seems to be established adequately by these reactions; however, the color is not accounted for.

Dibenzoylmethoxyethylene I(B), the structurally isomeric ether, and dibenzoylamino and chloroethylenes (VII and VIII) do not react under ordinary conditions with *o*-phenylenediamine. However, under more drastic conditions, namely, long continued refluxing with the reagents, dibenzoylmethoxyethylene gives IV with elimination of the methoxyl group, a reaction involving either the conjugated system or hydrolysis first to the reactive enol (the ether is known to be hydrolyzed or ammonolyzed easily).[1b] Dibenzoylaminoethylene VII under these conditions reacts very slowly giving IV, but the isomeric ether II or III(B) and also the *trans* chloro compound VIII, are stable.



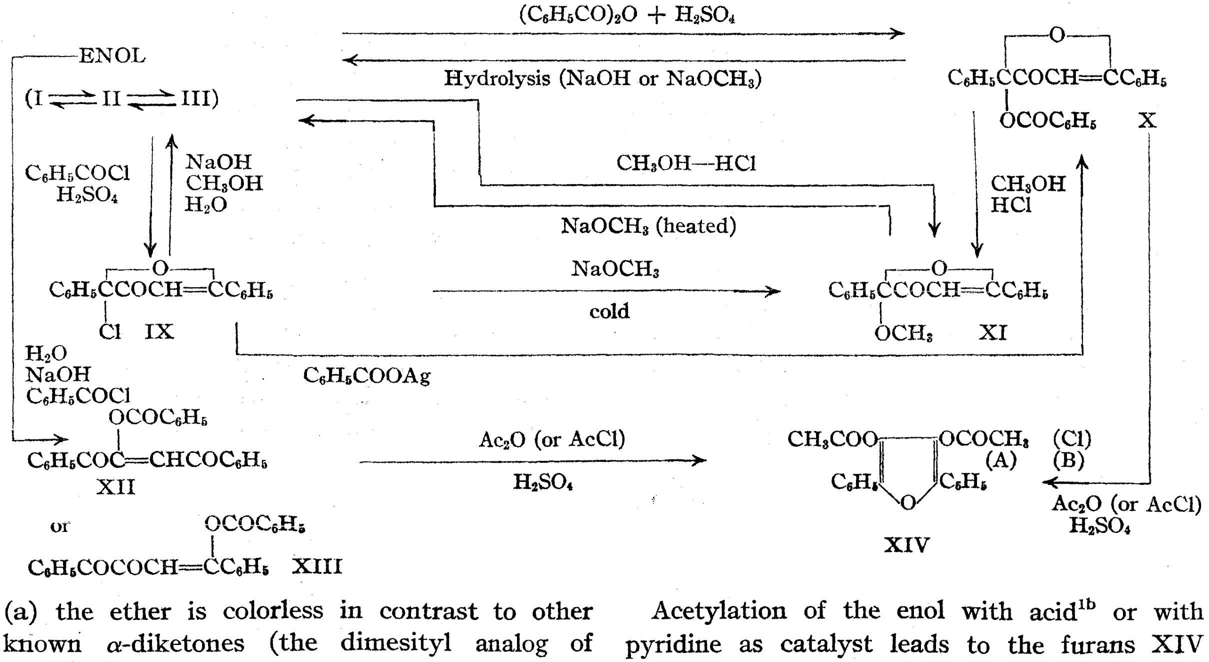
$C_6H_5C(NH_2){=}CHCOC_6H_5$ VII



$C_6H_5C(Cl){=}CHCOC_6H_5$ VIII

In regard to the bearing of these facts on the structure of the isomeric ether, the α-diketone formula II(B) seems to be excluded by the failure to react with *o*-phenylenediamine even under drastic conditions, and the cyclic formula III(B) is therefore the correct one. Other properties[1] of the ether support this conclusion: (a) the ether is colorless in contrast to other known α-diketones (the dimesityl analog of II(B) is bright yellow);[5] (b) it is not easily reduced by sodium hydrosulfite or zinc and acetic acid under ordinary conditions as would be expected of an α-diketone; (c) it does not react with acetyl chloride or acetic anhydride and sulfuric acid under ordinary conditions (as does dibenzoylmethoxyethylene I(B) and as presumably would an ether of formula II(B); and (d) it is only slowly hydrolyzed with alkali whereas the true enol ether, dibenzoylmethoxyethylene, and the two analogous 2- and 4-methoxynaphthoquinones[3] are hydrolyzed very rapidly under these conditions.

The chloro compound obtained by the action of thionyl chloride on either the enol or its methyl ether I(B) was previously assumed to be C_6H_5CO-$COCH{=}C(Cl)C_6H_5$.[1e] This compound must have the cyclic structure IX, however, in view of the following facts: (a) it is colorless; (b) it reacts readily with *o*-phenylenediamine to give the quinoxaline IV; (c) the chlorine is reactive as shown by the ease with which it is eliminated in the quinoxaline reaction and also in methanolysis to the cyclic ether III(B); and (d) the chlorine is replaceable readily by methoxyl by means of cold sodium methylate, giving the cyclic ether III(B) under conditions wherein the open chain enol ether I(B) is hydrolyzed directly to the enol.



Acetylation of the enol with acid[1b] or with pyridine as catalyst leads to the furans XIV (A and B). Studies on the enol salts, however, led to intractable products.

The action of benzoyl chloride and sulfuric

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(4) We are indebted to Dr. A. H. Blatt for furnishing samples of V and VI for purposes of identification.

(5) Lutz and Wood, unpublished results.

acid on the enol gave the cyclic chloro compound IX instead of the expected furan of the type XIV(B). Benzoic anhydride and sulfuric acid likewise failed to give the benzoyl analog of the furan XIV(A), but instead gave a cyclic benzoate X the structure of which follows from its synthesis from the cyclic chloro compound IX by means of silver benzoate, and from its failure to react with *o*-phenylenediamine, in contrast with the open chain enol benzoate XII which reacts readily. The cyclic benzoate (X) is very reactive as would be expected; methanolic hydrogen chloride converts it into the cyclic methyl ether XI, sodium methylate hydrolyzes it quickly to the enol, and acetic anhydride or acetyl chloride with sulfuric acid converts it into the diacetoxy or acetoxychlorofurans XIV (A) or (B).

Benzoylation of the sodium salt of the enol in aqueous alkaline medium gives yields as high as 50% of the enol benzoate. The nature of this product is evident from the ease of hydrolysis to the enol and benzoic acid by means of cold alkali. Of the two possible formulas, XII and XIII, the former is the more likely, particularly in view of the absence of color. It reacts readily with *o*-phenylenediamine giving the quinoxaline IV, with methanolic hydrogen chloride to give the cyclic ether XI, and with acetic anhydride or acetyl chloride and sulfuric acid to give the diacetoxy and acetoxychlorofurans XIV(A) or (B). The ease of replacement of benzoyl by acetyl shows that neither this reaction nor the analogous conversion to a β-benzoyloxyfuran could be used to distinguish between the two structures XII and XIII. Preliminary reduction experiments with this end in view have not been successful.

There was produced consistently in the benzoylation of the sodium enolate in isopropyl ether as solvent smaller yields (30% or less) of the enol benzoate XII together with 20–25% yields of a product derived from the carbon benzoyl compound. The studies of the latter series are not yet completed and will be the subject of a later paper.

We have evidence that the true open chain enol methyl ether II(B), which we have not yet been able to isolate and characterize, is formed in considerable amount during methylation of the enol with diazomethane. Both forms of the enol react similarly, even in petroleum ether, solvent conditions under which they appear to be reasonably stable. The yields of dibenzoylmethoxyethylene I(B) average 30–50%. The oily product at the beginning contains no unchanged enol as shown by the absence of the very characteristic red ferric chloride test. However, in the course of handling the crude mixtures in order to isolate the dibenzoylmethoxyethylene, free enol is regenerated, gives a strong ferric chloride test, and has been isolated in one instance. The quinoxaline test on these oils gave amounts of IV corresponding to total yields of about 15–30% (neither the ethers I(B) nor III(B) react under these conditions). These facts indicate the presence of an unstable enol derivative which is readily hydrolyzed to the enol and which appears to be the open chain ether II(B). This hypothesis is not unreasonable in view of the fact that the analog has since been isolated in the dimesityl series.[5] Further evidence for the presence of this compound in approximately the amounts indicated above was obtained by ozonizing the crude product after separation of the dibenzoylmethoxyethylene and isolating methyl benzoate in a yield of 20%. The cyclic ether III(B), if present, would have given this result, but it could hardly have been formed as a result of methylation of III with diazomethane; furthermore, it crystallizes easily, has never been isolated in this type of methylation, and could not possibly have been present in amounts sufficient to account for the above result. It seems to be established, therefore, that the ether II(B) as well as I(B) is formed in the methylation of the enol with diazomethane, and that the enol reacts partly in the sense of formula II(A) as well as I and III(A).[6]

The foregoing facts necessitate reconsideration of the structural relations of the two solid forms of the enol. Both isomers react readily and similarly with one equivalent of bromine, and with ferric chloride, in ethanol at −10–15°, and with diazomethane in petroleum ether, solvent conditions under which the two forms alone appear to be fairly stable. It is not certain, however, that they are both true enols in view of the great mobility of the equilibrium and probable catalytic effect of the reagents, and

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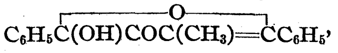
[6] In this connection it is noteworthy that since phenylglyoxylic acid was not found in significant amounts in the above ozonization of II(B), the discussion of results in the first paper (end of p. 1781, ref. 1b) is valid even though the methyl ether then under consideration (formula VIII of that paper) was really the cyclic compound III(B).

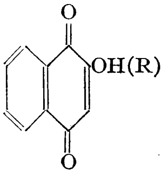
since a cyclic compound such as III(A) might react with bromine in much the same sense as the enol. The hypothesis that the two forms are *cis–trans* enols[1b] is unlikely, particularly in view of the fact that on methylation with diazomethane they give the same mixtures of the two structural and not stereoisomeric methyl ethers. The properties of the yellow form are in accord with an assumption of chelation between I(A) (*trans*) and II(A), with the possibility of actual existence of both isomers minimized or eliminated (through resonance). The colorless form can hardly be the triketone or the enol II(A) in view of the absence of color. The cyclic formulation III(A) for this isomer is the most reasonable one since, coupled with the assumption of chelation in the yellow form, it explains adequately why the two isomers always give the same results on methylation with diazomethane.

The formation of the cyclic ether III(B) upon alkylation of the sodium salt with dimethyl sulfate (reported in an earlier paper[1b]) was found to result not from direct alkylation but from hydrolysis of the sodium salt and catalytic etherification of the resulting enol through the action of alcohol and the acid generated by hydrolysis of dimethyl sulfate. In inert solvents the sodium salt does not react either with dimethyl sulfate or methyl iodide. In aqueous media, the alkylation was too slow to compete with hydrolysis of the reagent.

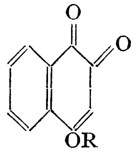
Alkylation was more conveniently studied using the silver salt and alkyl halides. With methyl iodide a 70% yield of the carbon–alkyl compound resulted, the gross structure of which was shown by hydrolytic fission to phenylglyoxylic acid and propiophenone. The oxygen–alkyl compound I(A) was formed also in approximately 10% yield. The new carbon–alkyl compound apparently has the cyclic structure  $C_6H_5C(OH)COC(CH_3){=}CC_6H_5$ (O bridging the two C atoms), XV (*cf.* ref. 2b), and will be considered in a later paper.

Ethylation of the silver salt with ethyl iodide gave a mixture from which were obtained yields of carbon- and oxygen–alkyl compounds of 50 and 20%, respectively. The carbon–alkyl compound (new) was identified by hydrolytic fission to phenylglyoxylic acid and butyrophenone. Propyl iodide also gave a carbon–alkyl product (45% yield, identified by hydrolytic fission); however, in this case we were unable to isolate a crystalline oxygen–alkyl compound from the residual oils.

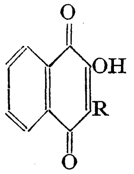
From the above results it would appear that there is nothing strikingly abnormal in the mode of alkylation in this series, contrary to the inference previously drawn from preliminary experiments.[1b] The yield of carbon–alkyl product, however, is relatively very high as compared with that in the alkylation of the α-diketones[7] and hydroxynaphthoquinone.[3]



XVI



XVII



XVIII

The analogy between the enol I(A) and hydroxynaphthoquinone XVI deserves emphasis. Both have the 1,2,4-triketone-enol system terminated by aromatic groups and both are rather strongly acidic. In both cases the silver salt is easily alkylated in contrast with the sodium salt. Hydroxynaphthoquinone gives mixtures of the two oxygen ethers XVI and XVII but does not give carbon–alkyl compounds (XVIII) with simple alkyl halides (methyl and ethyl) although considerable amounts are formed when more active unsaturated halides are used. In the case of diphenylbutanetrione enol, however, carbon-alkylation is the dominant reaction and alkylation at the enol oxygen-4 (formula IIB) was not observed although it may have occurred to a very small extent. Diazomethane reacts with hydroxynaphthoquinone to give exclusively the 2-oxygen ether, but in the case of our enol there is formed a mixture of the ethers I(B) and II(B). Catalytic etherification of I(A) leads to the formation of the cyclic ether III(B); however, with hydroxynaphthoquinone, where cyclization and chelation are excluded on steric grounds, only the 2-ether is formed. Both hydroxynaphthoquinone ethers XVI and XVII are hydrolyzed easily by alkali as are the enol ethers I(B) and II(B) (the 4-ethers in both series appear consistently to be more easily hydrolyzed than the 2-ethers). The cyclic ether III(B), in contrast with true enol ethers, is not hydrolyzed by alkali with the same degree of ease.

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[7] Kohler and Barnes, THIS JOURNAL, **56**, 211 (1934); Kohler and Weiner, *ibid.*, **56**, 434 (1934); Barnes and Payton, *ibid.*, **58**, 1300 (1936).

Experimental Part

The experiments on the two isomeric enols were largely repetitions of earlier experiments by methods described elsewhere, and since in most cases they are referred to specifically in the foregoing discussion, details are unnecessary.

The sodium salt of the enol is best prepared by treating an alcoholic solution with the calculated amount of sodium alcoholate, the salt being obtained as a yellow precipitate which is difficultly soluble in cold water but dissolves hot and does not crystallize out on cooling. Acidification generates the yellow form of the enol.

The sodium salt yielded unchanged enol after being subjected to the action of an excess of dimethyl sulfate under a variety of conditions including refluxing in inert solvents, benzene or isopropyl ether. Similarly, practically no alkylation resulted when experiments were conducted in aqueous media under various conditions of time, temperature and alkalinity.

When the sodium salt or the free enol is treated in alcohol with an excess of dimethyl sulfate, a nearly quantitative yield of the cyclic ether III (B) corresponding to the alcohol used as solvent is obtained regardless of whether dimethyl or diethyl sulfate is used. It is obvious that the dialkyl sulfate undergoes hydrolysis and the acid generated liberates the enol and catalyzes etherification.

The silver salt of the enol was obtained as a brilliant yellow precipitate by adding 2% silver nitrate solution to a cooled aqueous solution of the sodium salt. It is somewhat unstable and often turns dark on standing and drying. *Anal.* Calcd. for $C_{16}H_{11}O_3Ag$: Ag, 30.1. Found: Ag, 30.0. Alkylation with dimethyl sulfate in methanol or ethanol gave the cyclic alkyl ether corresponding to the solvent used. Apparently the alkylation is far too slow to avoid hydrolysis, liberation of the enol and catalytic etherification.

The quinoxaline reactions were carried out by dissolving the compound and an equal weight of *o*-phenylenediamine in alcohol and heating to boiling, the product crystallizing directly or on subsequent cooling of the solution. The products were recrystallized from ethanol. The following compounds were recovered unchanged under these conditions: I(B), III(B), VII, VIII, X and XIV(A). The compounds III(B), VIII, X and XIV(A) were recovered unchanged also after four hours of refluxing with the reagent. The enol, the enol benzoate XII, the cyclic chloro compound IX and the acetoxychlorofuran XIV(B) reacted immediately on boiling, the orange crystals of the quinoxaline IV appearing directly or upon seeding. Dibenzoylmethoxyethylene after four hours of refluxing with the reagent gave IV in good yield. Under these conditions dibenzoylaminoethylene VII gave largely unchanged material, and on six hours of refluxing with the reagents gave a 40% yield of IV.

2-Phenyl-3-phenacylquinoxaline, IV, is bright orange in color, even after careful purification including distillation in the vacuum oven. It is difficultly soluble in ethanol from which it was recrystallized; melting point 169–170° (corr.). *Anal.* Calcd. for $C_{22}H_{16}ON_2$: C, 81.5; H, 4.94. Found: C, 81.3; H, 5.15.

Oxidation was carried out by treating 2 g. of IV in 10 cc. of hot concd. acetic acid with 3 g. of chromic acid in 6 cc. of 50% acetic acid, the mixture being boiled for two minutes. The products were separated by successive extractions from an ether solution by sodium carbonate and by sodium hydroxide, giving a practically quantitative yield of benzoic acid (separated from V by extraction with hot water), 1.0 g. (79%) of VI, and a small amount of V.

2-Chloro-2,5-diphenyl-3-furanone (IX) was prepared by the action of benzoyl chloride containing a trace of concd. sulfuric acid on the enol. When shaken with cold sodium methylate solution for five minutes it is converted into III(B) in good yield. On standing for one hour in dilute methanolic sodium hydroxide solution, it is converted in good yield into the enol.

2-Benzoyloxy-2,5-diphenyl-3-furanone, X.—(a) Half a gram of IX with 2 g. of silver benzoate (freshly precipitated from alcoholic silver nitrate by means of sodium benzoate and washed with isopropyl ether) was suspended in 30 cc. of isopropyl ether and the mixture refluxed for ten hours. On filtering and working up the product 0.4 g. of nearly pure X was obtained.

(b) A mixture of 3 g. of enol, 9 g. of benzoic anhydride, and one drop of concd. sulfuric acid, was allowed to stand for one hour. The benzoic anhydride was decomposed with aqueous sodium bicarbonate solution. The residue on crystallization from isopropyl ether gave 2 g. of nearly pure X, m. p. 162–163° (corr.). *Anal.* Calcd. for $C_{23}H_{16}O_4$: C, 77.50; H, 4.53. Found: C, 77.49; H, 4.67.

The reactions outlined in the diagram were carried out in the usual way. The hydrolysis to the enol took place within a few minutes at room temperature.

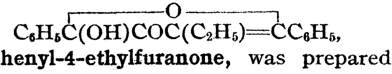
2-Benzoyloxy-1,2-dibenzoylethylene (dibenzoylethenol benzoate), XII (or XIII), was prepared in yields of 50% or less by adding benzoyl chloride to a well-stirred suspension of the enol in an excess of aqueous sodium hydroxide solution. The product, obtained as an oil, was recrystallized from isopropyl ether or ethanol. The alkaline solutions always contained considerable enol which was recovered on acidification; m. p. 139° (corr.). *Anal.* Calcd. for $C_{23}H_{16}O_4$: C, 77.50; H, 4.53. Found: C, 77.30; H, 4.57.

The conversion to III(B) was accomplished by allowing the benzoate to stand for several hours in methanol saturated with hydrogen chloride. Both sodium hydroxide in 80% methanol and sodium methylate solution quickly hydrolyzed it to the enol. On standing for one-half to one hour in acetic anhydride or acetyl chloride containing a trace of concd. sulfuric acid, followed by hydrolysis and recrystallization, good yields of XIV (A) and (B), respectively, were obtained.

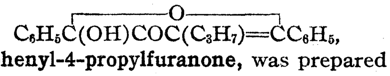
2-Hydroxy-2,5-diphenyl-4-methylfuranone, XV.—A mixture of 5 g. of the silver salt, 4 g. of methyl iodide and 35 cc. of isopropyl ether was refluxed for one hour. The solution was then filtered to remove silver halide, and extracted with 10% sodium hydroxide to remove the product, which is readily soluble in alkali. The alkaline solution was acidified and the crude product isolated by extraction with ether. The original isopropyl ether solution after the alkali extraction was evaporated and gave an oil from which 0.3 g. (about 10%) of dibenzoylmethoxyethylene was obtained. The carbon-alkyl product was purified by repeated crystallizations from isopropyl ether and melted at 143–144° (corr.), yield 70%. *Anal.* Calcd. for $C_{17}H_{14}O_3$: C, 76.7; H, 5.30. Found: C, 76.6; H, 5.47.

The carbon-alkyl compound does not react with diazomethane under ordinary conditions and gives no color test with alcoholic ferric chloride, but reacts readily with bromine and dissolves easily and directly in dilute sodium hydroxide.

Hydrolytic fission was effected by steam distillation of a barium hydroxide solution. Propiophenone was isolated from the distillate and identified as the semicarbazone by mixed melting point with an authentic sample. The barium hydroxide solution on acidification and extraction with ether gave phenylglyoxylic acid (also identified as the semicarbazone).



$C_6H_5C(OH)COC(C_2H_5){=}CC_6H_5$, **2-Hydroxy-2,5-diphenyl-4-ethylfuranone,** was prepared and isolated in 50% yield by following the above procedure using ethyl iodide. The yield of dibenzoylethoxyethylene obtained as a by-product was 20%. The carbon-alkyl compound was purified by repeated crystallizations from isopropyl ether; m. p. 113° (corr.). It is soluble in dilute sodium hydroxide. *Anal.* Calcd. for $C_{18}H_{16}O_3$: C, 77.1; H, 5.76. Found: C, 76.9; H, 5.93. Hydrolytic fission with barium hydroxide, carried out as described above, gave phenylglyoxylic acid and phenyl propyl ketone which were identified as the semicarbazones.



$C_6H_5C(OH)COC(C_3H_7){=}CC_6H_5$, **2-Hydroxy-2,5-diphenyl-4-propylfuranone,** was prepared as above using *n*-propyl iodide (yield 45%). From the non-acidic oily residues no crystalline *o*-alkyl product was obtained. The product was purified by repeated crystallization from isopropyl ether; m. p. 137.5° (corr.). It is soluble in sodium hydroxide. *Anal.* Calcd. for $C_{19}H_{18}O_3$: C, 77.5; H, 6.17. Found: C, 77.3; H, 6.20.

Hydrolytic fission carried out as above gave phenylglyoxylic acid and phenyl *n*-butyl ketone, identified as semicarbazones.

Summary

New studies including the application of the quinoxaline reaction have been made on 1,4-diphenyl-1,2,4-butanetrione enol and derivatives. These studies, together with reconsideration of known facts, show that the methyl ether obtained from the enol by catalytic etherification, and the chloro compound obtained by the action of thionyl chloride, have cyclic formulas.

The benzoylation of the enol under different conditions gives a cyclic oxygen-benzoyl compound, an open chain enol benzoate, and a carbon-benzoyl derivative.

Evidence is given for the simultaneous formation in considerable amounts of the true structurally isomeric enol ether, diphenyl-4-methoxy-1,2-butenedione in the methylation of the enol with diazomethane.

The bearing of the new facts on the structure of the two forms of the enol is discussed.

Alkylation of the silver salt leads to a mixture of oxygen and carbon-alkyl compounds, the latter type predominating.

The analogy between the enol and hydroxynaphthoquinone is discussed.

UNIVERSITY, VA. RECEIVED MAY 8, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Mechanism of Carbohydrate Oxidation. XXI.[1] The Synthesis of Glucosidoglyceraldehyde Derivatives

BY HAROLD W. ARNOLD AND WILLIAM LLOYD EVANS

In interpreting the results of the alkaline degradation of gentiobiose (6-glucosidoglucose), Evans and Hockett[2] postulated the intermediate formation of 3-glucosidoglyceraldehyde as the result of the fragmentation of the gentiobiose in an alkaline solution. It was with the ultimate purpose of testing this hypothesis that the synthesis of 3-glucosidoglyceraldehyde derivatives was undertaken.

The synthesis involved the condensation of acetobromo-*d*-glucose with glyceraldehyde benzyl-cyclo-acetal[3] (a compound of the type known to have an unblocked hydroxyl group on the third carbon atom) according to the procedure of Königs and Knorr[4] as improved by Kreider and Evans[1,5] with the formation of crystalline 3-β-*d*-glucosido-glyceraldehyde benzyl-cyclo-acetal tetraacetate (I). In order to test the applicability of Hudson's rules of isorotation to disaccharide derivatives containing the glyceraldehyde benzyl-cyclo-acetal residue, 3-β-*l*-arabinosidoglyceraldehyde benzyl-cyclo-acetal triacetate (II) was like-

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[1] No. XX of this Series, THIS JOURNAL, **58**, 1661 (1936).

[2] W. L. Evans and R. C. Hockett, THIS JOURNAL, **53**, 4384 (1931).

[3] H. O. L. Fischer and Erich Baer, *Ber.*, **65**, 337 (1932).

[4] W. Königs and E. Knorr, *ibid.*, **34**, 957 (1901).

[5] L. C. Kreider and W. L. Evans, THIS JOURNAL, **57**, 229 (1935).

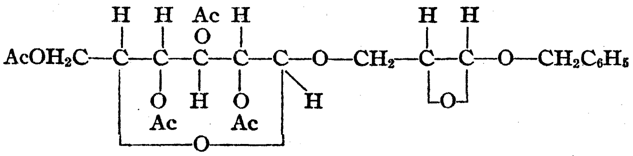
wise prepared by the condensation of acetobromo-*l*-arabinose with glyceraldehyde benzyl-cyclo-acetal.

Upon hydrogenation in the presence of palladium black, (I) yielded amorphous 3-β-*d*-glucosidoglyceraldehyde tetraacetate (III). The complete cleavage of glyceraldehyde benzyl-cyclo-acetal acetate and related compounds had already been demonstrated by Fischer and Baer.[3] More thorough studies by Richtmyer[6] had shown that only benzyl glycosides are completely split by catalytic hydrogenation.

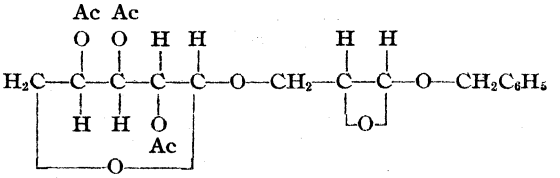
Refluxing of (III) with anhydrous pyridine, followed by acetylation, yielded a sirup which reacted with *p*-nitrophenylhydrazine to form the crystalline *p*-nitrophenylhydrazone of β-*d*-glucosidodihydroxyacetone pentaacetate.[5] The yield of this hydrazone indicated an 8–9% conversion of the glucosidoglyceraldehyde derivative to the corresponding glucosidodihydroxyacetone derivative. Fischer, Taube and Baer,[7] in similar studies of the action of pyridine on glyceraldehyde, found a maximum conversion to dihydroxyacetone of 49%.

In the course of experiments carried out in the attempt to improve the yield of glyceraldehyde benzyl-cyclo-acetal from glyceraldehyde, it was found that glyceraldehyde diacetate on treatment with titanium tetrachloride according to the method of Pacsu,[8] smoothly yielded acetochloroglyceraldehyde. This underwent the Königs–Knorr[4] reaction with benzyl alcohol to form what was apparently a mixture of isomeric benzyl glycoside acetates. From the mixture it was possible to separate the benzyl-cyclo-acetal acetate described by Fischer and Baer.[3]

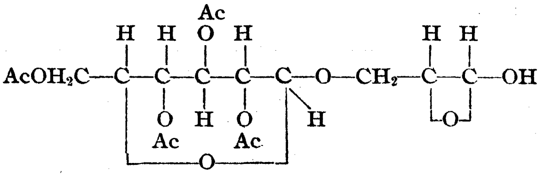
In formulating the compounds shown, the ethylene oxide formula has been ascribed to the glyceraldehyde residues. This has been done to conserve space and is not meant to imply that the glyceraldehyde derivatives described have this structure. Although many of the properties of dimeric glyceraldehyde and its simple derivatives can be accounted for on the basis of an associated ethylene oxide formula, more recent work[9] points to a dioxane ring structure for dimeric glyceraldehyde and its derivatives. The β-*d*-glucosidoglyceraldehyde benzyl-cyclo-acetal tetraacetate described in this paper appears to be almost entirely dimeric in benzene at the freezing point and almost wholly monomeric at the temperature of melted camphor.



(I) 3-β-*d*-Glucosidoglyceraldehyde benzyl-cyclo-acetal tetraacetate



(II) 3-β-*l*-Arabinosidoglyceraldehyde benzyl cyclo-acetal triacetate



(III) 3-β-Glucosidoglyceraldehyde-tetraacetate

The results obtained in the study of the alkaline degradation of glucosidoglyceraldehyde tetraacetate will be incorporated into a later paper.

Experimental Part

Preparation of Reagents and Starting Materials.—The crystallineglyceraldehyde used in this work was obtained from the laboratory of Dr. Fraenkel and Dr. Landau, Berlin-Oberschöneweide. It melted at 141°.

The acetobromo-*d*-glucose was prepared according to the procedure of Freudenberg.[10] It was recrystallized twice from anhydrous ether and extensively dried *in vacuo*.

The acetobromo-*l*-arabinose was prepared as described by Hudson and Dale.[11] It was purified as described above.

The glyceraldehyde benzyl-cyclo-acetal was prepared, with a few minor modifications, according to the method of Fischer and Baer.[3] The pyridine used was purified by refluxing and fractionating over barium oxide.

Other materials were prepared and purified as described by Kreider and Evans.[12]

3 - β - *d* - Glucosidoglyceraldehyde Benzyl - cyclo - acetal Tetraacetate.—The preparation of this compound was carried out in a three-necked flask fitted with a powerful mercury-sealed stirrer. One neck of the flask carried a

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(6) N. K. Richtmyer, This Journal, **56**, 1633 (1934).

(7) H. O. L. Fischer, Carl Taube and Erich Baer, *Ber.*, **60**, 479 (1927).

(8) Eugen Pacsu, *ibid.*, **61**, 1510 (1928); This Journal, **52**, 2563 (1930).

(9) H. G. Reeves, *J. Chem. Soc.*, 2477 (1927); M. Bergmann, A. Miekley and E. von Lippmann, *Ber.*, **62**, 1467 (1929); M. Bergmann and A. Miekley, *ibid.*, **62**, 2297 (1929); W. Discherl and E. Braun, *ibid.*, **63**, 416 (1930).

(10) K. Freudenberg, A. Noë and E. Knopf, *ibid.*, **60**, 241 (1927).

(11) C. S. Hudson and J. K. Dale, This Journal, **40**, 992 (1918); *cf.* P. A. Levene and A. L. Raymond, *J. Biol. Chem.*, **90**, 247 (1931).

(12) L. C. Kreider and W. L. Evans, This Journal, **58**, 797 (1936).

dropping funnel, the other a calcium chloride tube. The following mixture was introduced into the flask and rapidly stirred for thirty minutes: 11.0 g. of glyceraldehyde benzyl-cyclo-acetal (1 mol), 22.0 g. of silver carbonate, 50.0 g. of finely powdered "Drierite," and 120 cc. of benzene. A solution of 25.1 g. (1 mol) of acetobromo-*d*-glucose in 110 cc. of benzene was then slowly added through the dropping funnel, the initial rate of addition being somewhat faster than at the end. The addition required approximately thirty minutes. As the addition progressed there was a rapid evolution of carbon dioxide, a marked rise in temperature (10°), and a noticeable change in color. The mixture was stirred for at least five hours after the addition of the acetobromoglucose was complete. It was then filtered by suction and the residue repeatedly washed with small quantities of benzene. The benzene solution was then evaporated to dryness *in vacuo* at room temperature. The half crystalline residue was dissolved in the least possible volume of boiling ethyl alcohol. When allowed to cool the product precipitated in clumps of needles. After three recrystallizations from ethyl alcohol and two from methyl alcohol the melting point was constant at 172–173° (corr.). The weight of crystals (needles) was 15.5 g., corresponding to a yield of 50%, calculated on the basis of the acetobromoglucose used; $[\alpha]^{23}_D$ −19.9° (*c*, 1.7; $CHCl_3$).

Anal. Calcd. for $C_{16}H_{18}O_8(COCH_3)_4$: acetyl, 7.83 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 7.79 cc., 7.80 cc. *Mol. wt.* Calcd. for $(C_{24}H_{30}O_{12})_2$: 1020. Found: (cryoscopic in benzene) 995. Calcd. for $C_{24}H_{30}O_{12}$: 510. Found: (Rast) 562.

The compound is readily soluble in ether, chloroform, benzene, ethyl acetate and acetone. It is insoluble in water and petroleum ether, and only slightly soluble in cold methyl or ethyl alcohol. The substance reduces hot Fehling's solution only after hydrolysis by dilute mineral acid.

3-β-*l*-Arabinosidoglyceraldehyde Benzyl-cyclo-acetal Triacetate.—The procedure which was followed in preparing this compound was exactly the same as that described under the preparation of the corresponding β-*d*-glucosido derivative. The following quantities of reactants were used: glyceraldehyde benzyl-cyclo-acetal, 3.06 g. (1 mol); silver carbonate, 9.88 g.; "Drierite," 20.0 g.; acetobromo-*l*-arabinose, 5.8 g. (1 mol); benzene, 150 cc. The product was crystallized to constant melting point and rotation from methyl alcohol. The weight of the pure product (needles) was 0.51 g., corresponding to a yield of 7%, calculated on the basis of the acetobromoarabinose used; m. p. 142–143° (corr.) $[\alpha]^{22}_D$ +4.2° (*c*, 1.2; $CHCl_3$).

Anal. Calcd. for $C_{15}H_{17}O_7(COCH_3)_4$: acetyl, 6.84 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 6.78 cc.

3-β-*d*-Glucosidoglyceraldehyde Tetraacetate.—Because of the danger of hydrolysis of the glycosidic link in acid media, the cleavage of β-*d*-glucosidoglyceraldehyde benzyl-cyclo-acetal tetraacetate was carried out in purified methyl alcohol. The palladium catalyst was prepared according to the method of Tausz and von Putnoky.[13] The apparatus used was a modification of that described by Gattermann–Wieland.[14] The following procedure was followed in carrying out the hydrogenations. The catalyst and the solvent were introduced into the hydrogenation flask and rapidly shaken in a hydrogen atmosphere until absorption of hydrogen ceased. The sample was then introduced and the system flooded with hydrogen. The flask was again shaken until absorption of hydrogen ceased. At the beginning practically none of the substance was in solution, whereas, when hydrogen absorption was complete, the solution was homogeneous. At the end of a run the odor of toluene was very marked. The solution was filtered rapidly through a porous-bottomed crucible, care being taken to prevent contact of the catalyst with the air because of the danger of igniting the solvent vapors.

The results of two typical hydrogenations are tabulated below.

Wt. of compound, g.	3.21	4.00
Wt. of catalyst, g.	1.00	1.00
Vol. of CH_3OH, cc.	100	100
Vol. of H_2 absorbed (std. concns.), cc.	158	291
Theoretical vol. of H_2 (1 mol), cc.	144	176
Theoretical wt. of debenzylated compound, g.	2.70	3.30
Actual wt. of reaction product, g.	2.68	3.27

After removal of the catalyst by filtration, the filtrate and washings were evaporated *in vacuo* to about one-fourth their volume. The remaining solution was decolorized with Norite, chilled in ice for several hours, and filtered. The filter and all other vessels used were washed out repeatedly with methyl alcohol to ensure complete transference of the product. The solution was evaporated in a crystallizing dish to a thick, colorless sirup in a vacuum desiccator. This was redissolved in a small volume of chloroform and the solution again evaporated to dryness. The same treatment was repeated successively with pure chloroform, 50% chloroform and petroleum ether (30–60°), 20% chloroform in petroleum ether, and three times with petroleum ether. The dish was covered with a watch glass during these operations to prevent loss by spattering. After the foregoing treatment, the product could be powdered. Microscopic examination showed it to be amorphous. All attempts to bring about crystallization from a large number of solvents and combinations of solvents have failed up to the present.

Anal. Calcd. for $C_9H_{12}O_8(COCH_3)_4$: acetyl, 9.52 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 9.65 cc., 9.57 cc. *Mol. wt.* Calcd. for $(C_{17}H_{24}O_{12})_2$: 850. Found: (cryoscopic in benzene) 840.

The amorphous solid melts to a thick sirup at 63°. Since this amorphous substance was analytically pure, a determination of the specific rotation was thought to be of value. The following result was obtained: $[\alpha]^{24}_D$ −15.5° (*c*, 1.8; $CHCl_3$). Attempts to prepare crystalline derivatives by acetylation and benzoylation failed. Likewise did the attempts to prepare substituted phenylhydrazones. The substance rapidly reduces Fehling's solution in the cold.

Conversion of β-*d*-Glucosidoglyceraldehyde Tetraacetate to β-*d*-Glucosidodihydroxyacetone Pentaacetate.—The record of two experiments is given below. The

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(13) J. Tausz and N. von Putnoky, *Ber.*, **52B**, 1573 (1919).

(14) L. Gattermann and H. Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Co., New York, 1932, p. 367.

glucosidoglyceraldehyde tetraacetate was refluxed with anhydrous pyridine (drying tube) at a bath temperature of 135–140°. The solution was then cooled somewhat and 10 cc. of acetic anhydride was added. The mixture was then allowed to stand overnight. It was poured into 500 cc. of ice water which was then extracted with 200 cc. of chloroform in small portions. The chloroform solution was washed successively with dilute sulfuric acid, sodium bicarbonate solution and water. It was dried over calcium chloride. Removal of the chloroform left a thick sirup which could not be crystallized. It was taken up in ethyl alcohol and heated on the water-bath with a saturated ethyl alcohol solution of *p*-nitrophenylhydrazine. The solution was then allowed to concentrate spontaneously over a period of a week. At the end of this time, reddish-yellow crystals had separated out. These were recrystallized three times from 95% ethyl alcohol, giving pale yellow needles which melted at 187° (corr.). Mixed melting point with an authentic sample of the *p*-nitrophenylhydrazone of *β*-*d*-glucosidodihydroxyacetone pentaacetate was likewise 187°; $[\alpha]^{23}\text{D}$ −126.5°. In calculating the per cent. conversion, the reaction between the dihydroxyacetone derivative and *p*-nitrophenylhydrazine is assumed to be complete. Experimental losses are also neglected.

Wt. of glucosidoglyceraldehyde tetraacetate, g.	1.5	1.5
Vol. of pyridine, cc.	15	15
Time of refluxing, hrs.	2	3.5
Wt. of pure *p*-nitrophenylhydrazone, g.	0.18	0.20
Per cent. conversion	8.4	9.4

Acetochloroglyceraldehyde.—The results of a series of experiments on the action of titanium tetrachloride on dimeric glyceraldehyde diacetate are given below in tabular form.

The glyceraldehyde diacetate was dissolved in purified chloroform. A 10% solution of purified titanium tetrachloride in anhydrous, alcohol-free chloroform was rapidly added and the mixture protected from moisture by a drying tube. Immediately after mixing a lemon-colored addition compound precipitated out. The mixture was then refluxed on the water-bath or allowed to stand at room temperature. The precipitated solid gradually became darker in color, being almost black at the end of the reaction. The mixture was poured into a large volume of ice water. The chloroform layer was separated and the water layer repeatedly extracted with small portions of chloroform until the volume of chloroform solution amounted to 200 cc. per gram of diacetate used. The chloroform layer was washed several times with water and then with sodium carbonate solution. It was dried over calcium chloride. Evaporation of the chloroform under reduced pressure left a light brown-colored residue which was recrystallized by dissolving in the least possible quantity of boiling chloroform. When the solution had reached room temperature, an equal volume of petroleum ether (30–60°) was added and the mixture cooled in ice for several hours.

The pure compound crystallized in fine needles. It was insoluble in water and petroleum ether, sparingly soluble in chloroform, ether, and benzene at ordinary temperatures, and easily soluble in acetone.

SUMMARY OF RESULTS

Diacetate, g.	$TiCl_4$, g.	Time of refluxing, hours	Yield, %
1.0	1.0	4	49.7
4.0	4.0	4	35.0
4.5	4.8	6	15.4
1.0	1.0	14—rm. temp.	87.0
1.0	1.0	18—rm. temp.	83.3
1.0	1.0	23—rm. temp.	81.0

M. p. 174–175° (corr.). *Anal.* Calcd. for $C_3H_7O_3Cl$: Cl, 23.56. Found: Cl, 23.52.

Reaction of Acetochloroglyceraldehyde with Benzyl Alcohol.—A mixture of 2.1 g. of acetochloroglyceraldehyde, 6 g. of silver carbonate and 30 cc. of benzyl alcohol was shaken for eighteen hours at room temperature. At the end of this time it was heated on the water-bath for one hour. Following this it was cooled in ice for several hours before filtering. The residue was dried as far as possible by suction filtration, being washed with a little ice-cold ethyl alcohol to remove excess benzyl alcohol. It was then repeatedly extracted with boiling ethyl alcohol and finally with boiling chloroform, the alcohol and chloroform extracts being combined. The solvents were removed by a warm air stream, and the residual crystals recrystallized from the least possible volume of boiling 50% alcohol. The weight of crystals after the first recrystallization was 2.3 g. The melting range was very wide. Melting began at 110° and was complete at 135°. After five recrystallizations from the same solvent, the weight of the substance was 0.75 g. and the melting point was constant at 141–142° (corr.). A mixed melting point with glyceraldehyde benzyl-cyclo-acetal acetate, prepared according to the procedure of Fischer and Baer,[3] showed no depression.

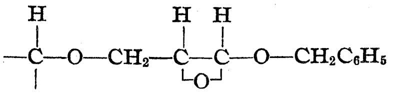
Anal. Calcd. for $C_{10}H_{11}O_3COCH_3$: acetyl, 4.50 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl (for substance melting at 110–135°), 4.44 cc.; (for substance melting at 141–142°) 4.45 cc.

By appropriate procedures it was possible to isolate from the mother liquors a small quantity of crystals melting at 109–110° (corr.). The quantity was not large enough for further work.

The results seem to point to the presence of two isomeric benzyl-cyclo-acetal acetates.

Discussion

In a manner similar to that suggested by Kreider and Evans[12] the rotations of *β*-*d*-glucosidoglyceraldehyde benzyl-cyclo-acetal tetraacetate and *β*-*l*-arabinosidoglyceraldehyde benzyl-cyclo-acetal triacetate may be considered in accordance with Hudson's views to be the sum of two components, A and B, A being used to designate that part of the rotation due to the group



$$-\overset{H}{\underset{|}{\overset{|}{C}}}-O-CH_2-\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}-O-CH_2C_6H_5$$

and B that due to the remainder of the molecule. Since *l*-arabinose has been shown by Isbell[15] to be

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(15) H. S. Isbell, *J. Chem. Ed.*, **12**, 96 (1935).

genetically related to *d*-glucose, the A values for the *d*-glucosido derivative and the *l*-arabinosido derivative should have the same sign. If the principle of optical superposition is valid, the A values should also have approximately the same magnitude. The B values for the two derivatives may be calculated from the rotations of the α- and β-forms of the fully acetylated parent sugars. The A values may then be calculated from the experimentally determined rotations of the two glycosido derivatives. The values for the molecular rotation of A as calculated by this method are: β-*d*-glucosidoglyceraldehyde benzyl-cyclo-acetal tetraacetate, A $-30{,}500$; β-*l*-arabinosidoglyceraldehyde benzyl-cyclo-acetal triacetate, A $-31{,}990$. The difference between the numerical values of Hudson's A for the two derivatives is very nearly equal to that reported by Kreider and Evans[12] for the corresponding dihydroxyacetone derivatives.

Summary

1. β-*d*-Glucosidoglyceraldehyde benzylcyclo-acetal tetraacetate and β-*l*-arabinosidoglyceraldehyde benzyl-cyclo-acetal triacetate have been prepared in crystalline condition.

2. Cleavage of β-*d*-glucosidoglyceraldehyde benzyl-cyclo-acetal tetraacetate by catalytic hydrogenation yields β-*d*-glucosidoglyceraldehyde tetraacetate as an amorphous solid with an acetyl number and a molecular weight in good accord with the theory.

3. Refluxing β-*d*-glucosidoglyceraldehyde tetraacetate in anhydrous pyridine, followed by acetylation, gives β-*d*-glucosidodihydroxyacetone pentaacetate in yields of 8–9%, based on the quantities of the *p*-nitrophenylhydrazone of the latter compound isolated.

4. Acetochloroglyceraldehyde has been prepared in the crystalline condition. This reacts with benzyl alcohol to yield what is apparently a mixture of isomeric glyceraldehyde benzyl-cyclo-acetal acetates.

COLUMBUS, OHIO RECEIVED JULY 11, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

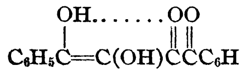
Hydroxy Polyketones. III.[1] Benzoylformoin

BY A. H. BLATT

In an earlier article[2] we described the alkylation of benzoylformoin and presented the evidence for a revision of the structures formerly assigned to its alkylation products. In this article we complete our description of the chemical behavior of the formoin and its derivatives.

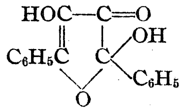
The chemistry of benzoylformoin is that of a tautomeric mixture of the ene-diol (I) and the dihydroxyfuranone (II). While certain of its reactions may be ascribed to the alternative ene-diol (III) and to the hydroxy ketone (IV), there are no reactions of the material which require the existence of these latter two forms and the entire behavior of the formoin can be accounted for on the basis of an equilibrium between (I) and (II). The reactions which form the basis for these conclusions will now be described.

Salt formation, oxidation and quinoxaline formation characterize benzoylformoin as an ene-diol. Werner described, without analytical data, a series of lakes obtained from the formoin and salts of several heavy metals.[3] Sidgwick[4] considers that these salts are derived from the completely chelated ene-diol (III) and that they contain two five-membered chelate rings. In the absence of all details as to the composition of the salts this conclusion seems to us to be somewhat hazardous. We have succeeded in securing a copper derivative of the formoin which is obviously derived from an ene-diol for its composition corresponds to the replacement of two atoms of hydrogen by one of copper. However,



$\overset{OH}{C_6H_5C}{=}C(OH)\overset{O}{C}\overset{O}{C}C_6H_5$

I



II

$C_6H_5COC(OH){=}C(OH)COC_6H_5$

III

$C_6H_5COCHOHCOCOC_6H_5$

IV

$C_6H_5COCOCOCOC_6H_5$

V

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[1] Second paper, THIS JOURNAL, **58**, 81 (1936). Shortly after the present article was submitted to the Journal a paper by Karrer and Litwan appeared [*Helv. Chim. Acta*, **19**, 829 (1936)] in which conclusions similar to ours about the structure of the formoins are advanced on the basis of iodine titrations.

[2] Blatt, THIS JOURNAL, **57**, 1103 (1935).

[3] Werner, *Ber.*, **41**, 1070 (1908).

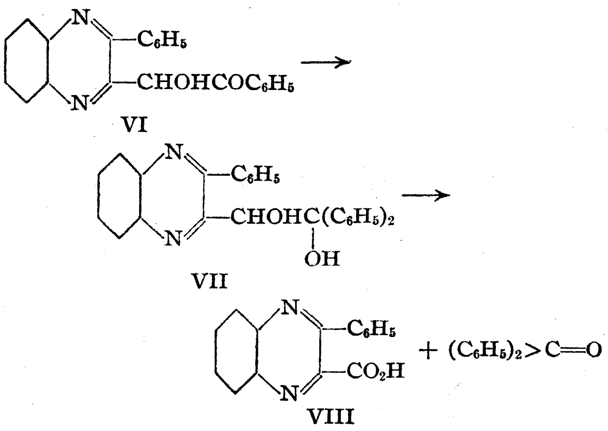
[4] Sidgwick, "Electronic Theory of Valence," Oxford University Press, Oxford, England, 1932, p. 245.

no indication as to which of the two possible ene-diols is involved in the salt formation is available from the metallic derivatives of the formoin.

The ease of oxidation of benzoylformoin is in agreement with its formulation as an ene-diol. The earliest work with the formoin showed that it was oxidized to diphenyl tetraketone (V) by nitric acid and by bromine.[5] It is also oxidized to the tetraketone by thionyl chloride. Quite recently, Karrer[6] has shown that the formoin is oxidized by iodine in acid solution and from the results of iodine titrations has concluded that it exists in solution to the extent of 57% as an ene-diol. We have not succeeded in isolating the tautomeric modifications whose existence is indicated by these titrations but we have found that the stable yellow crystalline formoin when vacuum distilled furnishes a deep red unstable liquid distillate which gradually reverts to the stable yellow modification. Since the color of the distillate is so similar to that of the alkaline solutions of benzoylformoin and to that of the unstable material which is first obtained on acidification of these alkaline solutions, we are of the opinion that the liquid is the ene-diol while the stable crystalline form is the dihydroxyfuranone. It is because of the greater volatility of the unstable modification that we have suggested the hydrogen bond (chelate linkage) shown in formula I.

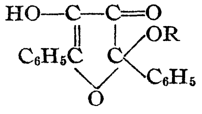
Benzoylformoin is also oxidized by copper acetate in aqueous acetic acid.[6] Since we had found that the closely related dibenzoylcarbinol on oxidation with copper acetate furnishes benzil instead of diphenyl triketone,[1] we sought the oxidation product of the formoin with this reagent. The product is benzil. Diphenyl tetraketone likewise furnishes benzil on oxidation with copper acetate, as does benzoin. From these results it is evident that not only are α-hydroxy ketones oxidized by copper acetate in an acid medium but also that the oxidative elimination of carbonyl groups from linear tri- and tetraketones is a general reaction. We have confirmed this by oxidizing 2,4,6-trimethylbenzoylformoin and find that the process is completely analogous and furnishes dimesityl diketone.

With o-phenylenediamine, benzoylformoin furnishes the quinoxaline (VI) whose structure was established by the following sequence of reactions.

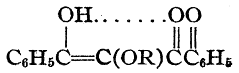


Quinoxaline formation may be ascribed to the hydroxy ketone tautomer (IV). We believe it is more reasonably considered as a reaction of the ene-diol (I) followed by ketonization and in a later paragraph we shall show that enolization of the hydroxy ketone system even in the quinoxaline (VI) can be brought about with surprising ease.

Alkylation and acylation of the formoin are predominantly the reactions of the furanone (II) but the course of these reactions can be directed by controlling the acidity or alkalinity of the reaction medium. Thus, alkylation with an alcohol and acid leads, as was shown earlier,[2] to cyclic derivatives such as (IX). Alkylation with methyl sulfate in sodium hydroxide solution, however, furnishes the open-chain ether (X, R = CH_3).



IX



$C_6H_5\overset{\overset{\displaystyle OH\cdots\cdots}{|}}{C}=C(OR)\overset{\overset{\displaystyle O}{\|}}{C}\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5$

X

Acetylation leads to three acetyl derivatives: a diacetate and two isomeric monoacetates. Acetic anhydride alone or containing sulfuric acid, acetyl chloride alone or in pyridine, all furnish the cyclic diacetate (XI, R = CH_3). The two acetyl groups in this substance are easily hydrolyzed either by acids or bases.[5] Treatment with o-phenylenediamine effects partial hydrolysis removing the enolic ester group to furnish the monoacetate (XII). That it is the enolic ester group which is eliminated is shown by the fact that the acetate (XIII) on treatment with o-phenylenediamine undergoes a parallel reaction to furnish the methoxyl compound (IX, R = CH_3). With acetic anhydride and sodium hydroxide the formoin yields an isomeric monoacetate (XIV).

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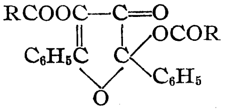
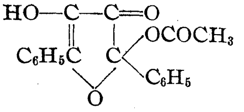
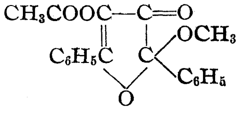
(5) Abenius, (a) *Bihang Till K. Sv. Vet.-Akad. Handl.*, **20**, 3 (1894); (b) *Ber.*, **27**, 706 (1894).

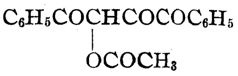
(6) Karrer and v. Segesser, *Helv. Chim. Acta*, **18**, 273 (1935); Karrer and Musante, *ibid.*, p. 1140.

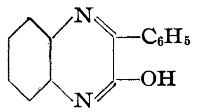
This monoacetate, like its isomer, may be hydrolyzed by acids or bases and with acetic anhydride and sulfuric acid forms the cyclic diacetate (XI). With *o*-phenylenediamine the monoacetate (XIV) furnishes the hydroxyquinoxaline (XV).


XI

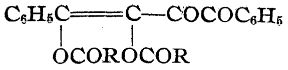

XII

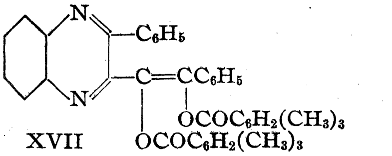

XIII


$$\underset{\displaystyle OCOCH_3}{C_6H_5CO\overset{|}{C}HCOCOC_6H_5}$$
XIV

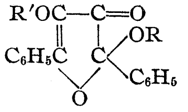

XV

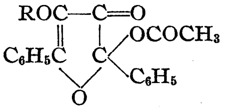
The acetyl derivatives of the formoin are so readily hydrolyzed that it is difficult to secure reliable information about them. In order to get around this difficulty, we treated benzoylformoin with 2,4,6-trimethylbenzoyl chloride, expecting that the resulting highly substituted acyl derivative would be relatively insensitive. This proved to be the case and we obtained a diacyl derivative of the ene-diol having the structure (XVI, R = 2,4,6-$(CH_3)_3C_6H_2$—) for it reacted with *o*-phenylenediamine to form the quinoxaline (XVII) which could be oxidized to the known hydroxyquinoxaline (XV). It is not improbable that acetylation with acetyl chloride in pyridine, which eventually leads to the diacetate (XI, R = CH_3), furnishes first a diacetate (XVI, R = CH_3) which is rearranged by acids to the product actually obtained, for the diacyl derivative (XVI, R = 2,4,6-$(CH_3)_3C_6H_2$—) is converted by prolonged treatment with acid to an isomer which does not react with *o*-phenylenediamine. The di-(trimethyl)-benzoate (XVI) in which no mobile hydrogen atom is present is the only derivative of the ene-diol to which a structure free from ambiguity can be ascribed.

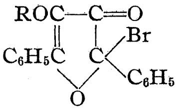

$$C_6H_5\underset{OCOR}{C}=\underset{OCOR}{C}-COCOC_6H_5$$
XVI

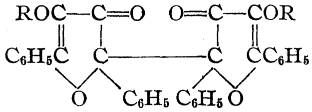

XVII

Considering next the dialkyl derivatives of benzoylformoin which have the structure (XVIII), we find that the glycosidic alkyl group is distinguished from the enolic alkyl group by its behavior toward acetic anhydride and sulfuric acid and toward hydrogen bromide in acetic acid. With the former reagent alkoxyl is replaced by acetoxyl to furnish the alkoxy acetate (XIX), isomeric with the previously mentioned acetate (XIII) and differing from it in that it is unaffected by *o*-phenylenediamine. With hydrogen bromide both the dialkyl derivatives (XVIII) and the alkoxy acetates (XIX) yield the bromofuranone (XX). The bromofuranone was not isolated in a pure state because it was always accompanied by the dimolecular product (XXI). The ease of formation of dimolecular products is even more pronounced in the case of our bromofuranones than with the analogous triphenylbromofuranone recently described by Kohler.[7] Our bromofuranones (XX) are converted to the dimolecular compounds by prolonged treatment with hydrogen bromide in acetic acid—a fact of particular interest in connection with recent observations on the reduction of α-bromo ketones by hydrogen bromide.[8]


XVIII


XIX


XX


XXI

The open chain monomethyl derivative of benzoylformoin, like benzoylformoin, shows the behavior of a tautomeric mixture of the two forms: (X, R = CH_3) and (XXII, R = CH_3). With *o*-phenylenediamine it furnishes the quinoxaline (XXIII), on acid methylation the dialkyl derivative (XVIII, R, R′ = CH_3), on acetylation the acetate (XIX, R = CH_3) and with hydrogen bromide the dimolecular product (XXI, R = CH_3). The ordinary crystalline pale yellow monomethyl derivative is probably the furanone (XXII, R = CH_3). On distillation it furnishes a red modification, presumably (X, R = CH_3), whose color is analogous to that of the alkaline

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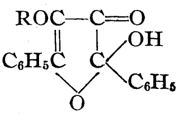
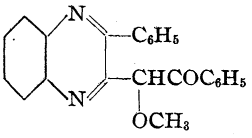
[7] Kohler, Westheimer and Tishler, THIS JOURNAL, 58, 264 (1936).

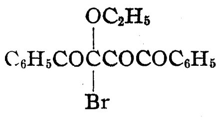
[8] Kröhnke and Timmler, *Ber.*, 69, 614 (1936).

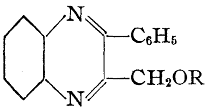
solutions of the ether and to the color of the first unstable product obtained by acidifying these alkaline solutions.


XXII


XXIII

The facts presented up to this point furnish a consistent picture of benzoylformoin and its open chain monoalkyl derivatives as ene-diol—hydroxyfuranone tautomers, and of its cyclic mono- and di-alkyl derivatives as alkoxyfuranones. There are two facts, however, which, while they are no better interpreted on any alternative formulation, are less concordant. The first is the stability of the formoin and its open chain monoalkyl derivatives toward alkali. While they are cleaved, as one would expect of α-diketones, by alkaline peroxide, they do not undergo a benzilic acid rearrangement with alkali alone. The second is the behavior of the open chain monoethyl derivative (X, R = C_2H_5, and XXII, R = C_2H_5). On acid alkylation, with hydrogen bromide, and with acetic anhydride and sulfuric acid it behaves like its methyl analog. With *o*-phenylenediamine, however, it does not give a quinoxaline analogous to (XXIII) but, instead, like the acetate (XIV) furnishes the hydroxyquinoxaline (XV). With bromine it yields a monobromo derivative for which no other structure than (XXIV) is reasonable but which is remarkably stable for a substance having such a structure.


$C_6H_5COC(OC_2H_5)(Br)COCOC_6H_5$
XXIV


XXV

Finally attention should be called to the behavior of the quinoxalines (VI) and (XXIII) toward sodium methylate. On treatment with this reagent they form intensely colored solutions reminiscent of those of the metallic derivatives of stilbene diol. These solutions gradually lose their color and furnish methyl benzoate, benzoic acid, the hydroxyquinoxaline (XV) and from the quinoxaline (VI) the carbinol (XXV, R = H), from the quinoxaline (XXIII) the ether (XXV, R = CH_3). The formation of methyl benzoate, the carbinol (XXV, R = H) and its methyl ether (XXV, R = CH_3) are obviously due to the addition of alcohol or alcoholate and subsequent cleavage—a process similar to the alcoholysis of dibenzoylcarbinol.[1] The formation of the hydroxyquinoxaline (XV) must be a result of an oxidation process.

Experimental

Benzoylformoin distils at about 240° at a pressure of 0.5 mm. The deep red distillate on standing or on solution in alcohol reverts to the ordinary yellow stable crystalline form. Our previous statement[2] that the formoin decomposed on melting is incorrect. The formoin undergoes gradual autoxidation on standing.

Salt Formation and Oxidation.—In ethereal solution shaken with copper acetate benzoylformoin furnishes a brown copper derivative of the ene-diol. For analysis the copper derivative was washed with ether and vacuum dried.

Anal. Calcd. for $C_{16}H_{10}O_4Cu$: Cu, 19.23. Found: Cu, 18.84.

When benzoylformoin was boiled with thionyl chloride a carmine red solution resulted. Evaporation of this solution over alkali in a desiccator left diphenyl tetraketone (V). The tetraketone crystallized from benzene in splendid scarlet crystals melting at 110–112° and was identified by a mixed melting point with a synthetic sample prepared by the nitric acid oxidation of benzoylformoin.[9] The product of the nitric acid oxidation is the tetraketone hydrate which is easily converted to the anhydrous material by high vacuum distillation.

When benzoylformoin was dissolved in 60% acetic acid and warmed at 80° for one hour with an excess of saturated aqueous copper acetate, then filtered hot from the precipitated cuprous oxide and diluted with water, an excellent yield of benzil was obtained. On similar treatment diphenyl tetraketone and benzoin also gave benzil.

When 2,4,6-trimethylbenzoylformoin[10] was oxidized in the same way with copper acetate the product melted at 117–118°. Since the melting point did not suffice to distinguish between the two possible products, dimesityl triketone[11] and dimesityl diketone,[12] the product was analyzed and found to be the diketone. (*Anal.* Calcd. for $C_{20}H_{22}O_2$: C, 81.6; H, 7.5. Found: C, 81.6; H, 7.67.) The yield is excellent and the process makes readily available this highly hindered diketone.

Quinoxaline Formation.—When 5.4 g. of benzoylformoin dissolved in 30 cc. of hot methanol was boiled for one hour with an excess (3.0 g.) of *o*-phenylenediamine, the solution on cooling deposited 4.7 g. of the quinoxaline (VI). For analysis the material was crystallized from acetic acid. It was sparingly soluble in the ordinary solvents and melted to a red liquid at 187–188°.

Anal. Calcd. for $C_{22}H_{16}O_2N_2$: C, 77.6; H, 4.7. Found: C, 77.36; H, 4.7.

To establish the structure of the quinoxaline (VI) it was converted to the glycol (VII) which was then oxidized.

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(9) Abenius and Söderbaum, *Ber.*, **24**, 3034 (1891).

(10) Gray and Fuson, THIS JOURNAL, **56**, 1367 (1934). We are indebted to Dr. R. C. Fuson for a sample of the formoin.

(11) Fuson, Matuszeski and Gray, *ibid.*, **56**, 2100 (1934).

(12) Kohler and Baltzly, *ibid.*, **54**, 4024 (1932).

For this purpose 1.7 g. of the powdered quinoxaline was added to an excess of magnesium-free phenylmagnesium bromide and the reaction mixture on decomposition with sulfuric acid furnished 1.9 g. of the glycol. The material, which was sparingly soluble in the ordinary solvents, crystallized well from benzene and petroleum ether in fine needles melting at 163–164°.

Anal. Calcd. for $C_{28}H_{22}O_2N_2$: C, 80.4; H, 5.3. Found: C, 80.7; H, 5.4.

When the quinoxaline glycol (VII) suspended in warm glacial acetic acid was oxidized with the calculated amount of chromic oxide, the reaction mixture taken up in ether, washed with water and extracted with sodium carbonate, the extract furnished on acidification 3-phenylquinoxaline 2-carboxylic acid (VIII)—identified by comparison with a sample prepared according to the directions of Wahl.[13] From the ether, by evaporation and steam distillation, benzophenone was obtained.

In order to be certain that no benzoic acid (which would show the presence of a quinoxaline isomeric with VI but having the positions of the hydroxyl and carbonyl groups interchanged) had been formed in the oxidation and had been lost by admixture with the quinoxaline acid (VIII), we did a second oxidation of the glycol (VII) using a large excess of chromic acid. In this oxidation the products were benzophenone and the hydroxyquinoxaline (XV).[14] The hydroxyquinoxaline being soluble in alkali hydroxides and insoluble in alkali carbonates permitted a chemical separation from any benzoic acid which might have been formed. No benzoic acid was found. We had previously assured ourselves by a separate experiment that the quinoxaline acid (VIII) was converted to the hydroxyquinoxaline (XV) by chromic oxide.

Acylation.—The cyclic diacetate (XI, R = CH_3) was described by Abenius, who obtained it from the formoin and acetic anhydride.[5] We find that it is prepared in quantitative yield by treatment of the formoin with acetic anhydride and a little sulfuric acid. Other methods of preparation have been described in the introduction. The cyclic diacetate is stable and since it can be hydrolyzed to the formoin with alkali and converted to the furanone ethers (IX) with alcoholic acid, it is useful for storing the formoin. We were unable using alkali hydroxides to effect partial hydrolysis of the diacetate. This was possible, however, with *o*-phenylenediamine. Thus, when 1.7 g. of the diacetate in 25 cc. of boiling benzene was heated for two hours with 0.6 g. of the diamine and the solvent then removed *in vacuo*, a yellow solid was obtained. After crystallization from alcohol or acetic acid the pale yellow product melted at 198°.

Anal. Calcd. for $C_{18}H_{14}O_5$: C, 69.7; H, 4.5. Found: C, 69.7; H, 4.8.

The cyclic monoacetate (XII) is converted by acetic anhydride and sulfuric acid to the diacetate (XI, R = CH_3). With methyl alcohol and hydrochloric acid it furnishes the cyclic ether (IX, R = CH_3) and with alcoholic alkali it furnishes benzoylformoin.

When 2.7 g. of the formoin in 40 cc. of water containing 0.8 g. of sodium hydroxide was shaken for two hours with 2 cc. of acetic anhydride, the deep red color of the solution disappeared and 3.0 g. of a colorless solid precipitated. After crystallization from dilute alcohol the product melted at 109–110°.

Anal. Calcd. for $C_{18}H_{14}O_5$: C, 69.7; H, 4.5. Found: C, 69.7; H, 4.4.

The open chain monoacetate (XIV or its enol) is converted to the cyclic diacetate (XI, R = CH_3) by acetic anhydride and sulfuric acid and on treatment with *o*-phenylenediamine furnishes the hydroxyquinoxaline (XV).

When 7.3 g. of 2,4,6-trimethylbenzoyl chloride was added to a cold solution of 5.4 g. of the formoin in 40 cc. of pyridine and the reaction mixture was left for forty hours then decomposed with iced dilute hydrochloric acid a mixture of a solid and a sticky oil was obtained. Ether was added and the solid, 4.4 g., was separated by filtration. The ether extract, after washing with dilute acid, was evaporated and furnished an additional 3.1 g. of the solid. The product after crystallization from acetic acid melted at 145°.

Anal. Calcd. for $C_{36}H_{32}O_6$: C, 77.1; H, 5.7. Found: C, 76.9; H, 5.8.

The di-(2,4,6-trimethyl)-benzoate of benzoyl formoin (XVI, R = 2,4,6(CH_3)$_3$$C_6H_2$—) is sparingly soluble in the ordinary solvents. When 0.5 g. of the material was suspended in 20 cc. of boiling methyl alcohol containing 0.2 g. of *o*-phenylenediamine and boiled for four and one-half hours, the solution after the usual ether extraction gave 0.2 g. of the quinoxaline (XVII). The very sparingly soluble quinoxaline was crystallized from acetic acid and melted at 182–183°. (*Anal.* Calcd. for $C_{42}H_{36}O_4N_2$: C, 79.7; H, 5.7. Found: C, 79.2; H, 6.0.) The quinoxaline was oxidized with chromic oxide in hot glacial acetic acid and furnished the hydroxyquinoxaline (XV), m. p. and mixed m. p.

In one preparation of the diacyl derivative (XVI, R = 2,4,6-(CH_3)$_3$$C_6H_2$—) we obtained two products: the 145° compound already described and an isomer which melted at 189°. (*Anal.* Calcd. for $C_{36}H_{32}O_6$: C, 77.1; H, 5.7. Found: C, 76.8; H, 5.6.) The formation of the 189° isomer could not be repeated but we found that when 0.5 g. of the 145° isomer suspended in 25 cc. of methyl alcohol and 2 cc. of concd. hydrochloric acid was boiled for two hours, it was converted into the 189° isomer. The 189° isomer did not react with *o*-phenylenediamine after six hours of boiling in an alcoholic suspension.

The alkylation products of benzoylformoin can also be acetylated with acetic anhydride and sulfuric acid. The glycosidic monomethyl derivative (IX, R = CH_3) furnishes the acetate (XIII) already described by Abenius.[5] When 1.6 g. of the acetate (XIII) in benzene solution was boiled for an hour with 0.54 g. of *o*-phenylenediamine, it regenerated the methoxyl compound (IX, R = CH_3). The cyclic dialkyl derivatives (XVIII) undergo replacement of the glycosidic alkoxyl group by acetoxyl on treatment with acetic anhydride and sulfuric acid. Thus, when 3.0 g. of the dimethyl derivative (XVIII, R, R′ = CH_3) was dissolved in 10 cc. of acetic anhydride containing a drop of sulfuric acid, the reaction mixture soon solidified. Decomposition with water furnished a quantitative yield of the methoxy acetate (XIX, R = CH_3) which melted, after crystallization from acetone, at 164–165° and which was

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[13] Wahl, *Bull. soc. chim.*, [4] **1**, 461 (1907).

[14] Buraczewski and Marchlewski, *Ber.*, **34**, 4009 (1901).

unaffected by *o*-phenylenediamine in benzene solution. (*Anal.* Calcd. for $C_{19}H_{16}O_5$: C, 70.4; H, 4.9. Found: C, 70.3; H, 5.0.) In similar fashion, the diethyl derivative (XVIII, R, $R' = C_2H_5$) furnishes with acetic anhydride and sulfuric acid, the ethoxy acetate (XIX, $R = C_2H_5$) which, after crystallization from alcohol, melts at 133°. (*Anal.* Calcd. for $C_{20}H_{18}O_5$: C, 71.0; H, 5.3. Found: C, 70.7; H, 5.1.)

That it is the glycosidic alkyl group which is replaced on treatment of the dialkyl derivatives with acetic anhydride and sulfuric acid is shown by the fact that when the open chain monoalkyl derivatives of benzoylformoin (X) or (XXII) are treated with acetic anhydride and sulfuric acid they furnish the same cyclic alkoxy acetates (XIX) as are obtained from the dialkyl derivatives. Thus the methyl derivative (XXII, $R = CH_3$) furnishes (XIX, $R = CH_3$) while the ethyl derivative (XXII, $R = C_2H_5$) furnishes (XIX, $R = C_2H_5$).

Reactions with Hydrogen Bromide in Acetic Acid.—On treatment with this reagent the formoin and all of its derivatives which do not contain an alkyl group in the position occupied by R′ in formula XVIII or R in formula XXII are destroyed and no definite products can be isolated. Derivatives of the formoin containing an alkyl group in the position indicated, for example the dialkyl derivatives (XVIII), the alkoxy acetates (XIX) and the monoalkyl derivatives (XXII) undergo replacement of alkoxyl, acetoxyl or hydroxyl by bromine with subsequent reduction of the resulting bromofuranones (XX) to the dimolecular products (XXI). Thus, the dimethyl derivative (XVIII, $R,R' = CH_3$), the methoxy acetate (XIX, $R = CH_3$) and the monomethyl derivative (XXII, $R = CH_3$), on solution in acetic acid and addition of a saturated solution of hydrobromic acid in acetic acid, gradually deposited a mixture of bromofuranone (XX, $R = CH_3$) and dimolecular product (XXI, $R = CH_3$). The dimolecular product interfered with the purification of the bromofuranone, so we contented ourselves with showing that the impure bromo compound could be converted to the dimolecular product by heating or by treatment in acetone solution with acidified potassium iodide. The dimolecular product was purified by crystallization from benzene and ligroin (70–90°) and from benzene alone. It melted at 226–227°.

Anal. Calcd. for $C_{34}H_{26}O_6$: C, 77.0; H, 4.9. Found: C, 76.9; H, 4.9.

The diethyl derivative (XVIII, $R,R' = C_2H_5$) and the monoethyl derivative (XXII, $R = C_2H_5$) with hydrogen bromide in glacial acetic acid furnish the ethoxy dimolecular product (XXI, $R = C_2H_5$). Purified by crystallization from benzene and ligroin, this dimolecular compound melted at 218–219°. (*Anal.* Calcd. for $C_{36}H_{30}O_6$: C, 77.4; H, 5.4. Found: C, 77.0; H, 5.5.) That it is the glycosidic alkyl group which is replaced in the reaction with hydrogen bromide is shown by the fact that ethyl methyl benzoylformoin (XVIII, $R = C_2H_5$, $R' = CH_3$) on treatment with this reagent furnishes the methoxy dimolecular product (XXI, $R = CH_3$).

The bromoethoxy compound (XXIV) has been described by Abenius.[5] It can be vacuum distilled without decomposition and is reduced by acidified potassium iodide to regenerate the monomethyl derivative (X or XXII, $R = CH_3$). With *o*-phenylenediamine the bromo compound gives the hydroxyquinoxaline (XV). Attempts to synthesize the bromo compound by adding ethyl bromide to diphenyl tetraketone were not successful.

The Action of Sodium Methylate on the Quinoxalines (VI) and (XXIII).—When 1.36 g. of the quinoxaline (VI) was dissolved in 30 cc. of methyl alcohol containing 1.6 g. of sodium an intensely purple colored solution resulted. The color of this solution faded very slowly in a stoppered container, rapidly when exposed to the air. In either case the odor of methyl benzoate was pronounced. After the color of the solution had bleached, water and ether were added. The aqueous layer was acidified, then made alkaline with sodium carbonate. The precipitate at this point consisted of 0.35 g. of the hydroxyquinoxaline (XV). The sodium carbonate filtrate was acidified and furnished 0.2 g. of benzoic acid. From the ethereal extract on evaporation there was obtained 0.5 g. of the quinoxalyl carbinol (XXV, $R = H$) which was purified by crystallization from ether and petroleum ether and from dilute methanol. It melted at 140–141° and could be distilled in a high vacuum.

Anal. Calcd. for $C_{15}H_{12}ON_2$: C, 76.3; H, 5.1. Found: C, 76.2; H, 5.2.

When the quinoxaline (XXIII)[2] was treated in similar fashion with sodium methylate, the alkaline solution was a vivid red. On working up the products of the reaction, methyl benzoate was identified by its odor, benzoic acid and the hydroxyquinoxaline (XV) by mixed melting points. The fourth product of the reaction, quinoxalyl carbinol methyl ether (XXV, $R = CH_3$), was obtained in much larger amounts than was the corresponding carbinol from the quinoxaline (VI). The ether was purified by high vacuum distillation and by crystallization from dilute methanol. It melted at 78–79°.

Anal. Calcd. for $C_{16}H_{14}ON_2$: C, 76.8; H, 5.6; OCH_3, 12.4. Found: C, 77.1; H, 5.7; OCH_3, 12.8.

The structures of the quinoxalyl carbinol and its methyl ether were established by etherification of the former to yield the latter and by oxidation of the carbinol to the known quinoxaline acid (VIII). Thus, 0.24 g. of the carbinol was dissolved in methyl iodide and boiled with a half gram of powdered sodium hydroxide for three hours. After removal of the methyl iodide, the reaction product was vacuum distilled and gave a quantitative yield of the methyl ether (XXV, $R = CH_3$). When 0.15 g. of the carbinol was oxidized in acetic acid with the calculated amount of chromic acid, the reaction mixture taken up in ether and washed with water, then extracted with sodium carbonate, the extract furnished on acidification 0.10 g. of the quinoxaline acid (VIII).

Summary

A description of the chemical behavior of benzoylformoin and its derivatives is presented. On the basis of this description it is concluded that the formoin and its open-chain monoalkyl derivatives are ene-diol hydroxyfuranone tautomers, while its cyclic mono- and dialkyl derivatives are alkoxyfuranones.

WASHINGTON, D. C. RECEIVED JULY 15, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

The Action of Alkali on Acylated Ketoximes. II.[1] Steric Hindrance to Alkaline Hydrolysis

BY A. H. BLATT AND R. P. BARNES

Although chemists have not agreed upon the relative importance to be assigned to steric factors in chemical reactions, they have recognized the existence of hindrance in the alkaline hydrolysis of esters since the early experiments of Victor Meyer.[2] The acylated ketoximes are esters of organic acids and oximes and as such one would expect that their alkaline hydrolysis would be subject to hindrance when the acyl group involved was properly substituted. Since we were unable to find any data bearing directly on this point, and since we had need of specific information on it, we have examined the behavior toward alkali of the benzoates and 2,4,6-trimethylbenzoates of benzophenone oxime and the α-oxime of *p*-chlorobenzophenone. In addition, in order to make certain that configuration played no part, we included the benzoates and trimethylbenzoates of both oximes of *p*-methoxybenzophenone.

As our interest was in the existence of hindrance rather than in the exact amount of hindrance, we have not made quantitative studies of reaction rates but have, instead, contented ourselves with comparative tests. Our procedure consisted in determining first the conditions under which an oxime benzoate was completely hydrolyzed. We then made parallel runs with the benzoate and the corresponding trimethylbenzoate under these previously determined conditions. As was to be expected, hydrolysis was suppressed by hindrance for, without exception, the 2,4,6-trimethylbenzoates were unaffected by the treatment which served to hydrolyze the benzoates completely.

The structures of the oxime benzoates employed were established both by their method of preparation and by their hydrolysis. The structures of the oxime trimethylbenzoates followed with near certainty from their method of preparation, for it is known that oximes of the benzophenone type on treatment with pyridine and an acid chloride furnish acylated oximes and not rearrangement products unless the acid chloride is derived from a strong acid—*e. g.*, benzenesulfonic acid. 2,4,6-Trimethylbenzoic acid is of the same order of strength but somewhat weaker than benzoic acid so that a rearrangement in the preparation of the trimethylbenzoates seemed most improbable.[3] Since, however, our experiments with the trimethylbenzoates were meaningless unless these substances had the structures assigned them, we have hydrolyzed all the trimethylbenzoates by prolonged heating with alcoholic hydrochloric acid. This treatment furnished in each case trimethylbenzoic acid and the ketone from which the oxime was derived, showing that our starting materials were acylated ketoximes. This precaution was particularly necessary in the case of the β-oxime of *p*-methoxybenzophenone for it gave two isomeric products on treatment with 2,4,6-trimethylbenzoyl chloride. Both isomers on acid hydrolysis furnished *p*-methoxybenzophenone and 2,4,6-trimethylbenzoic acid and neither isomer was hydrolyzed by alkali. Presumably this is a case of dimorphism but it is not absolutely certain.

The fact that the hydrolysis of these acylated ketoximes is subject to hindrance is strong presumptive evidence that it proceeds through an addition reaction. An observation which we made during the hydrolysis of the benzoates has confirmed this and has enabled us to show the nature of the addend. When the benzoates were hydrolyzed by treatment in alcoholic solution with aqueous sodium hydroxide and the reactions were stopped by pouring into large volumes of water, the products were not oxime and sodium benzoate but oxime and ethyl benzoate. The isolation of the small amount of ethyl benzoate formed was not feasible under the conditions of our experiments. Consequently, in order to establish the formation of an ester in the alkaline reaction medium, we hydrolyzed the *p*-phenylbenzoate of acetoxime (I) using methyl alcohol and aqueous sodium hydroxide. This gave methyl *p*-phenylbenzoate (II). In our opinion the only reasonable interpretation of these facts is that the alkaline hydrolysis of acylated ketoximes under the condi-

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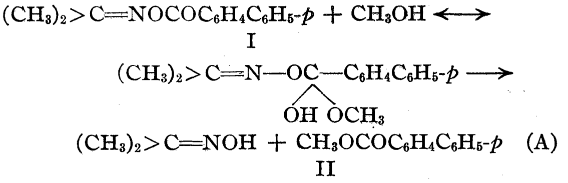
[1] First paper, THIS JOURNAL, **57**, 1330 (1935).

[2] Meyer, *Ber.*, **28**, 1263 (1895). Compare Freudenberg, "Stereochemie," Franz Deuticke, Vienna, 1933, p. 462.

[3] The dissociation constants at 25° of benzoic acid and 2,4,6-trimethylbenzoic acid are 6.15×10^{-4} and 3.7×10^{-4}, respectively. "International Critical Tables," Vol. VI, McGraw-Hill Book Co., Inc., New York City, 1929, pp. 249, 295.

tions of our experiments proceeds through the, probably reversible, addition of alcohol followed by cleavage of the intermediate addition product—the reaction series (A).



$$(CH_3)_2{>}C{=}NOCOC_6H_4C_6H_5\text{-}p + CH_3OH \longleftrightarrow$$

I

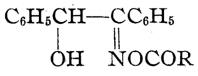
$$(CH_3)_2{>}C{=}N{-}\underset{OH\ \ OCH_3}{OC}{-}C_6H_4C_6H_5\text{-}p \longrightarrow$$

$$(CH_3)_2{>}C{=}NOH + CH_3OCOC_6H_4C_6H_5\text{-}p \quad \text{(A)}$$

II

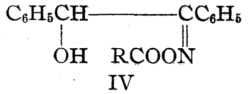
The application of this mechanism to the alkaline hydrolysis and alcoholysis of carboxylic esters is sufficiently obvious to make specific comment unnecessary.

With the existence of hindrance in the alkaline hydrolysis of acylated ketoximes thus established, we have made use of it in order to secure additional information about the two processes which take place when acylated benzoin oximes are treated with alkali. It has previously been shown[1] that acylated α-benzoin oximes (III) on treatment with alkali are cleaved to benzaldehyde, benzonitrile and the acid corresponding to the acyl group present, while the isomeric acylated β-benzoin oximes (IV) on similar treatment do not undergo cleavage but instead are hydrolyzed to oxime and acid.



$$\underset{OH}{C_6H_5CH}{-}\underset{NOCOR}{\overset{}{CC_6H_5}}$$

III



$$\underset{OH}{C_6H_5CH}{-\!-\!-\!-}\underset{RCOON}{CC_6H_5}$$

IV

To determine the effect of hindrance on these two processes we have examined the behavior toward alkali of the trimethylbenzoates of both benzoin oximes. The trimethylbenzoate of α-benzoin oxime (III, R = 2,4,6-$(CH_3)_3C_6H_2$—) on treatment with aqueous sodium hydroxide or alcoholic sodium carbonate cleaves, at least as readily as do the unhindered esters of this oxime, to benzonitrile, benzaldehyde and trimethylbenzoic acid. The trimethylbenzoate of β-benzoin oxime (IV, R = $(CH_3)_3C_6H_2$—) under the same conditions is unaffected. The application of these results to the acylated benzoin oximes is straightforward. Hydrolysis, here as in other acylated ketoximes, is the usual type of ester hydrolysis which proceeds through an addition reaction and which is stopped by hindrance. Cleavage, which is not affected by hindrance, obviously does not involve an addition reaction and must follow a quite different course.

The most probable course for the cleavage is one which is an application to the acylated α-benzoin oximes of the mechanism which Mills[4] has proposed for the action of alkali on aldoxime acetates. Stereoisomeric aldoxime acetates on treatment with alkali undergo cleavage to nitrile and acid or hydrolysis to aldoxime and acid. Mills has suggested that the first step in both cases is the loss of the aldehydic hydrogen atom as a proton. The resulting gap molecules will then, depending upon their configuration, either lose an acetate ion—cleavage—or undergo hydrolysis and regain a proton. This mechanism, applied to the acylated benzoin oximes with which we are dealing, involves the loss of the hydroxyl hydrogen atom as a proton from both isomers. It is in complete agreement with all the available facts insofar as the α-derivatives, those which cleave, are concerned. In the case of the β-derivatives we have already shown that the reaction involved is the usual type of ester hydrolysis proceeding through an addition reaction and we see no necessity for the assumption of the loss of a proton and the formation of gap molecules.

The essential difference between our point of view and that of Mills is that while Mills regards configuration as determining the behavior of the gap molecules once they are formed, we regard configuration as determining the ease of formation of the gap molecules. These alternatives can be tested by making use once more of the trimethylbenzoate of β-benzoin oxime (IV, R = 2,4,6-$(CH_3)_3C_6H_2$—). If configuration determines the behavior of the gap molecule, then this trimethylbenzoate should be unaffected by any alkaline treatment. If, however, configuration simply determines the ease of formation of the gap molecule then, since hydrolysis is stopped by hindrance, this trimethylbenzoate should cleave if the alkaline treatment is made sufficiently drastic. This latter is the case. The trimethylbenzoate of β-benzoin oxime, which is unaffected by the treatment which serves to cleave its α-isomer, is itself cleaved by alcoholic sodium hydroxide.

Experimental

The acylated oximes were prepared by mixing cold pyridine solutions containing equivalent amounts of oxime and acid chloride, allowing them to stand for twenty-four hours at room temperature and then pouring them onto ice and dilute hydrochloric acid. The benzoates solidified promptly; the trimethylbenzoates were generally obtained as oils which crystallized only after they had been dissolved

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[4] Mills, *Chemistry and Industry*, **51**, 750 (1932).

TABLE I

Substance, benzoate	Crystallized from	M. p., °C.	Analyses, %			
			Calcd.		Found	
			C	H	C	H
Benzophenone oxime 2,4,6-trimethyl-	Ethanol	136–137	80.46	6.1	80.8	6.3
p-Chlorobenzophenone *α*-oxime	Ethanol	114–115	71.55	4.2	72.0	4.4
p-Chlorobenzophenone *α*-oxime 2,4,6-trimethyl-	Ethanol	101–102	73.1	5.3	73.1	5.2
p-Methoxybenzophenone *α*-oxime	Ethanol	115–116	CH_3O,	9.35		9.29
p-Methoxybenzophenone *β*-oxime	Ethanol	85–86	CH_3O,	9.35		9.47
p-Methoxybenzophenone *α*-oxime 2,4,6-trimethyl-	Ethanol–water	102–103	CH_3O,	8.31		8.48
p-Methoxybenzophenone *β*-oxime 2,4,6-trimethyl-	Ethanol	120–121			CH_3O,	8.36
		75	CH_3O,	8.31	CH_3O,	8.22
Acetoxime *p*-phenyl-	Ether	132–133	75.9	5.9	75.45	5.7

in ether and shaken thoroughly with dilute acid. The solvents used for purification, with the melting points and analyses of the products, are given in Table I. The benzoate of benzophenone oxime has already been described.[5] A more detailed description of the trimethylbenzoates of the benzoin oximes is given later.

Attempts to determine whether the 75 and 120° trimethylbenzoates of the *β*-oxime of *p*-methoxybenzophenone were dimorphous were inconclusive because the melts of these isomers did not crystallize satisfactorily on cooling.

Each of the above 2,4,6-trimethylbenzoates was hydrolyzed by boiling its alcoholic solution to which a small amount of concd. hydrochloric acid had been added, for from two to six hours. Water was then added, the solutions were made alkaline with carbonate and steam distilled. The distillates contained in each case the ketone from which the oxime was derived, while the residual alkaline liquid furnished on acidification 2,4,6-trimethylbenzoic acid.

Since the procedure in most of the alkaline hydrolysis experiments was similar, a generalized description will suffice for all but the exceptional cases. After preliminary experiments had shown the time required for complete hydrolysis of a benzoate, a solution of 1.0 g. of that benzoate in a definite volume of alcohol was prepared. At the same time a solution of 1.0 g. of the corresponding trimethylbenzoate was made up in the same volume of alcohol. To these solutions equal volumes of 5% sodium hydroxide solution were added. Then, after both solutions had been left for a time sufficient to hydrolyze the benzoate, half of the solution containing the trimethylbenzoate was poured into a large volume of water while all of the solution containing the benzoate was similarly treated. The precipitates thus obtained, after filtering and drying, were identified by melting points and mixed melting points. Finally, after a much longer reaction time, the remaining half of the solution of the trimethylbenzoate was poured into water and worked up. In every case the product from the benzoates (reaction time from thirty to ninety minutes) consisted of oxime produced by hydrolysis. The alcoholic solutions smelled strongly of ethyl benzoate. In every case the product from the trimethylbenzoates (reaction time from thirty minutes to twenty-two hours) consisted of unchanged starting material.

When a solution of 1.2 g. of the *p*-phenylbenzoate of acetoxime (I) in 90 cc. of methyl alcohol and 10 cc. of sodium hydroxide was poured into water after standing for one hour, there was obtained a quantitative yield of methyl *p*-phenylbenzoate (II) which was identified by comparison with an authentic specimen of that ester.[6]

The 2,4,6-trimethylbenzoate of *α*-benzoin oxime crystallizes splendidly from ether and petroleum ether or alcohol and water in clusters of small needles which melt irregularly at about 92°. The material undergoes cleavage on heating so that the melting point is not sharp. Even on standing the material cleaves to such an extent that it is not possible to secure acceptable analytical results. Carbon and hydrogen determinations are both inconsistent and low, presumably as a result of autoxidation of the benzaldehyde formed by cleavage. In the absence of analytical data the structure of the material is based on its alkaline cleavage to furnish benzaldehyde, benzonitrile and trimethylbenzoic acid and its hydrolysis, on standing in alcoholic solution with hydrochloric acid at room temperature, to furnish benzoin.

The 2,4,6-trimethylbenzoate of *β*-benzoin oxime crystallizes from ether and petroleum ether and melts at 151°. This material is quite stable and does not decompose on standing. (*Anal.* Calcd. for $C_{24}H_{23}O_3N$: C, 77.2; H, 6.2. Found: C, 77.25; H, 6.2.)

The trimethylbenzoate of *α*-benzoin oxime is completely cleaved to trimethylbenzoic acid, benzaldehyde and benzonitrile by shaking for fifteen minutes with an excess of 5% aqueous sodium hydroxide. Shaken for fifteen minutes in alcoholic solution with one mole of aqueous sodium carbonate the same cleavage occurs. Identification of the cleavage products was made by the method used in earlier work.[1] The trimethylbenzoate of *β*-benzoin oxime is recovered unchanged after the treatments just described. However, when it is treated in alcoholic solution with an excess of 5% aqueous sodium hydroxide for fifteen minutes, it is cleaved to benzaldehyde, benzonitrile and trimethylbenzoic acid.

Summary

The hydrolysis of acylated ketoximes by alkali in aqueous alcoholic solution proceeds through an addition of alcohol and can be stopped by the introduction of hindrance in the acyl group. The cleavage of acylated ketoximes of the benzoin type by alkali is not affected by hindrance. The mechanism of the cleavage process is discussed.

WASHINGTON, D. C. RECEIVED JULY 20, 1936

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(5) Chapman and Harris, *J. Chem. Soc.*, 809 (1933).

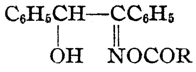
(6) Schlenk and Weickel, *Ann.*, **368**, 304 (1909).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

The Action of Alkali on Acylated Ketoximes. III. Hydrogen Bond Formation in Derivatives of the *o*-Hydroxybenzophenone Oximes

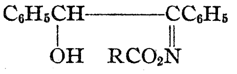
BY A. H. BLATT AND LILLIAN A. RUSSELL

In the earlier articles of this series[1] it was shown that, when hindrance does not intervene, the behavior of acylated benzoin oximes toward alkali is determined by their configuration. Acylated α-benzoin oximes (I) are cleaved by alkali while acylated β-benzoin oximes (II) are hydrolyzed. The mechanism of these two processes has been discussed but no explanation was advanced for the one-to-one correlation between configuration and mode of reaction. It is our purpose in this article to consider this latter point.



$$\begin{array}{ll} C_6H_5CH & \!\!-CC_6H_5 \\ | & \;\| \\ OH & NOCOR \end{array}$$

I



$$\begin{array}{ll} C_6H_5CH & \!\!-\!\!-\!\!-\!\!-CC_6H_5 \\ | & \qquad\;\| \\ OH & RCO_2N \end{array}$$

II

Since configuration is the determining factor, one seeks an explanation in terms of steric differences between the isomers. The most striking difference is the proximity in the α-series (I) of the unshared electron pair on the nitrogen atom to the hydroxyl group, and their separation in the β-series (II). We suggest, therefore, that the cleavage of acylated α-benzoin oximes is a consequence of incipient hydrogen bond formation (chelation) between the hydroxyl hydrogen atom and the spatially adjacent unshared electron pair on the nitrogen atom. The interaction between hydroxyl hydrogen and the unshared electron pair on nitrogen would be favored by their proximity in the α-series and it would be prevented in the β-series both by their separation and by the screening effect of the intervening acyl group. That such an interaction does take place is indicated by the infra-red absorption of the acetates of the benzoin oximes. The molal absorption area of β-benzoin oxime acetate (II, R = CH_3) approximates but is somewhat less than that of compounds containing a normal hydroxyl group, while the shape of the absorption curve shows some deviation from normal. α-Benzoin oxime acetate (I, R = CH_3), however, shows a marked suppression of hydroxyl group absorption and, more significant, a broad absorption curve.[2]

The acylated benzoin oximes, though useful as suggesting the explanation which we have just presented, are not of assistance in testing it. The requirements for complete hydrogen bond formation are well established: a system, capable of resonance, made up of a hydroxyl group and a conjugated system of double bonds terminating in oxygen or nitrogen. Such a system is not present in the acylated benzoin oximes though they contain one which approaches it and which constitutes a borderline case. Derivatives of the *o*-hydroxybenzophenone oximes, however, do meet exactly the requirements for hydrogen bond formation and, if our explanation is valid, stereoisomeric pairs of acylated *o*-hydroxybenzophenone oximes should show a difference in their chemical behavior comparable to that shown by stereoisomeric acylated benzoin oximes, while one isomer should show complete hydrogen bonding detectable by appropriate physical methods.

We have verified these consequences by an examination of the acetates of both oximes of *o*-hydroxybenzophenone and of both oximes of 2-hydroxy-5-methylbenzophenone. The isomeric oximes of *o*-hydroxybenzophenone were available as a result of the work of Kohler and Bruce;[3] we were able to obtain the previously unknown isomer of 2-hydroxy-5-methylbenzophenone oxime by applying the method of conversion of Kohler and Bruce to the known oxime. Since the two pairs of isomeric oximes thus available show perfectly parallel behavior, it will only be necessary to describe one pair and we shall confine our discussion with few exceptions to the acetates of the oximes of *o*-hydroxybenzophenone.

On treatment with excess sodium hydroxide the acetates of both *o*-hydroxybenzophenone oximes are hydrolyzed to the parent oximes. This perhaps means that under these conditions hydrolysis takes place more rapidly than cleavage. More likely, however, it indicates that salt formation occurs at the phenolic hydroxyl group and destroys the hydrogen bond. In either case,

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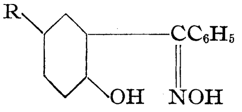
(1) Barnes and Blatt, THIS JOURNAL, **57**, 1330 (1935); Blatt and Barnes, *ibid.* **58**, 1900 (1936).

(2) The measurements of the infra-red absorption of these acetates have been published: Hilbert, Wulf, Liddel and Hendricks, *ibid.*, **58**, 548 (1936). We are indebted to Dr. Oliver Wulf and his associates of the Bureau of Chemistry and Soils of the U. S. Department of Agriculture for the measurements and for discussing with us their interpretation. We are, of course, responsible for the particular interpretation presented here.

(3) Kohler and Bruce, *ibid.*, **53**, 1569 (1931).

hydrolysis is most convenient for it permits one to relate the configurations of the acetates to those of the parent oximes by a chemical transformation. With sodium carbonate, that is, under conditions comparable in this series to the use of sodium hydroxide with the benzoin oxime acetates, differences in behavior are observed. The acetate (IV, R = H) undergoes a Beckmann rearrangement to furnish the benzoxazole (V, R = H)—a process which is the counterpart here of the cleavage of α-benzoin oxime acetate, for in both reactions the bond between the α-carbon atom and the carbon atom of the C=N group is broken. The acetate (VIII, R = H) on treatment with sodium carbonate undergoes hydrolysis to the parent oxime (VII, R = H) just as does β-benzoin oxime acetate. On pyrolysis, the acetate (IV, R = H) furnishes cleanly the benzisoxazole (VI, R = H). Pyrolysis of the stereoisomeric acetate (VIII, R = H) is not a smooth process; it furnishes in small yields a mixture of products from which it is possible to isolate the isoxazole (VI, R = H).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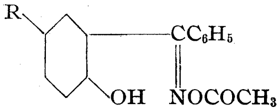
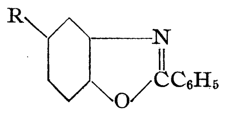
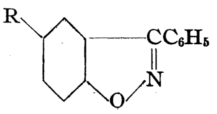
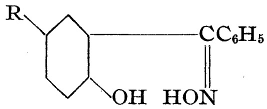
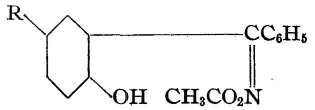

IV


V


VI


VII


VIII

The behavior of the acetates (IV, R = H) and (VIII, R = H) on pyrolysis is particularly interesting in view of earlier attempts at ring closure made with the parent oximes. Meisenheimer and Meis,[4] who were unable to dehydrate the oxime (VII, R = H) to the isoxazole (V, R = H), concluded that such a dehydration would take place only in the, then unknown, isomer (III, R = H) where it would result from the operation of residual valence forces. Kohler and Bruce,[3] who first prepared the oxime (III, R = H), found that it could not be dehydrated to the isoxazole and this, together with the observation of v. Auwers and Jordan[5] that the oxime of 2,2'-dihydroxybenzophenone could not be converted to an isoxazole, seemed to discredit pretty thoroughly Meisenheimer's suggestion. However, Lindemann[6] found that the acetates of a number of *o*-hydroxybenzaldoximes and *o*-hydroxyacetophenone oximes furnished isoxazoles on pyrolysis. Lindemann in no case had isomeric oxime acetates. Our results with the acetates of the *o*-hydroxybenzophenone oximes and the 2-hydroxy-5-methylbenzophenone oximes show clearly that pyrolysis to an isoxazole is a smooth reaction only when the acylated oximino group is *anti* to the hydroxyl group. And, although no *trans* dehydration of an oxime to a heterocyclic compound has yet been observed, the assumption that a *trans* ring closure of an oxime *derivative* may take place, for example, in the Beckmann rearrangement of α-benzil dioxime[7] becomes much more plausible.

It is clear from the foregoing description that the difference in chemical behavior—hydrolysis *vs.* cleavage—which was observed with the isomeric benzoin oxime acetates is also found in the isomeric *o*-hydroxybenzophenone oxime acetates. It remains to be shown that cleavage is associated with the presence of a hydrogen bond in the molecule. Our evidence on this point is from two sources: infra-red absorption and solubility. Dr. Oliver Wulf and his associates at the Bureau of Chemistry and Soils of the U. S. Department of Agriculture, have determined the infra-red absorption of the four acetates (IV, R = H and CH_3) and (VIII, R = H and CH_3). They find that the acetates (IV, R = H and CH_3), in which the hydroxyl group and acetylated oximino group are spatially distant with respect to each other, show no absorption in the hydroxyl region. The acetates (VIII, R = H and CH_3), in which the hydroxyl group and acetylated oximino group are spatially adjacent with respect to each other, show normal hydroxyl group absorption. Their data for the acetate (VIII, R = CH_3) are shown graphically in Fig. 1.[8] Since the work of these investigators[9] has shown that the disappearance of hydroxyl group absorption is a criterion of hydrogen bond formation between hydroxyl hydrogen

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[4] Meisenheimer and Meis, *Ber.*, **57**, 289 (1924).

[5] Von Auwers and Jordan, *ibid.*, **58**, 26 (1925).

[6] Lindemann and co-workers, *Ann.*, **449**, 63 (1926); **456**, 275, 284 (1927); *J. prakt. Chem.*, [II] **122**, 214 (1929).

[7] Compare Blatt, *Chem. Rev.*, **12**, 229 (1933).

[8] The data for the acetates (IV, R = H and CH_3) and (VIII, R = H) are presented in an article by Hendricks, Wulf, Hilbert and Liddel, THIS JOURNAL, **58**, 1991 (1936).

[9] Hilbert, Wulf, Liddel and Hendricks, *Nature*, **135**, 147 (1935). See also references 2 and 8.

and either carbonyl oxygen or trivalent nitrogen, their results establish definitely the existence of hydrogen bonds in the acetates (IV, R = H and CH_3) and their absence in the acetates (VIII, R = H and CH_3).

In connection with this discussion of the infra-red absorption data we wish to point out that it furnishes a new and absolute method for determining the configuration of oximes of the type under consideration. The results obtained by this method as applied to the oxime acetates can be related to the parent oximes by the fact that each oxime furnishes a single acetate from which the parent oxime can be cleanly regenerated. When the configurations of the oxime acetates, as determined by their infra-red absorption, are related back to the parent oximes, it is found that the configurations thus obtained are in complete agreement with those obtained from the Beckmann rearrangement of the oximes on the assumption of a *trans* shift of groups during rearrangement.

The conclusions from infra-red absorption are supported by the solubilities of the four acetates under discussion. The acetates (IV, R = H and CH_3) are soluble in carbon tetrachloride to the extent of forming one-tenth molar solutions at room temperature. The stereoisomeric acetates (VIII, R = H and CH_3) are so sparingly soluble that it is not possible to prepare one one-hundredth molar solutions in this solvent under the same conditions. While we realize that the use of solubility in assigning structure must be made with proper caution, in a case such as this where the solubilities of stereoisomers are being compared it seems legitimate to conclude that the tenfold greater solubility of the acetates (IV, R = H and CH_3) in a non-polar solvent like carbon tetrachloride indicates the disappearance of the polar hydroxyl group in these acetates. Corroborating the solubilities in carbon tetrachloride are those in alcohol where the acetates (VIII, R = H and CH_3) possessing a polar hydroxyl group are more soluble than their stereoisomers (IV, R = H and CH_3).

The material presented in this article furnishes a firm foundation for the suggestion that the alkaline cleavage of acylated oximes of the α-benzoin and *o*-hydroxybenzophenone types is a consequence of hydrogen bond formation in these substances. In addition, it makes possible a study of the chemical effects which accompany hydrogen bond formation. It is obvious from our results that hydrogen bond formation between oxygen and nitrogen is completely conditioned by steric factors. Because of this and because of the existence in isomeric forms of compounds containing an unsaturated trivalent nitrogen atom, it is possible for the first time to secure and study isomers which differ from each other only in that one contains a hydrogen bond while the other does not.[10] It has already been shown that occurrence of hydrogen bonding is accompanied by ease of cleavage of the molecule. It is also true that hydrogen bond formation in the *o*-hydroxybenzophenone oxime acetates is accompanied by a decrease in the acidity of the phenolic hydrogen atom. It is our intention to continue the study of systems where hydrogen bonding between oxygen and nitrogen can take place so as to secure additional information about the chemical effects which accompany it. It is our hope that a more complete knowledge of these chemical effects will be of use in the development of a physical interpretation of the hydrogen bond.

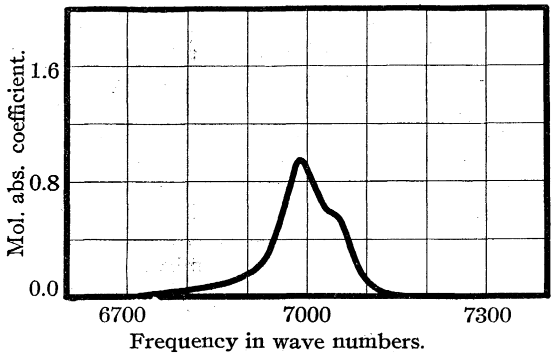

Fig. 1.—Infra-red absorption of *anti* phenyl 2-hydroxy-5-methylphenyl ketoxime acetate.

Experimental

A. Derivatives of *o*-Hydroxybenzophenone

Preparation of *syn*-Phenyl 2-Hydroxyphenyl Ketoxime Acetate (IV, R = H).—To 5.0 g. of the oxime (III, R = H)[11] was added 10 cc. of acetic anhydride. On gentle warming the oxime dissolved and on cooling the acetate

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[10] The existence of isomers of this type has been postulated by Pauling, THIS JOURNAL, **58**, 94 (1936), in connection with the infra-red absorption of certain ortho substituted phenols. However, the isomerism predicted by Pauling would result from two different configurations of the hydroxyl group while the isomers with which we are dealing result from different configurations of the atom to which the hydroxyl hydrogen atom is bonded.

[11] The preparation of this oxime is much more satisfactory if twice the quantity of hydroxylamine hydrochloride recommended by Kohler and Bruce,[3] is employed. Compare the directions given below for *syn*-phenyl 2-hydroxy-5-methylphenyl ketoxime.

crystallized. Decomposition of the excess anhydride with water and crystallization of the product from alcohol furnished 3.5 g. of pure acetate, melting at 96–97°.

Anal. Calcd. for $C_{15}H_{13}O_3N$: C, 70.6; H, 5.1. Found: C, 70.6; H, 4.9.

Action of Sodium Hydroxide on the Acetate (IV, R = H).—When 0.5 g. of the acetate was shaken with 10 cc. of 5% sodium hydroxide a slight yellow color developed but much of the solid did not dissolve. On addition of 20 cc. of alcohol a clear yellow solution was obtained. After five minutes it was diluted with water, iced and acidified with dilute hydrochloric acid. The resulting colorless precipitate, which weighed 0.35 g., melted at 110–125°. Mixed with the *syn* oxime (III, R = H), m. p. 142–143°, it melted at 133–138°, and mixed with the *anti* oxime (VII, R = H), m. p. 140–141°, it melted below 105°. A single crystallization of the product from benzene and ligroin furnished the pure *syn* oxime (III, R = H).

Action of Sodium Carbonate on the Acetate (IV, R = H).—When a solution of 0.5 g. of sodium carbonate in 5.0 cc. of water was added to 0.5 g. of the acetate in 25 cc. of alcohol there was a transient yellow color while a small amount of material precipitated. After five minutes, the addition of 70 cc. of water precipitated 0.35 g. of a colorless solid which melted at 80–85°; mixed with 2-phenylbenzoxazole (V, R = H)[12] it melted at 95–100°, and mixed with 3-phenylbenzisoxazole (VI, R = H)[13] it melted below 65°. Crystallization from alcohol furnished the pure benzoxazole, m. p. and mixed m. p. 102–103°.

Pyrolysis of the Acetate (IV, R = H).—When 0.2 g. of acetate was slowly heated in a Späth bulb connected to an oil pump it began to decompose at about 65° while between 140–150° a pale yellow oil distilled. There was almost no charring in the bulb. The distillate dissolved in 2 cc. of hot alcohol, gave on cooling 0.1 g. of 3-phenylbenzisoxazole (VI, R = H) melting at 83–84°. The melting point of the product was not lowered by admixture with a synthetic sample of the benzisoxazole but a mixture of the product and 2-phenylbenzoxazole (V, R = H) melted below 70°.

Preparation of *anti*-Phenyl 2-Hydroxyphenyl Ketoxime Acetate (VIII, R = H).—To 2.4 g. of the oxime (VII, R = H)[14] 8 cc. of acetic anhydride was added. The reaction was worked up as with the *syn* acetate (IV, R = H) and crystallization of the product from 15 cc. of alcohol and 10 cc. of water furnished 2.1 g. of pure acetate which melted at 156°.

Anal. Calcd. for $C_{15}H_{13}O_3N$: C, 70.6; H, 5.1. Found: C, 70.57; H, 4.9.

Action of Sodium Hydroxide on the Acetate (VIII, R = H).—When 0.5 g. of the acetate was shaken with 10 cc. of 5% sodium hydroxide all save a trace of the material dissolved. After fifteen minutes the solution was filtered, diluted, iced and acidified. It furnished 0.4 g. of the *anti* oxime (VII, R = H), melting at 140–141°, and whose melting point was not lowered by admixture with the *anti* oxime.

Action of Sodium Carbonate on the Acetate (VIII, R = H).—A solution of 0.5 g. of sodium carbonate in 5 cc. of water was added to 0.5 g. of the acetate in 25 cc. of alcohol. A pale yellow color developed and a slight precipitate, apparently inorganic, was formed. After fifteen minutes, the addition of 70 cc. of water gave a clear solution. Careful acidification with dilute hydrochloric acid furnished 0.35 g. of the *anti* oxime melting at 140–141°. The melting point of the product was not lowered by admixture with the *anti* oxime (VII, R = H) but it was lowered to 115–120° by admixture with the *syn* oxime (III, R = H).

Pyrolysis of the Acetate (VIII, R = H).—When 0.2 g. of the acetate was distilled in vacuum there was much charring. The yellow oily distillate dissolved in 1 cc. of alcohol and diluted with water furnished 0.07 g. of a colorless solid which melted at 72–78° and whose melting point was raised by admixture with 3-phenylbenzisoxazole and with 2-phenylbenzoxazole. The solid behaved like a mixture of the oxazole and isoxazole. Crystallization from alcohol and water furnished 0.03 g. of 3-phenylbenzisoxazole (VI, R = H) melting at 79–81° with preliminary softening. Mixed with pure benzisoxazole (83–84°) the recrystallized material melted at 82–84°, mixed with the pure benzoxazole (102–103°) it melted at 67–70°.

B. Derivatives of 2-Hydroxy-5-methylbenzophenone

Preparation of *syn*-Phenyl 2-Hydroxy-5-methylphenyl Ketoxime (III, R = CH_3).—Since the preparation and purification of this oxime are reported to be quite troublesome,[15] we present the following procedure based on that of Kohler and Bruce for the unmethylated analog. Ten grams of 2-hydroxy-5-methylbenzophenone is shaken with 80 cc. of 40% potassium hydroxide. The solid dissolves and an orange-yellow potassium derivative separates. The reaction mixture is then cooled and shaken while 15.0 g. of hydroxylamine hydrochloride is added over a period of forty-five minutes. When no more heat is evolved the flask is stoppered and shaken mechanically for four hours or left to stand overnight. The resulting clear yellow solution is then diluted, iced and acidified with dilute hydrochloric acid. The crude oxime, thus precipitated, weighs 10.1 g. and melts at 127–135°. Crystallization from 25 cc. of benzene and an equal volume of ligroin (70–90°) furnishes 8.2 g. of pure oxime melting at 135–136°. The oxime develops a bright yellow color on exposure to direct sunlight.

Preparation of *syn*-Phenyl 2-Hydroxy-5-methylphenyl Ketoxime Acetate (IV, R = CH_3).—To 2.0 g. of the oxime (III, R = CH_3) there was added 4 cc. of acetic anhydride. Solution was effected by warming and the acetate crystallized on cooling. Purified by crystallization from 25 cc. of alcohol the acetate melted at 125–126°; yield, 1.8 g.

Anal. Calcd. for $C_{16}H_{15}O_3N$: C, 71.4; H, 5.6. Found: C, 71.6; H, 5.6.

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(12) Prepared according to Ladenburg, *Ber.*, **9**, 1526 (1876), and melting at 102–103°.

(13) Prepared according to Kohler and Bruce, This Journal, **53**, 646 (1931), and melting at 83–84°.

(14) The gummy by-products formed in the conversion of the *syn* to the *anti* oxime (*cf.* ref. 3) can be removed conveniently by incompletely neutralizing the strongly alkaline reaction mixture, after dilution with water, with carbon dioxide. This precipitates the by-products so that on acidification of the filtered solution with dilute hydrochloric acid the *anti* oxime is obtained as a colorless, crystalline solid.

(15) (a) Von Auwers and Jordan, *Ber.*, **58**, 34 (1925); (b) Von Auwers and Czerny, *ibid.*, **31**, 2694 (1898).

Action of Sodium Hydroxide on the Acetate (IV, R = CH_3).—When 0.5 g. of the acetate was shaken with 10 cc. of 5% sodium hydroxide, the material dissolved in part to furnish a yellow solution. Addition of 20 cc. of alcohol effected solution, and on dilution with water and acidification with hydrochloric acid 0.4 g. of crude *syn* oxime was obtained. The crude product melted at 110–120°; mixed with the *syn* oxime it melted at 120–133° and, on crystallization from benzene and ligroin, furnished pure *syn* oxime melting at 135–136°.

Action of Sodium Carbonate on the Acetate (IV, R = CH_3).—A solution of 0.5 g. of sodium carbonate in 5 cc. of water was added to 0.5 g. of the acetate in 25 cc. of alcohol. A slight yellow color developed and a small amount of material precipitated. After fifteen minutes the addition of 70 cc. of water precipitated 0.35 g. of a colorless solid which melted at 80–88°. A mixture of this material and 2-phenyl-5-methylbenzoxazole (V, R = CH_3)[16] melted at 90–95°, while a mixture with 3-phenyl-5-methylbenzisoxazole (see below) melted below 65°. Crystallization from alcohol furnished the pure benzoxazole, m. p. and mixed m. p. 102–103°.

Pyrolysis of the Acetate (IV, R = CH_3).—When 1.0 g. of the acetate was pyrolyzed the product distilled at about 160° in an oil pump vacuum. Taken up in 4 cc. of alcohol the solution deposited on cooling 0.5 g. of impure 3-phenyl-5-methylbenzisoxazole (VI, R = CH_3). On crystallization from alcohol the pure benzisoxazole, melting at 92–93°, was obtained. Identification was made by a mixed melting point with a synthetic sample.

Synthesis of 3-Phenyl-5-methylbenzisoxazole (VI, R = CH_3).—A mixture of 2-chloro-5-methylbenzophenone and 2-methyl-5-chlorobenzophenone was prepared from *p*-chlorotoluene according to the directions of Heller.[17] Since the 2-chloro-5-methylbenzophenone did not crystallize, the mixture of isomers was treated with hydroxylamine and then with alkali according to the procedure of Kohler and Bruce for the preparation of 3-phenylbenzisoxazole.[13] The reaction mixture was then extracted with ether, the ether removed and the residue vacuum distilled. The fraction boiling at about 160° when dissolved in alcohol slowly deposited the characteristic large crystals of the isoxazole which melted at 92–93° and which were identical with the previously described pyrolysis product.

Anal. Calcd. for $C_{14}H_{11}ON$: C, 80.4; H, 5.26. Found: C, 80.2; H, 5.3.

Preparation of *anti*-Phenyl 2-Hydroxy-5-methylphenyl Ketoxime (VII, R = CH_3).—Strongly alkaline solutions at the boiling point convert the *syn* oxime (III, R = CH_3) into a mixture of the *syn* and *anti* forms. Fortunately the *syn* modification is precipitated from its alkaline solutions by carbon dioxide before the *anti*, so that the isolation of the *anti* form from the mixture presents no special difficulties. Our preferred procedure consists in boiling for two hours 1.0 g. of the pure *syn* oxime with 40 cc. of 40% sodium hydroxide. At the end of the first hour a clear yellow solution is obtained; at the end of the second hour a precipitate is suspended in the alkaline liquid. The hot alkaline reaction mixture is diluted with cold water to 300 cc., 50 g. of crushed ice added and a rapid stream of carbon dioxide passed in for from an hour to an hour and a quarter. At this point the yellow solution is filtered from a small flocculent precipitate of the *syn* oxime which is rejected. To the filtrate, 150 g. of crushed ice is added and then dilute hydrochloric acid is added with stirring until a vigorous evolution of carbon dioxide occurs. At this point the precipitation of the *anti* oxime is complete and it is unnecessary to add additional acid. The reaction mixture at no time is acid to litmus. If no seed is available the *anti* oxime precipitates as a gray curdy mass; once seed is available, the precipitate is lighter in color and granular in form. From three such runs 2.0 g. of crude *anti* oxime is obtained. The material is purified by crystallization from benzene (using 2.5 cc. per gram of solid) by diluting with an equal volume of ligroin (70–90°). The pure *anti* oxime melts at 136–137°, almost the same point as the *syn* modification, but mixtures of the two melt below 115°. The *anti* oxime precipitated from alkaline solutions picks up an electric charge very readily and is difficult to handle.

Anal. Calcd. for $C_{14}H_{13}O_2N$: C, 74.0; H, 5.7. Found: C, 74.5; H, 5.65.

Beckmann Rearrangement of the *anti* Oxime (VII, R = CH_3).—A solution of 1.0 g. of the *anti* oxime in 25 cc. of absolute ether was cooled while 1.0 g. of phosphorus pentachloride was added. After one hour, after which time there was no increase in the amount of precipitate, the reaction mixture was poured on ice and the ether layer was separated. Evaporation of the ether, after appropriate washing and drying, left a sticky brownish residue which dissolved completely in 5% sodium hydroxide. Acidification of the alkaline solution and crystallization of the precipitate from dilute alcohol furnished *p*-cresotinic anilide melting at 160–162° and whose melting point was not lowered by mixture with a synthetic sample of the anilide (m. p. 162–163°).[18]

Preparation of *anti*-Phenyl 2-Hydroxy-5-methylphenyl Ketoxime Acetate (VIII, R = CH_3).—Two grams of crude *anti* oxime was warmed with 4 cc. of acetic anhydride for half a minute. The oxime dissolved and the reaction mixture while still warm solidified. After cooling, water was added and the crude acetate was crystallized from dilute alcohol; yield 2.1 g. The pure *anti* acetate melted at 157–158°.

Anal. Calcd. for $C_{16}H_{15}O_3N$: C, 71.4; H, 5.6. Found: C, 71.24; H, 5.9.

Action of Sodium Hydroxide on the Acetate (VIII, R = CH_3).—When 0.5 g. of the acetate was shaken with 10 cc. of 5% sodium hydroxide, all save a few specks dissolved. After thirty minutes the pale yellow solution was diluted, iced and acidified with dilute hydrochloric acid. The precipitate thus obtained weighed 0.4 g. and melted at 135–136° and its identity as the *anti* oxime was established by mixed melting points with the *syn* and *anti* oximes.

Action of Sodium Carbonate on the Acetate (VIII, R = CH_3).—When 0.5 g. of sodium carbonate was added to 0.5 g. of the acetate in 25 cc. of alcohol, there was a transient deep yellow color and a slight inorganic precipitate. After fifteen minutes, the addition of 70 cc. of

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[16] Prepared by a Beckmann rearrangement of the *syn* oxime, compare ref. 15, and melting at 102–103°.

[17] Heller, *Ber.*, **46**, 1500 (1913).

[18] *p*-Cresotinic acid, Zeltner, *J. Chem. Soc.*, **104**, 726 (1913); *p*-cresotinic anilide, reference 15(a), p. 34.

water formed a clear pale yellow solution. Acidification with dilute hydrochloric acid gave 0.4 g. of the *anti* oxime melting at 120–125°; mixed with the *anti* oxime it melted at 128–133° and mixed with the *syn* oxime it melted below 110°. Crystallization from benzene and ligroin gave the pure *anti* oxime.

Pyrolysis of the Acetate (VIII, R = CH_3).—When 0.2 g. of the acetate was vacuum distilled, it charred badly and the yield of distillate, a yellow oil, was poor. Dissolved in alcohol and diluted with water it gave 0.1 g. of a solid melting by 70° and whose melting point was raised by admixture with either the isoxazole (VI, R = CH_3) or the oxazole (V, R = CH_3). Careful crystallization from alcohol gave a small amount of 3-phenyl-5-methylbenzisoxazole (VI, R = CH_3) melting at 91–92° and whose melting point was not lowered by mixing with the pure benzisoxazole, m. p. 92–93°, but which was lowered to 70° by mixing with the oxazole, m. p. 102–103°.

Summary

It has been suggested that the cleavage of acylated α-benzoin oximes by alkali is a consequence of incipient hydrogen bond formation in these compounds. By an examination of acylated *o*-hydroxybenzophenone oximes it has been shown that hydrogen bond formation, sterically conditioned, does take place and that its occurrence is accompanied by behavior comparable to that observed in the acylated α-benzoin oximes. It is pointed out that the existence of stereoisomers, only one of which contains a hydrogen bond, makes possible a study of the chemical effects associated with hydrogen bonding.

WASHINGTON, D. C. RECEIVED JULY 20, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane–Water Mixtures from Electromotive Force Measurements. I. Standard Potentials

BY HERBERT S. HARNED AND JOHN OWEN MORRISON[1]

The further development of the physical chemistry of ionized solutes and ionic equilibria requires a knowledge of the variation of the fundamental thermodynamic property, the relative partial molal free energy, as a function of all the intensive variables. Such a comprehensive study of many electrolytes by different methods of measurement is a tremendous task, only to be carried out by many investigators over a long period of time. As a part of this general scheme, we have undertaken in this Laboratory a comprehensive study of the relative partial molal free energy of a single electrolyte as a function of its concentration, the temperature and dielectric constant of the solvent medium over as wide a range of values of these variables as will be found possible.

To achieve this purpose, the cell

$$H_2\ (1\ \text{atm.})\ |\ HCl\ (m),\ X\%\ \text{Dioxane},\ Y\%\ H_2O\ |\ AgCl\text{–}Ag \qquad (1)$$

is peculiarly adapted. The cell reaction is well known and the electrodes are very reproducible. Dioxane–water mixtures because of their complete miscibility and because of the low dielectric constant of pure dioxane (∼2) afford a wide range of variation of the dielectric constant. These properties have been shown to be of great value by Kraus and Fuoss[2] and Fuoss and Kraus,[3] who measured conductances of some electrolytes in these mixtures.

As part of this program, Åkerlöf and Short[4] have determined the dielectric constant of dioxane–water mixtures from 0 to 80°. The present communication contains electromotive force measurements of the above cells containing 20, 45 and 70% dioxane, respectively. Measurements have been made from 0 to 50° at 5° intervals, and from them the standard potentials of the cell from 0 to 50° inclusive have been calculated.

Experimental Procedure

In order to obtain electromotive forces in these mixtures with an accuracy equal to that obtained by Harned and Ehlers in water[5] and Harned and Thomas[6] in methanol–water mixtures, it was necessary to develop a new type of cell and a specialized technique. It was found that complete air elimination in all-glass apparatus was essential. Any contact of vapor or liquid in the cells with rubber rendered the measurements erratic and uncertain. Upon elimination of these difficulties, very accurate results may be obtained with a potentiometer circuit and a high sen-

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[1] This communication contains material from a dissertation presented by John Owen Morrison to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

(2) Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933).

(3) Fuoss and Kraus, *ibid.*, **55**, 1019 (1933).

(4) Åkerlöf and Short, *ibid.*, **58**, 1241 (1936).

(5) Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

(6) Harned and Thomas, *ibid.*, **57**, 1666 (1935); **58**, 761 (1936).

sitivity galvanometer in solutions of dielectric constant ranging from 80 to 10. With a quadrant electrometer or an amplified galvanometer circuit, we have reason to believe that accurate results may be obtained in media of dielectric constant of the order 5, or even less.

Dioxane was purified by distillation over sodium and subsequent recrystallization. The freezing point of the material used was always within 11.76–11.78°, a value which agrees with the value 11.78° reported by Kraus and Vingee.[7]

The composition of the water–dioxane mixtures prepared from this material was known to within ±0.01%. The hydrochloric acid content of any mixture employed was known to within less than ±0.05%.

The hydrogen electrodes, consisting of platinum foils 0.4 cm. by 2.5 cm., were plated with platinum black. The silver–silver chloride electrodes were those designated by Harned[8] as type 2.

All electromotive forces were measured by an Eppley Feussner type calibrated potentiometer and Leeds and Northrup HS galvanometer. Saturated Weston cells certified by the Eppley Laboratory were used as final standards of electromotive force. The correction of pressure to 1 atm. hydrogen was made by the usual method. The solvent vapor pressures were determined by Mr. Dale Dreisbach of the Morley Chemical Laboratory of Western Reserve University, who employed the method of Hovorka and Dreisbach.[9] These were placed at our disposal by Mr. Dreisbach, for which kindness we are most grateful. The temperature control was ±0.02°.

Cells were run in triplicate. If the values of E deviated from the mean by more than ±0.05 mv., they were discarded. Each set of cells was measured over a temperature range of 25°. One series was begun at 25° and measured at 5° intervals up to 50°, then brought back to 25°. Although six to twelve hours had elapsed between the two readings at 25°, during which the cells were rather severely treated, the difference between the two readings at 25° never exceeded 0.1 mv. and was in most cases less than 0.05 mv. A second series of cells were begun at 25°, reduced to 0°, and finally brought back to 25°. The agreement of the two readings at 25° was excellent. Indeed, in some cases after sufficient experimental skill was acquired, cells were measured at 25°, reduced to 0° by 5° changes in temperature, brought back to 25°, raised to 50° by 5° changes in temperature, and then finally lowered to 25°. The agreement of the three measurements at 25° was very good (~0.05 mv.) even though the measurements had been extended over periods of twenty-four to thirty-six hours.

Electromotive Forces

Since the cells containing the solution of a given composition were measured at eleven temperatures, a table of all the original data is too voluminous for presentation. In its place, we have resorted to the expedient of expressing the results by the quadratic equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (2)$$

E is the cell electromotive force at the centigrade temperature, t; E_{25} the electromotive force at 25°; and a and b are constants. m is the molality of the acid (moles per 1000 g. solvent). The solvent consisted of X% by weight dioxane and Y% by weight of water. Table I contains the constants of the equation at the molalities actually employed in 20, 45 and 70% dioxane–water mixtures. These values were determined by the method of least squares. In the fifth column of the table, the maximum deviation, Δ_M, between the observed and calculated results is given.

TABLE I

CONSTANTS OF EQUATION (2): $E = E_{25} + a(t - 25) + b(t - 25)^2$

E = Electromotive Force of the Cell

H_2 (1 atm.) | HCl (m), X% dioxane – Y% water | AgCl–Ag

m	E_{25}	$a \times 10^6$	$(-b \times 10^6)$	Δ_M	Δ_A
X = 20%					
0.0031249	0.50385	268.727	3.665	0.08	0.03
.0047459	.48340	199.618	3.561	.11	.05
.007088	.46398	133.673	3.629	.05	.02
.009760	.44839	80.436	3.567	.07	.03
.019132	.41618	− 21.891	3.672	.07	.02
.030042	.39473	− 81.927	3.562	.04	.02
.045631	.37505	−150.418	3.397	.05	.02
.06847	.35601	−210.327	3.565	.07	.03
.11469	.33183	−276.982	3.404	.11	.07
.18726	.30863	−343.436	3.215	.06	.03
X = 45%					
0.0031321	0.46879	− 62.127	3.409	0.05	0.02
.005136	.44542	−133.454	3.239	.03	.01
.006804	.43242	−173.636	3.205	.08	.03
.010099	.41426	−224.836	3.155	.05	.02
.020305	.38278	−316.527	3.135	.02	.01
.032601	.36186	−373.727	3.016	.10	.03
.05412	.33964	−438.818	3.040	.03	.01
.07741	.32420	−479.818	2.967	.04	.01
.11172	.30808	−520.945	2.862	.05	.02
.18442	.28593	−580.636	2.812	.03	.01
X = 70%					
0.0031639	0.38934	−577.200	2.852	0.03	0.015
.0051877	.36993	−622.818	2.630	.03	.02
.006950	.35878	−651.327	2.716	.09	.04
.009612	.34669	−673.709	2.606	.05	.015
.019270	.32142	−732.945	2.417	.05	.02
.032031	.30321	−772.473	2.315	.06	.025
.05633	.28315	−815.582	2.250	.03	.01
.07735	.27163	−842.382	2.186	.04	.02
.11362	.25726	−875.109	2.189	.04	.015
.17753	.24002	−916.509	2.090	.05	.015

In the sixth column, Δ_A represents the average deviation, or the sum of the magnitudes of the deviations at the eleven temperatures divided by eleven. Equation (2) is applicable over the temperature range of 0 to 50°.

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[7] Kraus and Vingee, THIS JOURNAL, **56**, 511 (1934).

[8] Harned, *ibid.*, **51**, 416 (1929).

[9] Hovorka and Dreisbach, *ibid.*, **56**, 1664 (1934).

It is clear that a quadratic equation affords a very close representation of the results. The data in the two solvents richer in dioxane are somewhat more consistent than in the 20% mixtures. Since the 20% mixtures were the first to be studied, we attribute this greater consistency to the skill acquired with longer experience with the technique.

The Evaluation of the Standard Potentials

As expressed by Harned and Thomas,[6] the electromotive force of cell (1) in a mixture of any composition may be expressed by

$$E = E_0 + \frac{RT}{F}\ln y - \frac{2\,RT}{F}\ln \gamma\, m = E' - 2\,k\log \gamma\, m \tag{3}$$

E_0 is the standard potential in water, E_0' the standard potential in the solvent in question and k equals 2.3026 RT/F. γ and m are the activity coefficient and molality of the acid, respectively. In water, $y = 1$, $E_0 = E_0'$. The term containing y is a measure of the medium effect.

Since the law of Debye and Hückel is to be employed in the evaluation of E_0', it is necessary to use the rational activity coefficient, f, which is related to γ according to the equation

$$a = \gamma\, m = f\, N\, s' \tag{4}$$

where a is the relative activity, and N is the mole fraction of the acid, s' a constant factor required to take care of the convention that f becomes unity in a given solvent when N or m equal zero. From this we find that

$$\log \gamma = \log f + \log s' - \log (1 + 0.002\, m\, G_0) + \log 0.001\, G_0 \tag{5}$$

where G_0 "the mean molecular weight" of solvent is given by

$$G_0 = 100\Big/\left(\frac{X}{M_1} + \frac{Y}{M_0}\right) \tag{6}$$

M_1 and M_0 are the molecular weights of dioxane and water, respectively. According to equation (5), f equals unity when m equals zero only when $\log s' = -\log 0.001\, G_0$, or $s' = 1/0.001\, G_0$. Imposing this condition, equation (5) becomes

$$\log \gamma = \log f - \log (1 + 0.002\, m\, G_0) \tag{7}$$

It also follows that

$$E = E' - 2\,k\log \gamma\, m = E' - 2\,k\log s' - 2\,k\log N f = E_0'' - 2\,k\log N f \tag{8}$$

where E_0'' is the standard potential on the mole fraction scale. We note that the standard potential, E_0'', on the f scale differs from that on the γ scale by the term $2\,k \log 0.001\, G_0$. We shall employ the Debye and Hückel limiting equation with a linear term, namely

$$\log f = -\frac{1.843 \times 10^6}{(DT)^{3/2}}\sqrt{c} + B\,c = -u\sqrt{c} + B\,c - \ldots \tag{9}$$

Combining equations (3), (7) and (9) and rearranging, we obtain

$$E + 2\,k\log m - 2\,k\,u\sqrt{c} - 2\,k\log (1 + 0.002\, G_0\, m) = E' = E_0' - Bc \tag{10}$$

a convenient form for purposes of extrapolation. If the left of equation (10) which we represent by E' be plotted against c, its value at zero c is the desired standard potential, E_0'.

For c we have substituted md_0 where d_0 is the density of the pure solvent. This will cause no error in extrapolation since at the limit ($m = 0$), it is strictly true. The values of the densities of the dioxane–water mixtures, at the desired compositions and temperatures, were obtained from suitable graphs of the density data of Mr. Dale Dreisbach of Western Reserve University. We thank Mr. Dreisbach for placing these results at our disposal before publication.

The values of the dielectric constants of the mixtures required for the computation of the limiting slopes, u, were taken from the data recently obtained in this Laboratory by Åkerlöf and Short.[4]

Table II contains the values of the densities, the dielectric constants and the limiting slopes, which combined with the electromotive force data in Table I made possible the computation of the left side of equation (10). Values of all fundamental constants employed in these computations were those adopted by the "International Critical Tables."

The actual plots of E' *versus* c uniformly exhibited a slight curvature which nearly vanished in the neighborhood of the intercept. The uncertainty in reading the values at the intercept was estimated to be of the order of ±0.05 mv. All experimental results were plotted without any sort of experimental smoothing. In the case of the 20% series, the plotted points differed from the plot used for extrapolation only at the lowest acid concentration ($m \sim 0.005$). In the cases of the 45 and 70% series, the extrapolations were made directly through the large majority of points. Of the points not lying directly on the plots, less than 10% were farther distant than 0.2 mv., and for not a single point was the deviation greater than 0.3 mv.

TABLE II

DENSITIES, DIELECTRIC CONSTANTS AND LIMITING SLOPES FOR 20, 45 AND 70% DIOXANE-WATER MIXTURES

	$X = 20\%$			$X = 45\%$			$X = 70\%$		
t, °C.	d_0	D	u	d_0	D	u	d_0	D	u
0	1.0271	69.16	0.6989	1.0505	44.28	1.364	1.0619	20.37	4.373
5	1.0245	67.39	.7072	1.0467	43.05	1.385	1.0570	19.81	4.437
10	1.0219	65.68	.7156	1.0431	41.86	1.406	1.0522	19.25	4.510
15	1.0193	64.01	.7245	1.0393	40.70	1.429	1.0474	18.72	4.581
20	1.0167	62.38	.7339	1.0356	39.57	1.453	1.0426	18.20	4.657
25	1.0141	60.79	.7437	1.0319	38.48	1.477	1.0378	17.69	4.738
30	1.0115	59.94	.7540	1.0282	37.41	1.503	1.0332	17.20	4.820
35	1.0090	57.73	.7648	1.0246	36.37	1.530	1.0285	16.72	4.907
40	1.0063	56.26	.7760	1.0210	35.37	1.557	1.0239	16.26	4.995
45	1.0038	54.83	.7877	1.0173	34.39	1.586	1.0194	15.80	5.092
50	1.0014	53.43	.7999	1.0139	33.43	1.616	1.0149	15.37	5.185

The values obtained for the electrode potential of the cell E'_0 are given in Table III. These results were then expressed by the quadratic equation

$$E_0 = E'_{0(25)} + a_0\,(t - 25) + b_0\,(t - 25)^2 \qquad (11)$$

The constants were evaluated by the method of least squares. The deviations between the observed values and those computed by equation (11) are indicated by the numbers in parentheses immediately following the result. These deviations are given in hundredths millivolt and are positive when the calculated is greater than the observed value. The constants of equation (11) are given at the bottom of the table.

TABLE III

STANDARD POTENTIALS

	$X = 20$	$X = 45$	$X = 70$
t, °C.	E'_0	E'_0	E'_0
0	0.21983 (−4)	0.18940 (−5)	0.10783 (−4)
5	.21689 (−7)	.18445 (6)	.09982 (−3)
10	.21369 (−2)	.17947 (3)	.09152 (11)
15	.21033 (−3)	.17434 (−1)	.08337 (−6)
20	.20682 (−2)	.16910 (−10)	.07475 (8)
25	.20315 (−4)	.16344 (7)	.06620 (−2)
30	.19920 (+4)	.15780 (6)	.05720 (17)
35	.19510 (+8)	.15205 (−1)	.04855 (−15)
40	.19092 (+4)	.14612 (−5)	.03930 (−3)
45	.18650 (+4)	.14000 (−7)	.03005 (−8)
50	.18196 (−1)	.13355 (8)	.02040 (11)

	$E'_{0(25)}$	$a_0 \times 10^6$	$b_0 \times 10^6$
$X = 20$	0.20311	− 757.0	−3.58
$X = 45$	.16351	−1114.5	−3.24
$X = 70$	.06618	−1745.6	−3.25

Our experience indicates that there is little doubt as to the reproducibility and reliability of the experimental results. An uncertainty arises in the extrapolation in the more concentrated dioxane solutions which is due to the fact that we have employed the Debye and Hückel function when perhaps a more extended function containing a factor to account for ionic association would be better. We shall reserve such considerations for future discussion when more results in media of low dielectric constant are available. The discussion of different extrapolations in pure methyl alcohol solutions ($D = 31.5$) given by Harned and Thomas[6] is a partial answer to this difficulty. Their computations indicate that our standard potentials are very near the true values.

Summary

1. Measurements of the cells

H_2 (1 atm.) | HCl (m), $X\%$ dioxane, $Y\%$ H_2O | AgCl–Ag

have been made at 5° intervals from 0 to 50° in solutions containing 20, 45 and 70% dioxane and hydrochloric acid at various concentrations between 0.003 and 0.2 M.

2. From these the standard electrode potentials have been evaluated.

NEW HAVEN, CONN.

RECEIVED JULY 6, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of Acetic Acid in Dioxane–Water Mixtures

BY HERBERT S. HARNED AND GEORGE L. KAZANJIAN[1]

Accurate determinations of the ionization constants of weak electrolytes in media other than water are scarce. Harned and Embree[2] have obtained the ionization constant of acetic acid in 10 and 20% by weight methanol–water mixtures from suitable electromotive force measurements. The 20% methanol mixtures possess a dielectric constant of approximately 70 which is not far from that of water. In order to determine this ionization constant over a much wider range of variation of the dielectric constant, we have measured the cells

$$H_2\ (1\ \text{atm.})\ |\ \text{HAc}(m_1),\ \text{NaAc}(m_2),\ \text{NaCl}(m_3),\ X\%\ \text{dioxane}–Y\%\ H_2O\ |\ \text{AgCl–Ag} \quad (1)$$

containing 20, 45 and 70% by weight of dioxane at 5° intervals from 0 to 50°. The dielectric constants of these solvents at 25° are 60.79, 38.48 and 17.69, respectively. From these results, the ionization constant of the acid has been evaluated by the method of Harned and Ehlers.[3]

Experimental Results

The measurements of these cells were made in the manner described by Harned and Morrison.[4] The only detail different from their procedure consisted in the preparation of the buffered acetic acid solution, and the subsequent preparation of the cell solutions.

An approximately 1 *M* hydrochloric acid was standardized by gravimetric analysis. Its strength was estimated to have been known to ±0.02%. A 1.5 *M* sodium hydroxide solution free from carbon dioxide was standardized by weight titration by means of the hydrochloric acid solution. All weighings were reduced to vacuum. These titrations checked to within ±0.02%.

Glacial acetic acid was distilled three times in an all-glass still, the first two times from a 2% solution of chromic anhydride. The middle fraction of the third distillate was diluted with conductivity water to form an approximately 3 *M* solution. The strength of this solution was determined by weight titration against the standard sodium hydroxide solution. Deviations from the mean of several titrations were not more than ±0.03%.

Carefully purified sodium chloride dried in a muffle furnace at 500° was employed.

From these standard solutions a stock buffer solution was prepared. Six kilograms of the standard acetic acid solution was weighed in a bottle on a balance sensitive to less than one gram. To this was added an approximately equal weight of the standard sodium hydroxide solution to produce a buffer containing acetic acid and sodium acetate at nearly equal molalities. Then sufficient sodium chloride was weighed and introduced so as to make its molality equal to that of the sodium acetate. To prevent any change in concentration, the bottle containing the solution was equipped with a bulb containing the solution. It was estimated that the acetic and sodium acetate concentrations were known to within ±0.05%. The error in salt concentration was considerably less than this.

The cell solutions were prepared from this stock buffer solution, conductivity water and dioxane purified as described by Harned and Morrison. About 1800 cc. of solution was prepared in 2-liter solution flasks. Allowing for the water to be added in the buffer solution, about 20 g. less than the desired amount of water was weighed into the solution flask on a balance sensitive to about 0.02 g. Next was added the buffer solution from a weight buret. Finally, the dioxane was introduced and weighed. Vacuum corrections were applied to all weights and the amount of water required to adjust the solvent composition to the desired water–dioxane ratio was added. Errors in the weighings were less than 1 part in 500. The solvent composition was known to within 0.02%. The electrolyte concentration was known to within ±0.05%. All concentrations of electrolytes are expressed in moles per 1000 g. of solvent.

These solutions were rendered air free by the passage of hydrogen.[4] The cell technique and electrode preparation was also carried out according to their directions.

Measurements of electromotive forces were made with an Eppley–Feussner type calibrated potentiometer and with Weston cells frequently calibrated against standard Eppley saturated Weston cells. A Leeds and Northrup Type H. S. galvanometer was employed.

The first readings of the electromotive forces were taken from 6 to 8 hours after the cell had been started. Readings were then taken at one-half hour intervals until constancy was obtained, then the temperature was changed. Two series of measurements were made for each concentration, one from 0 to 25° at 5° intervals, and the other from 25 to 50°. The cells were measured in triplicate. In the 20% dioxane solutions the reproducibility was of the order of ±0.05 mv. In the 45% dioxane solution, the agreement was within ±0.1 mv. Sometimes difficulties were encountered at temperatures from 40 to 50°. In general, the results at the lower temperatures were somewhat more reliable. In the 70% series, the electromotive forces were reproducible to ±0.05 mv. in most cases. In the more dilute solutions, the electromotive forces were more difficult to measure because of the higher internal resistance of the cells. It was possible in all cases,

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[1] This communication contains material from a Dissertation presented to the Graduate Faculty of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

[2] Harned and Embree, THIS JOURNAL, **57**, 1669 (1935).

[3] Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

[4] Harned and Morrison, *ibid.*, **58**, 1908 (1936).

however, to estimate the electromotive forces with a certainty of 0.05 mv.

We have expressed the results by the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (2)$$

In many cases, the first order differences of E showed no tendency to vary with the temperature so that the constant b was zero. In the other cases b was of a small magnitude. In Table I, E_{25} and the constants a and b are given. In the fifth column of the table, the maximum deviation, Δ_M, between the observed results and those computed by equation (2) are given. In the last column, the average magnitude of the deviations, Δ_A, is given. It is apparent that Δ_A is for all cases 0.06 mv. or less. The range of applicability of equation (2) is from 0 to 50°.

TABLE I

CONSTANTS OF EQUATION (2)

X = % by weight of dioxane

m_1, m_2, m_3 = moles per 1000 g. solvent

$m_2 = m_3 = 1.034\ m_1$

m_1	E_{25}	$a \times 10^6$	$b \times 10^6$	Δ_M(mv.)	Δ_A(mv.)
		X = 20			
0.010918	0.63156	683	−0.64	0.09	0.05
.019677	.61683	641	− .64	.11	.03
.04744	.59450	555	− .64	.14	.06
.07627	.58236	513	− .64	.07	.04
.10582	.57400	480	− .64	.11	.05
		X = 45			
0.011026	0.65217	568	0	0.15	0.04
.019983	.63706	515	0	.12	.03
.05173	.61258	423	−0.36	.16	.05
.10910	.59304	337	− .60	.11	.03
		X = 70			
0.005809	0.68806	420	0	0.10	0.05
.010909	.67144	356	0	.09	.05
.020968	.65404	300	0	.05	.02
.05164	.62937	216	0	.06	.015
.07862	.61774	172	0	.14	.03
.09986	.61081	144	0	.14	.04

The Ionization Constant

The equation for the electromotive force of the cell may be transposed to

$$\frac{F}{2.303\ RT}(E - E_0') + \log\frac{(m_1 - m_H)m_3}{(m_2 + m_H)} = \log\frac{\gamma_H\gamma_{Cl}\gamma_{HAc}}{\gamma_H\gamma_{Ac}} - \log K = -\log K'^{(2)(3)} \qquad (3)$$

where E_0' is the molal electrode potential of the cell, K the ionization constant of acetic acid, and γ and m are the activity coefficients and molalities of the species indicated by subscripts.[2,3] In order to evaluate K, the left side of this equation, $-\log K'$, was computed from the observed molalities, the observed electromotive forces, and the values of E_0' determined by Harned and Morrison.[4] Since K is of the order of 10^{-6} or less, $(m_1 - m_H)$ and $(m_2 + m_H)$ may be replaced by m_1 and m_2, respectively, without causing an error greater than the experimental. $(-\log K')$ was then plotted against the ionic strength, μ, and $(-\log K)$ was read off the intercept at zero μ.

The characteristics of the extrapolation are shown by Fig. 1 where the extrapolation plots of the 20, 45 and 70% series at 25° are shown. In the case of the 20% series, the plot through the points at the four highest concentrations is a straight line which has been continued to the intercept. The point at the lowest concentration lies somewhat below this plot. We feel justified in giving less weight to this result since the function plotted should yield a straight line at low concentrations. In the cases of the 45 and 70% series, the plots have been drawn through the points. There is a slight curvature at the higher concentrations which seems to disappear as the ionic strength decreases. The slope of the 20% curve is slightly positive, that of the 45% curve is slightly negative, while that of the 70% plot is negative. The extrapolation plots at all other temperatures were similar to these.

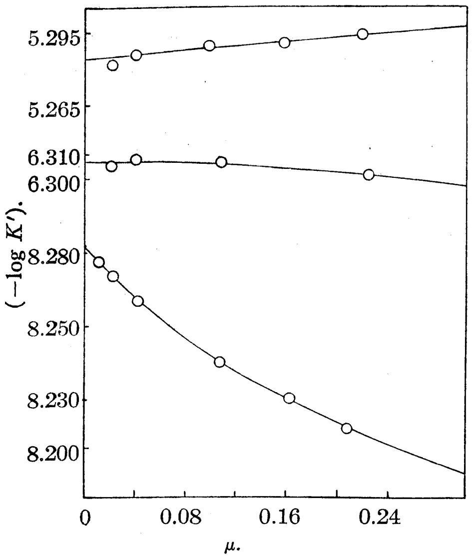

Fig. 1.—Extrapolation plots: diameters of circles correspond to 0.2 millivolt.

It is difficult to estimate the accuracy of this determination of the absolute value of $(-\log K)$. At 25°, an error corresponding to 0.1 mv. corresponds to an error of 0.002 to 0.003 in $(-\log K)$, or an uncertainty of 0.5 to 0.7% in the value of

K. The determination of K is estimated to be better than ±0.7% but not better than ±0.3%. The results in the more concentrated dioxane solutions appear to be the more consistent.

In Table II, the values of K are given at all temperatures at which measurements were made. We observe that K is in molality units. To convert to moles per liter of solution, it is only necessary to multiply by the solvent density. Thus, $K_c = Kd_0$. Examination of the values of K shows that in all solvents this quantity increases, passes through a maximum, and then decreases with increasing temperature. This fact is in accord with the behavior of weak electrolytes in aqueous solution.

TABLE II

IONIZATION CONSTANTS, OBSERVED AND CALCULATED BY EQUATION (5)

	$X = 20$		$X = 45$		$X = 70$	
	$D_{25} = 60.8$		$D_{25} = 38.5$		$D_{25} = 17.7$	
	$K \times 10^6$, obsd.	$K \times 10^6$, calcd.	$K \times 10^7$, obsd.	$K \times 10^7$, calcd.	$K \times 10^9$, obsd.	$K \times 10^9$ calcd.
0	4.77	4.77	4.74	4.75	5.17	5.18
5	4.88	4.89	4.83	4.84	5.25	5.25
10	4.99	4.99	4.91	4.90	5.27	5.29
15	5.07	5.05	4.93	4.94	5.31	5.29
20	5.10	5.10	4.96	4.94	5.25	5.27
25	5.13	5.11	4.93	4.92	5.22	5.21
30	5.09	5.10	4.87	4.87	5.11	5.13
35	5.04	5.05	4.80	4.79	5.04	5.02
40	4.97	4.98	4.69	4.69	4.88	4.88
45	4.89	4.87	4.54	4.56	4.70	4.72
50	4.78	4.75	4.39	4.41	4.50	4.54

Constants of Equation (4)

$X = 20$; $\Theta = 24.6$, $\log K_m = \bar{6}.7088$, $K_m = 5.12 \times 10^{-6}$
$X = 45$; $\Theta = 18.5$, $\log K_m = \bar{7}.6942$, $K_m = 4.95 \times 10^{-7}$
$X = 70$; $\Theta = 13.4$, $\log K_m = \bar{9}.7237$, $K_m = 5.29 \times 10^{-9}$

Harned and Embree[5] have shown that the equation

$$\log K - \log K_m = -p(t - \Theta)^2 \qquad (4)$$

expresses quite well the temperature variation of ionization constants of weak acids, bases and ampholytes in aqueous solution. K_m is the value of K at its maximum, Θ the characteristic temperature at which K is a maximum, and t is the centigrade temperature. p is a constant for all the electrolytes and has a value of 5.0×10^{-5}. Harned and Embree[2] also showed that the ionization constant of acetic acid in some methyl alcohol–water mixtures could be computed by this equation. They thus extended the range of applicability to a medium of dielectric constant of 70. The present results which extend to media of dielectric constant of the order of 18 are excellent for testing the further extension of the equation of Harned and Embree.

Equation (4) may be transposed to

$$\log K = [\log K_m - p\Theta^2] + 2p\Theta t - pt^2 \qquad (5)$$

($\log K + pt^2$) was plotted against t using the values of K given in Table II. Straight lines were obtained for the results in all the dioxane–water mixtures which proved the validity of the equation. From these graphs K_m and Θ were evaluated. Values of these quantities are given at the bottom of the table, and values of K computed by means of equation (5) are also given for purposes of comparison. The numerical equations for K in the three mixtures, obtained from equation (5) are

$$X = 20;\ \log K = \bar{6}.6785 + 0.00246\, t - 5 \times 10^{-5} t^2 \qquad (6)$$
$$X = 45;\ \log K = \bar{7}.6771 + 0.00185\, t - 5 \times 10^{-5} t^2 \qquad (7)$$
$$X = 70;\ \log K = \bar{9}.7147 + 0.00134\, t - 5 \times 10^{-5} t^2 \qquad (8)$$

respectively. The agreement between observed and calculated values is excellent. The maximum deviation is 0.6% for the 20% series and 0.5% for the 45% series. In the case of the 70% series, the maximum deviation is 0.4% except for the value at 50° where a 0.9% deviation is observed.

We have not tabulated the heat of ionization, ΔH. According to equation (4), this quantity is given by

$$\Delta H = 4.575 \times 10^{-4}\, T^2 (t - \Theta) \qquad (9)$$

The accuracy of the evaluation of ΔH depends on the accuracy with which Θ can be determined. An error in Θ of 1° will cause an error of 32 cal. at 0° and 48 cal. at 50°.

Summary

1. Measurements of the cells

$$H_2\ (1\ \text{atm.})\ |\ HAc(m_1),\ NaAc(m_2),\ NaCl(m_3),\ X\%\ \text{dioxane},\ Y\%\ H_2O\ |\ AgCl\text{–}Ag$$

have been made at 5° intervals from 0 to 50° in dioxane–water mixtures containing 20, 45 and 70% by weight of dioxane. The dielectric constants of these solvents at 25° are 60.8, 38.5 and 17.9, respectively.

2. From these data, the ionization constant of acetic acid, in each of the three solvents, has been computed at 5° intervals from 0 to 50° by the method of Harned and Ehlers.[3]

3. These values have been employed to test the empirical equation found by Harned and Embree[5] to express the variation of the dissociation constants of all weak electrolytes with the temperature.

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[5] Harned and Embree, THIS JOURNAL, **56**, 1050 (1934).

The results of this investigation indicate that this general equation without any modification may be valid in non-aqueous solutions. It may at least be said that the Harned and Embree equation is able to reproduce the experimental results in solutions covering a wide range of dielectric constant, extending from 80 in aqueous solutions to 15.4 in a solvent containing 70% dioxane by weight at 50°.

NEW HAVEN, CONN. RECEIVED JULY 25, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

A Redetermination of the Protium–Deuterium Ratio in Water[1]

BY NORRIS F. HALL AND THOMAS O. JONES

Since Bleakney and Gould[2] gave 5000 as the H/D ratio in rain water, several attempts[3] have been made to check this value by preparing water free from deuterium and comparing its density with that of ordinary water. Most of these fall roughly into two groups, resulting in values either near 5500 or near 9000.

Lewis in 1933[4] calculated the value 6500 on the basis of his first electrolytic fractionations. Recently Applebey and Ogden[5] have suggested an upper limit of 7000 on the basis of electrolyses and the assumption of "reasonable" values of the electrolytic separation factor. The opinion has been expressed[6] that Applebey's results definitely discredit values of the H/D ratio in the neighborhood of 9000. By most workers[7] Johnston's recent value ($-18.3\ \gamma$ in density, equivalent to a ratio of 5800) appears to be accepted as the most probable. We have now redetermined this ratio by a method which involves no extrapolation, and in which the final value is approached from both the light and heavy side.

Plan of Work

We prepared nearly deuterium-free water electrolytically by two methods. The first involved the recombination of the electrolytic gases according to the method used by Taylor, Eyring and Frost.[8] We shall refer to this method as "mixed recovery."

In one experiment 55 liters of Lake Mendota water was electrolyzed in potassium hydroxide solution with iron cathodes to about 70% of the original volume, and the 16 liters of water collected was reëlectrolyzed. This procedure was repeated five times until the volume of the last condensate was 150 ml. The amount collected at each stage was about 30% of the preceding volume. In a later experiment this process was independently repeated through four stages of electrolysis.

In the second method, called "separation recovery," we collected the hydrogen separately and burned it in ordinary air. Calculations of the equilibrium constant at high temperatures indicated that exchange effects in the flame could not introduce density differences in the burned water as great as 1 γ, and at the time this work was undertaken the results of Dole, Titani and Greene[9] were not available to us, so that we assumed that air oxygen and surface water oxygen had the same isotopic composition.

By this method two runs were made. In one run (III) through four stages using bell type cells, 30 liters of water was reduced to 150 ml. In the second (run IV), V-type cells (Fig. 1) with a loose plug of glass wool as a diaphragm were used. The initial and final volumes were 24 liters and 400 ml., respectively, and the electrolysis was carried again through four stages.

Because the results of the two types of electrolysis described did not agree, and because we expected on the basis of Johnston's work[3] a displacement of the oxygen isotope ratio during mixed recovery electrolysis, we decided to normalize the oxygen isotope content of some of our samples by equilibration against the standard

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[1] Presented at the Kansas City meeting of the American Chemical Society, April 15, 1936.

[2] Bleakney and Gould, *Phys. Rev.*, **44**, 265 (1933) (5000).

[3] Urey and Teal, *Rev. Modern Phys.*, **7**, 40 (1935) (5000); H. L. Johnston, THIS JOURNAL, **57**, 484, 2737 (1935) (5800); Ingold, Ingold, Whitaker and Whitlaw-Gray, *Nature*, **134**, 661 (1934) (9000); Tronstad, Nordhagen and Brun, *ibid.*, **136**, 515 (1935) (5500); Morita and Titani, *Bull. Chem. Soc. Japan*, **10**, 257 (1935) (5500); Christiansen, Crabtree and Laby, *Nature*, **135**, 870 (1935) (8400).

[4] Lewis and Macdonald, *J. Chem. Phys.*, **1**, 823 (1933).

[5] M. P. Applebey and G. Ogden, *J. Chem. Soc.*, 163 (1936).

[6] S. Glasstone, *Ann. Rep. Chem. Soc.*, **32**, 42 (1935).

[7] *Cf.* E. H. Riesenfeld and T. L. Chang, *Ber.*, **69A**, 1305, 1307, 1308 (1936).

[8] Taylor, Eyring and Frost, *J. Chem. Phys.*, **1**, 823 (1933).

[9] M. Dole, THIS JOURNAL, **57**, 2731 (1935), *J. Chem. Phys.*, **4**, 268 (1936); Morita and Titani, *Bull. Chem. Soc. Japan*, **11**, 36 (1936); C. H. Greene and R. J. Voskuyl, THIS JOURNAL, **58**, 693 (1936).

water through the medium of carbon dioxide gas. This was done as described below. As a valuable check on the density measurements, the index of refraction of many of the samples was determined.

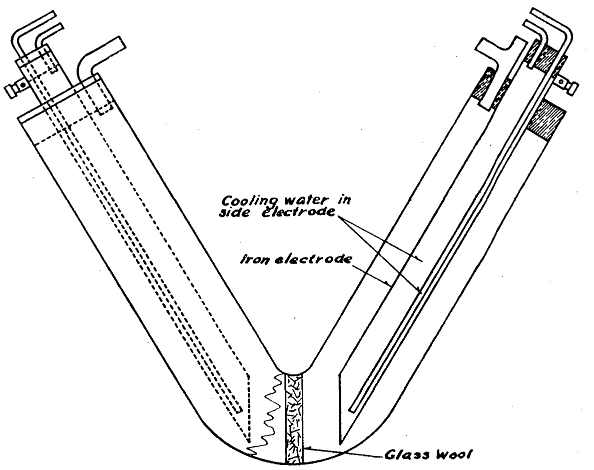

Fig. 1.—Electrolytic cell for separation recovery.

Experimental

1. Purification of Samples.—Each sample of water was distilled three times, once from alkaline permanganate in an all-glass still with a very short (1.27 cm.) Hempel column to trap spray, once from a drop of phosphoric acid through a 10-cm. Widmer column, and finally through a simple quartz still directly into the density apparatus or the interferometer cell. Small equal head and tail fractions were discarded. All the samples and the standard water were treated in exactly the same manner.

2. Density Measurements.—A magnetically controlled buoyancy apparatus (Fig. 2) was used, similar in principle to that described by Lamb and Lee.[10] The totally submerged quartz float was about 13 cm. long and had a volume of 8.2383 cc. at 25°. A cobalt–steel permanent magnet was sealed in the bottom of the float and held permanently in place with wax. The sample tube had a volume of about 60 cc. and had a bottom ground flat inside to which the magnetic float was attracted by the field of the coil beneath the sample tube. It was found that the float centered itself automatically and reproducibly in the field of the coil. The tube and connections were of Pyrex with metal parts of brass. The coil was held rigidly fixed below the tube by a brass and wax collar. By slowly reducing the current through the coil the exact voltage was found which just prevented the float from rising. The apparatus was calibrated by successively adding weighed platinum rings to the top of the float and measuring the e. m. f. required to hold the float against the bottom of the vessel. From the weight differences, the e. m. f. differences and the volume of the float and rings, it was found that one millivolt corresponded to a density change of 9.22 γ. This factor was found to be constant over the total density range studied (some 150 γ). The apparent precision of a single reading was 0.1 γ, and the measurement could be repeated at different times on the same samples to 0.2 or 0.3 γ. The apparatus was submerged in a thermostat which was constant to ±0.005°. The fluctuations in the apparent density of a given sample as it stood in the bath were hardly detectable, but measurements were always made at the crests of the bath temperature fluctuations.

Each sample was evacuated to remove dissolved air, opened to the atmosphere, closed, brought to temperature in the thermostat, opened and closed once more. This procedure removed the bulk of the dissolved air, but permitted small amounts to redissolve. No effect on the density from this source could be detected. Preliminary measurements showed that increases of barometric pressure produced an apparent density increase of 0.1 γ per cm. Since control measurements on the standard water were always made within a few hours of the measurements of an unknown sample, corrections from this source were always within the precision of the measurements themselves and were not applied.

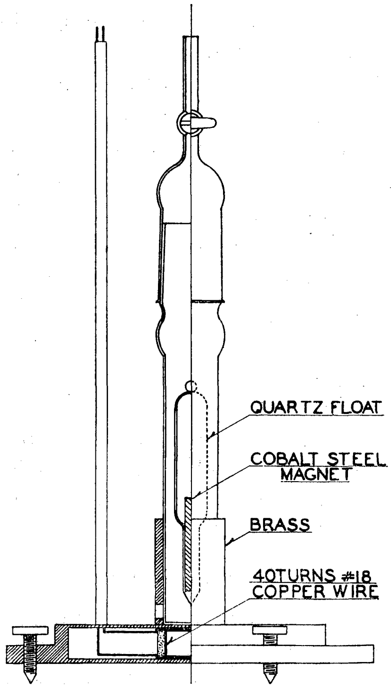

Fig. 2.—Density apparatus.

3. Carbon Dioxide Equilibration.—Saturating towers of a type described by Kraus[11] were used and filled with glass pearls. The gas current acting as an air lift circulated the water over the pearls and gave very efficient scrubbing. The gas was first scrubbed with a large quantity of the standard water which was frequently renewed. It was next thoroughly dried and then saturated by long and repeated contact with the unknown sample. As it left the sample the gas passed through reflux condensers and freezing traps to recover any water carried out, and this was united with the main sample. The density of the standard water was not affected by carbon dioxide treatment in this way.

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(10) A. B. Lamb and R. E. Lee, **This Journal**, **35**, 1666 (1913).

(11) C. A. Kraus, and H. C. Parker, *ibid.*, **44**, 2429 (1922).

4. Index of Refraction Measurements.—We fortunately were able to secure the loan for a time from the U. S. Forest Products Laboratory of a Rayleigh gas interferometer, through the courtesy of Dr. Alfred J. Stamm whose assistance is gratefully acknowledged. For this instrument a liquid cell-pair was constructed of Pyrex consisting of a 90-cm. long tube 3 cm. wide within which a 1-cm. tube was sealed by means of side inner seals (Fig. 3). Plate glass windows were cemented on the parallel ground ends. The standard water was placed in the larger tube and the sample in the smaller one. The whole cell was immersed in a water thermostat. Readings could be repeated to three or four scale divisions, so that the instrument was sensitive to refractive index differences of about 2×10^{-8}.

TABLE I

REMOVAL OF DEUTERIUM FROM WATER

I. Mixed Recovery

(1) Electrolysis stage	(2) $-\Delta d \times 10^6$	(3) $-\Delta d \times 10^6$ after CO_2 treatment	(4) $\Delta n \times 10^7$	(5) $-\Delta' d$ calcd. from $\Delta n \times 10^6$
Ia	14.0		[a]	
	13.8			
Ib	21.2		6.05	15.8
	21.4		6.3	
Ic	23.3		5.85	
	23.5		6.05	15.5
	23.7			
	24.6			
Id	24.0		[a]	
	24.1			
	25.5			
Ie	25.4		6.05	16.3
	24.8		6.3	
	24.6			
IIa	17.1	15.0	6.05	15.2
	17.2		7.0	
IIb	20.3	16.0	6.6	15.7
	20.3		6.8	
IIc	22.1	16.6	6.8	15.9
IId	25.4	16.5	6.7	15.9
			6.9	
II. Hydrogen Burned in Air				
IIIa	6.8			
	6.5			
IIIb	8.3			
	8.2			
IIIc	10.4			
	10.6			
	11.8			
IIId	12.0			
	11.9			
IVa	7.6	13.6		
IVb	8.1	16.3		
IVc	8.9	16.4		
IVd	8.9	16.7		

[a] In runs Ia, Id the amount of water available was too small for a determination of Δn.

Results

The columns of Table I show (1) the run (Roman numeral) and stage of electrolysis (small letter) referred to; (2) the difference in d^{25}_{25} between the purified electrolyzed sample and the purified standard water; (3) the same difference after the sample had been equilibrated with carbon dioxide and repurified; (4) the difference in index of refraction between the purified sample and the purified standard water (in run II these measurements were made on the samples which had been treated with carbon dioxide); (5) the specific gravity difference calculated from the measurement of n. In columns 2, 3 and 4 of Table I, each figure represents an individual determination. In calculating the values in column 5, the mean of the corresponding experimental values was used in each case. These results are also exhibited in Fig. 4, in which, however, only the mean values appear. The two upper curves represent the density differences obtained in runs III and IV by separation recovery. The lower two curves are the results of runs I and II by mixed recovery. The small circles and crosses on the middle curve show the values for all samples treated with carbon dioxide. The large circles give the values calculated from the index of refraction measurements.

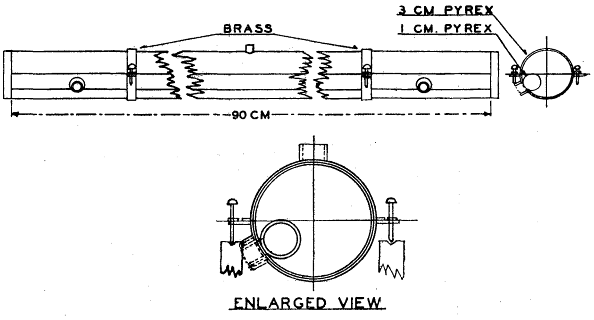

Fig. 3.—Interferometer cell.

For comparison with the water of Lake Mendota, we also made some density determinations on water from Lake Michigan, on the artesian well water of the Madison City supply, and on two samples of sea water taken from the Atlantic near the S. E. corner of Martha's Vineyard island.

TABLE II

Sample	$\Delta\gamma$		
Lake Michigan	+0.3	+0.4	+0.2
Madison City Water	−0.2	−0.3	
Atlantic Ocean I	+1.4	+1.8	
Atlantic Ocean II	+1.4	+1.6	

Table II gives the density differences of these samples from Lake Mendota water.

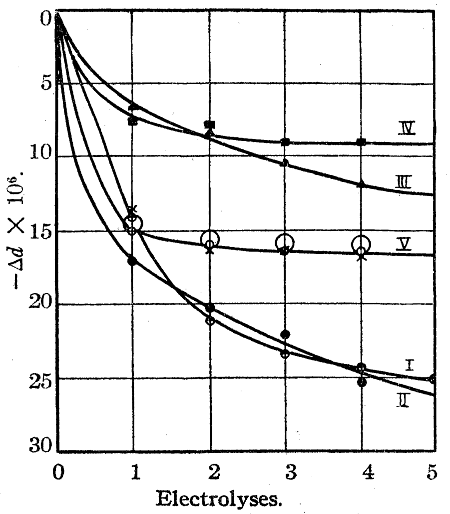

Fig. 4.—Removal of deuterium from water: ●, II knallgas water; ◓, I knallgas water; ○, V knallgas water; after carbon dioxide treatment; O, calcd. from interferometer; ▲, III hydrogen burned in air; ■, IV hydrogen burned in air; ×, air water after carbon dioxide treatment.

Discussion of Results

(a) **Mixed Recovery.**—Runs I and II are in substantial agreement with the results of Johnston[3] in that they seem to show composite density decrements due to (1) the progressive removal of all the deuterium, (2) a more or less steady but incomplete removal of O^{18}. Our results differ from his in that the decrement due to O^{18} removal does not seem to be constant and reproducible from stage to stage and run to run. Since the electrode surface and other conditions may be expected to vary with time, a completely constant fractionation factor for oxygen seems hardly to be expected. If our results are treated by Johnston's method of extrapolation to stage zero to correct for O^{18} removal, the residual density difference depends on the method of extrapolation. For these and other reasons, we have preferred to rely on the carbon dioxide method of restoring the original O^{18}/O^{16} ratio, rather than on correcting for its displacement by the electrolysis. Our average density decrease per stage due to oxygen in run II is 2.0 γ compared to the value 1.6 γ given by Johnston. (There is, of course, no reason why the gross separation factor in the two cases should be identical.)

(b) **Carbon Dioxide Equilibration.**—When samples from the mixed recovery electrolysis (run II) were treated with equilibrated carbon dioxide for several days, they showed in every case an *increase* in density (*i. e.*, an approach to the density of the original water). After removal from the apparatus, purification and density determination, the samples were returned to the apparatus and treated with carbon dioxide for several days more. The treatment was continued in every case until there was no further measurable change in density. The final values obtained (run II, column 3, Table I) point clearly to 16.5 ± 0.5 γ as the best value for the density decrement of deuterium-free water.

(c) **Separation Recovery.**—In two runs by this method density decreases of only about 12 and 9 γ, respectively, were obtained in four stages of electrolysis and burning. Since nearly all the deuterium (accounting for a density decrease of 10–15 γ) must have been removed in the first stage, the only way of accounting for this large excess density is to assume either that the nearly pure protium becomes reënriched in deuterium at each stage, or else that the oxygen isotope ratio has been significantly altered. To test the latter hypothesis, the samples from run IV were equilibrated with carbon dioxide against the standard water, and all showed further *decreases* in density (*cf.* columns 2 and 3, Table I). These decreases, which average 7.4 γ for the four stages, are in the direction, are of the order of magnitude to be expected from the work of Dole and others, since the oxygen of the original water had been replaced by (heavier) air oxygen in the burned water. The value found (7.4 γ) lies between those given by Dole and by Morita and Titani.[9] The indicated value for the density decrease of deuterium-free water is here again 16.5 $\pm$ 0.5 γ in complete agreement with the "mixed recovery" value.

(d) **Interferometry.**—Index of refraction measurements furnish independent evidence of the removal of deuterium from water, since unlike the density the value of n is relatively independent of changes in the amount of O^{18}.

It may be inferred from earlier work[3,12] that if $-\Delta d$ is the difference in density at 25° between two samples of water low in deuterium and normal as to oxygen isotope ratio, then $-10^6\Delta d$

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(12) D. B. Luten, Jr., *Phys. Rev.*, **45**, 161 (1934); L. W. Tilton and J. K. Taylor, *Bur. Standards J. Research*, **13**, 207 (1934).

should equal about (1062/453) × $10^7 \Delta n$ where Δn is measured with white light at the same temperature. Applying this factor 2.34 to the measured index of refraction differences in run II, column 4, we obtain the calculated density differences in column 5, which are somewhat lower than the measured values (col. 3). This suggests that the factor 2.34 may be a little low. Best agreement would be secured by using the value 2.39. The extra handling and purification of the samples with the attendant dangers of fractionation or contamination may be responsible for the slight lack of agreement found, or the error may reside in the density and index of refraction work of others on which the calculation is based. In any event, the total discrepancy is less than 1 part per million in the density, and is probably within the error of the refractive index determinations.

Run I was made before we had begun to use the equilibration method, and therefore the index of refraction measurements were made on samples of which the O^{18} content had been lowered by electrolysis. This should have caused a decrease in the observed Δn, so that a positive correction should be applied to the Δn figures in Table I, run I, column 4. Subtracting from the observed value of $-\Delta d$ for stage Ib the hypothetical value 16.0 γ and correspondingly subtracting 16.5 from the observed value in stages Ic and Ie, we get the values 5.3, 7.0, and 8.6 as the decreases due to O^{18} removal. Multiplying these by the factor 0.073 to convert $10^6\ \Delta d$ into $10^7\ \Delta n$, we have as O^{18} corrections +0.4, +0.5 and +0.6. Adding these to the observed $10^7\ \Delta n$ values and multiplying by the conversion factor 2.39 we arrive at the values 15.8, 15.5 (and 16.3) which may be compared with the directly measured values 16.0 and 16.6 in run II and 16.3 and 16.4 in run IV. We thus have two fully independent and two partly independent series of values, obtained in two different ways, all of which are consistent with the value 16.5 ± 0.5 γ for the decrease in specific gravity of water due to complete removal of deuterium without disturbance of the oxygen isotope ratio. If this result is accepted, and the value 1.1074 is correct for the specific gravity of pure deuterium oxide (oxygen normalized) at 25°, the protium–deuterium ratio in Lake Mendota water becomes 6400 ± 200. (This computation takes account of the non-additivity of volumes found by Luten[12] as does the calculation of Δn just given.)

Since the measurements reported in Table II indicate in connection with many published results of others that Lake Mendota water has about the same density as surface fresh water everywhere, the value 6400 may perhaps be taken as the correct value for such water in general.

Using this ratio, Aston's recent redetermination of the physical atomic weights of the hydrogens and the Mecke–Childs conversion factor, the physical atomic weight of ordinary hydrogen becomes 1.0083 and the chemical value 1.0081.

This work was furthered by grants from the Research Committee of the University, whose aid is gratefully acknowledged.

Summary

1. Surface water from Lake Mendota (Madison, Wis.) was freed from deuterium by repeated electrolysis with recombination of the electrolytic gases. When the *deficiency* in O^{18} thus caused had been restored by carbon dioxide equilibration against the original water, the density loss due to deuterium alone was 16.5 γ.
2. The same water was electrolyzed in stages and the electrolytic hydrogen burned in air. The *excess* of O^{18} thus introduced was removed in the same way, and the density loss was again 16.5 γ.
3. Index of refraction measurements on the equilibrated water indicated that the entire decrease was due to deuterium.
4. Index of refraction measurements on electrolyzed but not equilibrated water gave values consistent with the postulated displacement of the oxygen isotope ratio.
5. The protium–deuterium ratio in surface fresh water inferred from these results is 6400 ± 200, confirming Lewis' early estimate.
6. Both the lower and the higher values of this ratio reported in the literature may possibly be due to actual differences in the water studied, but it is believed that many of them rest upon inadequate correction for alteration in the oxygen isotope ratio.

MADISON, WISCONSIN RECEIVED JULY 16, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Influence of Combustion Conditions on the Density of Water Formed from Commercial Hydrogen and Oxygen

BY W. HEINLEN HALL AND HERRICK L. JOHNSTON

It was suggested in an earlier paper[1] that conditions at the time of combination of hydrogen and oxygen might influence the density of the water formed, particularly if the two gases were not present in the stoichiometric proportions. A further check on this point appeared of interest because of the possible significance of such an effect in the determination of isotope ratios.

To accomplish this a number of experiments have been carried out, with oxygen and hydrogen from commercial tanks. The gases were either combined by ignition in a small blowtorch of glass, to produce a flame, or the mixed gases reacted on a catalyst surface of platinized asbestos. The water vapor was condensed, the water purified[2] and its density determined to roughly 1 p. p. m. by the submerged float method. Precautions[3] were taken to avoid possible errors due to barometric variations or to changes in weight or volume of the glass float. Combustions were made out of contact with air.

The results of these experiments are given in Table I, where they are classified with respect to the conditions of combustion. As shown, the catalyst was employed under three sets of conditions. III represents conditions similar to those in our earlier work,[4] in which the catalyst chamber was heated to 300° and the mixed gas passed slowly through a loose plug of the platinized fiber. Reaction took place over a large area of catalyst[5] surface, without incandescence, and there was relatively long contact between the mixture of steam and the gas introduced in excess. The conditions in IV were similar, except that the catalyst chamber was not heated. An approximate temperature of 100° was maintained by the heat of reaction. In the experiments listed under II the mixed gases were directed onto a small area of the catalyst by a capillary which almost touched the asbestos. This resulted in a much more localized reaction with the result that incandescence was produced in a small zone adjacent to the capillary. In reality combustion probably occurred as a homogeneous gas phase reaction in a thin flame adjacent to the catalyst surface. In this series of experiments the walls of the catalyst chamber were cooled with water, which condensed the steam and thus removed it from the active zone.

TABLE I

Condition of combustion	Volume of O_2 per unit volume of H_2	Sample	Densities relative to normal water ΔT	Δd (p. p. m.)
I Flame at tip of glass blowtorch				
(a) Stoichiometric proportions	0.5	A3	+0.010	+2.6
(b) Oxygen in excess	4	A1	+ .010	+2.6
	0.7	B2	+ .012	+3.1
(c) Hydrogen in excess	.06	A2	+ .006	+1.6
II Glowing catalyst in water-cooled copper tube				
(a) Oxygen in excess	0.75	A5	+0.013	+3.4
(b) Hydrogen in excess	.2	A4	+ .013	+3.4
III Catalyst at 300° in heated Pyrex tube				
(a) Oxygen in excess	1.0	A8	−0.002	−0.5
	1.0	B3	− .020	−5.2
(b) Hydrogen in excess	0.1	A6	+ .018	+4.7
	.16	A7	+ .021	+5.5
	.25	B5	+ .021	+5.5
IV Catalyst at 100° in uncooled Pyrex tube				
(a) Oxygen in excess	1	B4	−0.014	−3.7
(b) Hydrogen in excess	0.125	B1	+ .025	+6.5

The columns in the table refer to: proportions in which the gases were supplied from the tanks, measured by flowmeters; identifying sample numbers, with the letters A and B used to distinguish two different pairs of oxygen and hydrogen tanks used in the investigations; and the temperatures of floating equilibrium and corresponding density increments, relative to purified samples of Columbus city water.

Interpretation and Discussion of Results

The low density of sample A2 may indicate a slight effect, due to excess hydrogen, in the flame experiments. However, the effect, if present, is no greater than the limits of error of the determination. Nor is the density of the water pro-

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[1] Hall and Johnston, THIS JOURNAL, **57**, 1515 (1935).

[2] Snow and Johnston, *Science*, **80**, 210 (1934).

[3] Johnston, THIS JOURNAL, **57**, 484 (1935).

[4] The same lot of platinized asbestos was used in all of the catalyzed experiments of the present work as was used in the early investigation.

[5] Analysis of the gas which came from the catalyst in one experiment, with an initial mix of 27 parts oxygen to 73 of hydrogen, showed that the oxygen removal was 95% complete.

duced from the "B" pair of tanks significantly different from that of the "A" pair. We take 2.5, the average of the four samples secured in the flame combustions, as the value best representative of the hydrogen and oxygen in the tanks and use this as a reference point to measure the effect of the various conditions accompanying the catalytic experiments.

The consistently high values (2 to 4 parts per million relative to the flame experiments) obtained with excess hydrogen in series III and IV are well outside the experimental error and are opposite in sign to effects which might be anticipated on the basis of comparative reaction velocities of light and heavy hydrogen.[6] They may be accounted for by the exchange reaction

$$H_2O(g) + HD = HDO(g) + H_2 \qquad (1)$$

for which platinum is observed to be a catalyst.[7] Equilibrium constants for this reaction are 2.0 and 1.38 at 100 and 300°, respectively.[7b] Table II records the relative densities to be expected with equilibrium fully attained.[8]

TABLE II

EQUILIBRIUM DENSITIES (CALCULATED) FOR THE RUNS WITH HYDROGEN IN EXCESS

Sample	Hydrogen steam ratio	Density above normal water, p. p. m.
A6	4.0	7.6
A7	2.1	6.7
B5	1.0	5.4
B1	3.0	13.5

Failure to attain full equilibrium, particularly at the lower temperature, is to be expected since the time of contact with the catalyst was much shorter than that found by A. and L. Farkas[7b] for complete equilibrium.

With excess oxygen, under the conditions pertaining to series III and IV, densities are consistently low (3 to 8 parts per million). Although the exchange reaction

$$H_2O^{18} + O^{16}O^{16} = H_2O^{16} + O^{16}O^{18} \qquad (2)$$

would lead, qualitatively, to water of low density, the quantitative effect of this reaction could not exceed approximately 0.3 p. p. m. in the experiment at 300°, or about 1 p. p. m. at 100°.[9] The low densities must therefore be the result of higher reaction velocities of $O^{16}O^{16}$ as compared with $O^{16}O^{18}$. It is evident that platinum is a much poorer catalyst for the exchange of oxygen with water than for the exchange of hydrogen with water.

The results in Series II are probably to be accounted for on the theory that here we are dealing with a homogeneous gas phase reaction in which the isotope proportions remain unchanged, as in the flame, and that rapid removal of water vapor from the gas phase prevents a subsequent hydrogen exchange with sample A4.

The Density of Atmospheric Oxygen

These experiments confirm a reinterpretation[10] of an observation reported in our previous paper.[1] The fact that tank hydrogen burned in air (flame) produced water of higher density than that resulting from reaction of the same tank hydrogen with oxygen from normal water (catalyst) was attributed by us to the relative proportions in which the gases were brought together in the two combustions. On the basis of the present work we see that the density of samples 4(a, b) of the earlier work were probably *high* to the extent of about 2.7 parts per million due to the hydrogen exchange reaction on the catalyst. With this correction applied the discrepancy between samples (4) and (5) of that work is *increased* to give a difference of 6.6 p. p. m. The combustion in atmospheric oxygen gave the water of higher density. This is in good agreement with independent work of Dole,[10] who reports 6.0 p. p. m. greater density for water produced by combustion of hydrogen with atmospheric oxygen than for water produced by combustion of the same hydrogen with oxygen from normal water.

The conclusions in the earlier paper respecting the O^{18} and O^{17} enrichment of water from commercial electrolytic cells are not changed by the results reported here. Since the conditions of combustion were the same with samples 2 and 3 (a, b) the influence of the hydrogen exchange reaction must have canceled out in the comparisons of densities.

Summary

Density comparisons of water produced by

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(6) H. W. Melville, *J. Chem. Soc.*, 797 (1934).

(7) (a) Horiuti and Polanyi, *Nature*, **132**, 819 (1933); (b) A. and L. Farkas, *Trans. Faraday Soc.*, **30**, 1071 (1934).

(8) The hydrogen was produced by electrolysis of water and should be nearly normal unless the electrolyte was newly prepared. The oxygen was produced by the fractionation of air and might be expected to contribute, in itself, a density abnormality of about 6 p. p. m. (*cf. seq.*) except for some probable isotope separation in its production. For purposes of this computation we have taken the hydrogen as normal (H/D ratio of 5800) and have credited the 2.5 p. p. m. abnormality to the oxygen alone.

(9) This calculation is based on the enrichment factors computed by Urey and Greiff [THIS JOURNAL, **57**, 321 (1935)] and on an O^{16}/O^{18} ratio of approximately 500.

(10) Malcolm Dole, *J. Chem. Phys.*, **4**, 268 (1936).

combustion of hydrogen and oxygen from commercial cylinders show: (1) that the proportions in which the gases are brought together for reaction results in no significant change in the isotopic composition of either hydrogen or oxygen if the combustion occurs in a flame.

(2) That changes of isotopic composition sufficient to affect the density of the resulting water by several parts per million may occur if the combination takes place on a platinum catalyst. With oxygen in excess the density of the resulting water may be low and appears to be accounted for by lower reaction velocities of oxygen molecules containing the heavier isotopes. With hydrogen in excess the resulting water was found, under certain conditions, to be high in density. This appears to be the consequence of an incomplete exchange reaction between steam and the excess hydrogen.

An exchange reaction between steam and molecular oxygen does not appear to be significantly catalyzed by platinum at 300°.

Previous data[1] corrected for the hydrogen exchange are in quantitative agreement with Dole's discovery[10] that water produced from hydrogen and atmospheric oxygen is denser by about 6 parts per million than water produced by combination of the same hydrogen with oxygen obtained from normal water.

COLUMBUS, OHIO RECEIVED JUNE 29, 1936

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF STANFORD UNIVERSITY]

Kinetics of the Vapor Phase Reaction of Mercury and Halogens

BY RICHARD A. OGG, JR., HENRY C. MARTIN AND PHILIP A. LEIGHTON

There appears to have been but little study of the familiar combination of mercury with halogens. In particular, no evidence has as yet been adduced to show that such a reaction can take place other than at the surface of liquid mercury. It is desired to report the preliminary results demonstrating the occurrence of a rapid vapor phase combination of mercury and bromine and to discuss the kinetics of this process.

The method previously described[1] for demonstrating visually the evaporation of mercury was extended to observe qualitatively the reaction of mercury vapor with halogens. A dish of warm liquid mercury was interposed between a mercury "resonance" lamp and a fluorescent screen. The ascending vapor was manifested as a dark shadow on the screen. Introduction of a small dish containing liquid bromine or warm iodine crystals into the space above the liquid mercury caused the shadows to vanish, only to reappear after removal of the halogen.

Estimates of the rate of the mercury–bromine reaction were made by an adaptation of the "diffusion flame" method employed by Frommer and Polanyi[2] in their studies of sodium vapor reactions. Mercury vapor (at a known partial pressure of some 0.01 to 0.1 mm.) carried in dry air at atmospheric pressure was allowed to flow through a nozzle into a reaction cell filled with air at atmospheric pressure and bromine vapor at a partial pressure of some 10 to 40 mm. The reaction zone was maintained at approximately 110°.

Quartz windows allowed a beam of light from a mercury "resonance" lamp to traverse the reaction zone and by means of quartz lenses an image of the nozzle and surrounding region was cast upon a fluorescent screen. With suitable rates of flow (a linear nozzle velocity of about 1 cc./sec.) the reaction "flame" was observed as a circular shadow projecting from the nozzle image. Visual estimation was made of the light absorption in various parts of the "flame," and compared with that in blank experiments in which air containing mercury vapor at various known concentrations was allowed to flow into the bromine-free cell. In this manner a rough estimate could be made of the total number of mercury atoms present in the mercury–bromine "flame." The reciprocal of the mean life of the mercury atoms in the "flame" divided by the bromine concentration yields the bimolecular velocity constant.

The mercury–bromine reaction appeared to be one of the first order with respect to each reactant. Upper and lower limits for the velocity constant under the above conditions were estimated as

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(1) P. A. Leighton and W. G. Leighton, *J. Chem. Education*, **12**, 139 (1935).

(2) L. Frommer and M. Polanyi, *Trans. Faraday Soc.*, **30**, 519 (1934).

10^7(mole/cc.)$^{-1}$ sec.$^{-1}$ and 10^5 (mole/cc.)$^{-1}$sec.$^{-1}$, respectively. Experiments were also made on the temperature coefficient. The temperature of the reaction cell was rapidly lowered from 120 to 50°, other conditions (rate of flow, concentrations of reactants) being maintained constant. No appreciable change could be observed in the size of the "flame" shadow. This result allows a conservative estimate of some 5 kcal. as the upper limit of the activation energy, and it may well be zero. A few experiments with mercury–iodine "flames" indicated the rate to be essentially the same as that of the mercury–bromine reaction. The reaction products were mercuric bromide and iodide, respectively.

These preliminary results allow decision between the only two plausible mechanisms for the mercury–bromine reaction. The first mechanism embodies two consecutive metatheses, of which the first would be rate determining.

$$\mathrm{Hg} + \mathrm{Br_2} \longrightarrow \mathrm{HgBr} + \mathrm{Br} \qquad (1)$$

$$\mathrm{HgBr} + \mathrm{Br_2} \longrightarrow \mathrm{HgBr_2} + \mathrm{Br} \qquad (2)$$

The second mechanism involves only an association.

$$\mathrm{Hg} + \mathrm{Br_2} \longrightarrow \mathrm{HgBr_2} \qquad (3)$$

The heat of dissociation of HgBr is given by Sponer[3] as 25.4 kcal. per mole. Using the accepted value of 45.2 kcal. per mole for the heat of dissociation of bromine, reaction (1) is seen to be endothermic by 19.8 kcal. Hence the corresponding activation energy would be at least this great. Experimentally the observed activation energy is nearly zero. Further, a bimolecular reaction having a normal collision rate [10^{14} (mole/cc.)$^{-1}$sec.$^{-1}$] and an activation energy of 19.8 kcal. would have at 110° a rate constant of only some 10^3(mole/cc.)$^{-1}$sec.$^{-1}$—a value much smaller than the lower limit estimated for the experimental value. Hence it may be concluded that the mechanism involving reactions (1) and (2) plays no appreciable role, and that the observed mercury–bromine reaction is due to the association reaction (3). Exactly similar considerations obtain for the mercury–iodine reaction.

An association reaction such as (3) may be slower than the collision rate for three reasons: (a) activation energy may be required; (b) there may be "steric hindrance"; (c) triple collision with a third body (in this case an oxygen or nitrogen molecule) may be necessary. Were the slowness of the observed mercury–bromine reaction due only to factor (a), the activation energy would be from 12 to 15 kcal., corresponding, respectively, to the upper and lower limits of the velocity constants. The extreme smallness of the observed activation energy leads to the conclusion that the second and third factors are more important.

As an approximate estimate of the rate of triple collision the rate constant for the recombination of bromine atoms in the presence of a third body may be chosen. For a considerable number of different molecules this constant has a value[4] of approximately 10^{15}(mole/cc.)$^{-2}$sec.$^{-1}$. At 110° and atmospheric pressure the concentration of air molecules is some 4×10^{-5}(mole/cc.). Hence if reaction (3) occurred at every triple collision the apparent bimolecular velocity constant would be some 4×10^{10}(mole/cc.)$^{-1}$sec.$^{-1}$. Since this value is over a thousand-fold greater than the estimated upper limit of the velocity constant for the mercury–bromine reaction, it is entirely consistent to assume that the association reaction (3) occurs only on collision with a third body. Theoretical considerations[5] indicate that association reactions which form a triatomic molecule should require triple collisions. The design of the apparatus was not such as to allow experimental test of the above conclusion by studying the dependence of the mercury–bromine reaction upon the concentration of inert gas. In future study of the reaction it is planned to make this test.

Assuming the mercury–bromine reaction to be a three-body process, it is seen that the efficiency of triple collisions is relatively small. The experimental results do not allow decision as to whether this is due to activation energy or "steric hindrance." Were the activation energy 5 kcal., the calculated rate at 110° would be reduced by a factor of some seven hundred.

It is interesting to compare the above results on the mercury–bromine and mercury–iodine association reactions with the studies of Polanyi[6] on the initiation of hydrogen–chlorine reaction chains by atoms of zinc, cadmium and mercury. At 300° zinc and cadmium atoms were found to initiate chains, presumably by processes analogous to reaction (1) above. The respective velocity constants were estimated as some 10^{10} and

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(3) H. Sponer, *Z. physik. Chem.*, **B11**, 425 (1931).

(4) K. Hilferding and W. Steiner, *ibid.*, **B30**, 399 (1935).

(5) L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932.

(6) M. Polanyi, *Trans. Faraday Soc.*, **24**, 606 (1928).

10^9(mole/cc.)$^{-1}$sec.$^{-1}$, respectively. This is not inconsistent with the assumption that zinc and cadmium atoms can combine with chlorine by association processes analogous to reaction (3). Presumably these reactions would also require triple collisions and have rate constants of the same order as those found for mercury–bromine and mercury–iodine association. Hence under the experimental conditions employed by Polanyi (total gas pressures of a few mm.), the bimolecular velocity constants for the zinc–chlorine and cadmium–chlorine association reactions may be estimated as at most some $10^5 - 10^6$(mole/cc.)$^{-1}$sec.$^{-1}$. This is very much smaller than the experimentally observed velocity constants for the metathetic reactions, and hence the association plays a negligible role. With mercury atoms and chlorine it appears that the reverse situation obtains, since it can be shown that the process analogous to reaction (1) is about equally endothermic for all halogens. This conclusion is in agreement with the observation of Polanyi that mercury atoms do not initiate chains in hydrogen–chlorine mixtures.

Summary

1. It has been shown that mercury atoms enter into a rapid vapor phase reaction with halogens.

2. At 110° and in the presence of air at atmospheric pressure the mercury–bromine reaction appears to be of the first order with respect to each reactant, and the velocity constant lies between 10^7 and 10^5(mole/cc.)$^{-1}$sec.$^{-1}$.

3. The temperature coefficient is very small, an upper limit of 5 kcal. being estimated for the activation energy.

4. It appears that the mercury–bromine reaction must take place as an association process, most probably in triple collisions with molecules of inert gas. The efficiency of triple collisions appears to be relatively small.

STANFORD UNIVERSITY, CALIF. RECEIVED JULY 27, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, ALABAMA POLYTECHNIC INSTITUTE]

Photography of Minima in the Magneto-Optic Apparatus

BY GORDON HUGHES

The work of Allison[1] and others on the magneto-optic apparatus has been called into criticism by several investigators[2–4] due to their inability to operate the magneto-optic apparatus successfully. In the face of the many admitted complexities and difficulties encountered in its use the failure of some might be readily expected. The purpose of this investigation has been to develop a completely objective method for the study of the minima of light intensity in the apparatus and thus demonstrate, beyond doubt if possible, the reality of the minima and the validity of the visual results previously obtained with the apparatus. During the course of this study several photographic methods have been employed with only partial success. Their failure has been due entirely to mechanical difficulties. The method described here is free of these inherent defects and with it consistent positive results have been obtained. This method has been made as completely automatic as possible in an effort to reduce the personal factor to a minimum. Since the results obtained by this photographic method may be interpreted into fairly accurate quantitative measurements, this work has had the added purpose of determining the quality of the minima under varying conditions in an effort to improve them for visual work.

Experimental Technique

Methods have been devised[2–4] for testing the presence of minima by comparing the light through the apparatus with a sample of light brought to one side of the coils and then joined with the main beam. In these methods one is never sure that both beams suffer the same optical conditions at all times. The Wollaston prism was employed in this study since with it there is no doubt that the treatment of both beams is optically identical. That is to say, the intensity ratio of the two beams is independent of variations in the intensity of the incident light. It has the further advantage that its use doubles the absolute intensity change for the effect, on the hypothesis that the effect is a rotation of the plane of polarization of the incident light.

The apparatus was essentially identical with the conventional one used for visual work except for the substitu-

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(1) Allison and Murphy, THIS JOURNAL, **52,** 3796 (1930).

(2) Slack, *J. Franklin Inst.*, **218,** 445 (1934).

(3) McPherson, *Phys. Rev.*, **47,** 310 (1935).

(4) Farwell and Hawkes, *ibid.*, **47,** 78 (1935).

tion of the Wollaston prism, W in Fig. 1, for the analyzing Nicol prism. Before photographic work was started sufficient work had been done visually with the Wollaston to show that minima could be observed with this type of prism as well as with the Nicol prism. The lens L_2 focused the two images of the single vertical slit S sharply on the photographic plate P_2. The Nicol prism N was set with its plane of polarization at an angle of 45° to the horizontal. The Wollaston prism mounted in a revolving head was turned to an angle midway between the angles of extinction of each of its two beams. This procedure gave two ribbon-like beams in a horizontal plane of nearly equal intensity falling on the photographic plate.

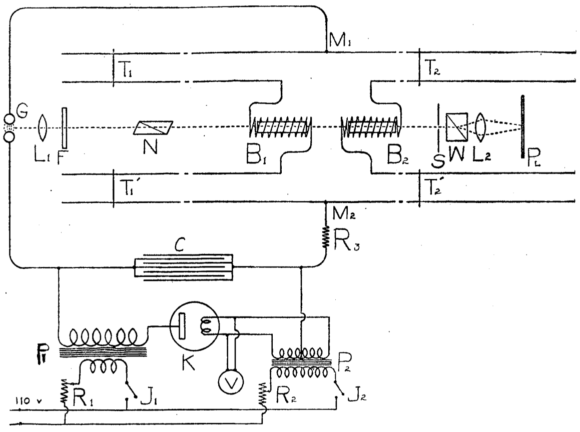

Fig. 1.—Magneto-optic apparatus.

The camera consisted of a simple frame to hold the plate which could be racked along the horizontal track by steps of 4 mm. With this horizontal motion it was possible to take 16 to 20 pictures in a row and a vertical motion of the plate in the frame permitted several rows on a plate. The time of exposure for each picture was made uniform by a synchronous motor timing device which gave to each exposure two and two-thirds seconds or some multiple of that time. At the same time the interval between exposures was kept at a constant one and one-third seconds. Eastman Hyperpress plates were used in this study since only a small amount of blue light was available for an exposure. The Hyperpress plates served admirably when developed with the contrast developer recommended for their use.

The magnesium 4481 Å. line was used. Short exposures were desirable in order that the electrodes of the spark gap should not overheat nor burn away appreciably from one exposure to the next. Exposures which gave a rather dense blackening were found to give more consistent results than those which were less dense. Plates which were not properly exposed were not included in the summary of results below.

The microphotometer employed in determining the densities of the exposures was of the conventional design with vacuum thermocouple and short-period high-sensitivity galvanometer. It was equipped with recording drum and glass scale so that the densities could simultaneously be recorded and measured directly from the galvanometer deflection on the glass scale. Most of the determinations were read directly from the scale as this was less time consuming than recording and then measuring the microphotometer traces.

The electrical system as shown in Fig. 1 is the same as that used for visual work except for the introduction of R_3, an electrolytic resistance of 130 ohms which effectively damped out oscillations in the electrical circuit and made the spark breakdown at G much steadier as well.

The breakdown at G was analyzed by means of a high-speed rotating mirror mounted on a Beams pneumatic top. The light, first focused on a narrow slit, was reflected from the mirror onto a photographic plate. Microphotometer traces of these exposures are shown in Figs. 2 and 3. The time scale is approximate only since no accurate measure of the speed of the top was made. Figure 2 is the type of breakdown obtained when R_3 was not present and shows the highly oscillatory nature of the current in the trolley system and coils. Figure 3 is the breakdown with R_3 inserted. Its damping value is apparent. Photographs of minima were attempted with both types of spark and it was found that only the damped spark gave positive results.

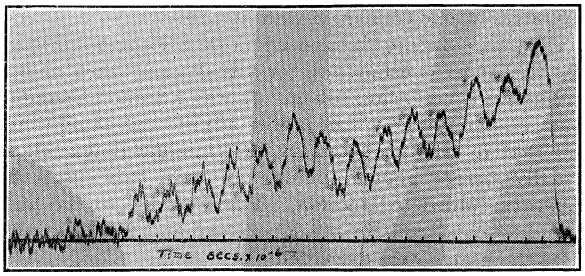

Fig. 2.—Normal spark discharge used for visual work.

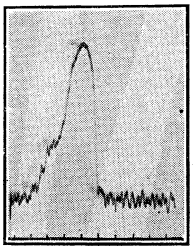

Fig. 3.—Spark discharge with damping resistance.

Since the results of visual work preclude any possible large change in light intensity to be photographed, it was apparent that a true picture of any real effect could be obtained only from the average effect in a large number of pictures. Under optimum conditions, the variable factors, intensity of light, current in the coils, and the optical condition of the liquids, would remain constant from one exposure to the next. It was with these variations in view that exposures were made in rapid succession first with the trolley contacts T_2 and T_2' at the proper position for a minimum and then off this position, alternating for possibly 16 to 20 pictures in a row. The number of rows of pictures starting with an "off" about equalled the number starting with an "on." The "on" position for any given compound had been determined previously from repeated visual observation. In determining a desirable "off" position, a position was taken which was known to be free of minima as shown from a chart of all known minima or a solution of the material to be examined was placed in the apparatus and the regions of the scale on either side of the minimum position were scanned visually to find one location free of minima. In the cases of the compounds used: for lithium chloride the "off" position was 2.1 cm. ahead of the "on" position, for cupric chloride the "off" was 0.9 cm. back of the "on" position, for phosphoric acid "off" was 1.05 cm. ahead of "on." The concentration of compound for all but a few pictures was 1 to 2 parts in 10^5 parts of water. This relatively high concentration was necessary since the Wollaston prism was set so that its two beams were at 45° angles to the plane of the polarizing nicol. Bishop, Dollins and Otto[5] report a reduced sensitivity of the apparatus at this point.

In every case water blanks were photographed prior to compounds. The compound to be studied was added to the same tube which had contained the water blank in order that the optical system should remain intact for all exposures of one compound and its blank.

The particular apparatus used for the photographic work was in almost constant use for visual work when photographs were not being taken. It was assumed therefore that the apparatus was in proper adjustment at all times and that it was not necessary that minima be examined visually before photographing. In only two cases the apparatus failed to function. This was due to the high humidity conditions in the laboratory and for these two cases the plates were discarded.

Discussion of Results

Figure 4 is an enlarged reproduction of some of the exposures on a typical plate. In the top row every other pair of lines represents an "on" exposure. Alternate pairs of lines were made when the trolley was on the position of a minimum and the other pairs when the trolley was off this position as described above. Since the two beams making lines A and B were of nearly equal intensities and were polarized at 45° angles to the light from the polarizing nicol, any rotation of the plane of the light before it reached the Wollaston would have caused a dimming of one of the beams and a brightening of the other. On the assumption that there was a change in the plane of polarization on passing through a minimum, there should have been a momentary difference in the density ratio of the lines A and B as this position was crossed.

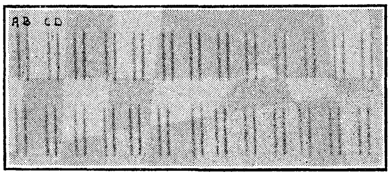

Fig. 4.—Enlarged reproduction of typical plate.

Figure 5 is a typical microphotometer trace showing only the peaks or maximum density points for a picture similar to Fig. 4.

TABLE I

MICROPHOTOMETER READINGS H_3PO_4 10^{-5} G./CC. FROM DENSITOMETER TRACES

On minimum			Off minimum		
A cm.	B cm.	A–B cm.	C cm.	D cm.	C–D cm.
3.60	5.00	1.40	3.50	5.05	1.55
3.40	5.30	1.90	3.65	5.30	1.65
4.00	5.05	1.05	3.65	5.45	1.80
3.35	5.05	1.70	2.60	4.85	2.25
3.20	4.75	1.55	3.15	4.90	1.75
3.15	5.10	1.95	2.80	4.95	2.15
3.80	5.35	1.55	2.90	4.80	1.90
3.25	5.25	2.00	3.35	5.50	2.15

Mean "on" 1.63 cm. Mean "off" 1.90 cm.

Difference "off" – "on" = 1.90 – 1.63 = 0.27 cm. = G

From Glass Scale

On minimum			Off minimum		
A cm.	B cm.	A–B cm.	C cm.	D cm.	C–D cm.
29.90	28.55	1.35	30.00	28.45	1.55
30.10	28.20	1.90	29.85	28.15	1.70
29.50	28.40	1.10	29.80	28.00	1.80
30.20	28.40	1.80	30.90	28.60	2.30
30.30	28.70	1.60	30.35	28.50	1.75
30.30	28.35	1.90	30.70	28.50	2.20
29.70	28.10	1.60	30.60	28.70	1.90
30.25	28.20	2.05	30.10	27.95	2.15

Mean "on" 1.66 cm. Mean "off" 1.92 cm.

Difference "off" – "on" = 1.92 – 1.66 = 0.26 cm. = G

Table I presents a set of measurements made on the microphotometer trace of Fig. 5 and the reading on the glass scale for the same plate. The base line in Fig. 5 from which the peaks were measured is arbitrary and is on the opposite side of the peaks from the zero of the glass scale.

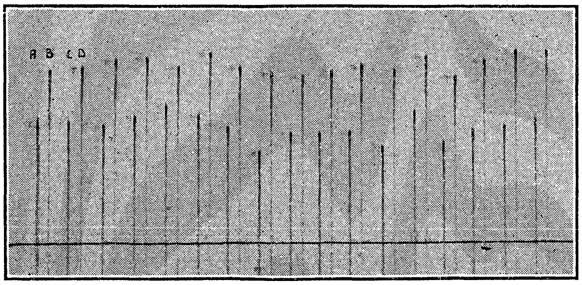

Fig. 5.—Microphotometer trace of maximum density points of typical plate.

The readings on the glass scale are presented to demonstrate the reliability of density measurements made in this manner when compared to the generally accepted method of measuring microphotometer traces. That nearly exact duplication is shown is sufficient justification for the direct measurement of the galvanometer deflection.

The value of G in the above table represents a difference in density which should be obtained if the minima have been photographed. The value

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(5) Bishop, Dollins and Otto, THIS JOURNAL, **55**, 4365 (1933).

in centimeters as recorded has no absolute significance since the measurements were made only to show a difference in density "on" and "off" minima and are not a measure of this difference in absolute terms. Table II presents the results of water blanks photographed just prior to the photographs recorded in Table I. The photographs of the acid solution were made with the acid in the identical tube which had contained the blank placed in the apparatus in the same position as the blank. Several series of pictures were made in which different cells were used for the solution and the blank. These blank pictures were not comparable with solution pictures since the collimation of the light was different for different cells.

TABLE II

DENSITOMETER READINGS FOR WATER

	On minimum			Off minimum	
A cm.	B cm.	A–B cm.	C cm.	D cm.	C–D cm.
17.70	16.35	1.35	17.50	16.40	1.10
17.65	16.30	1.35	17.60	16.30	1.30
17.50	16.35	1.15	17.40	16.20	1.20
17.40	16.20	1.20	17.40	16.20	1.20
17.80	16.50	1.30	17.85	16.50	1.35
17.50	16.50	1.00	18.00	16.55	1.45
18.00	16.50	1.50	17.80	16.50	1.30
17.55	16.45	1.10	17.80	16.65	1.15
Mean "on" 1.24 cm.			Mean "off" 1.26 cm.		

Difference "off" – "on" = 1.26 – 1.24 = 0.02 cm. = G

If the minima are characteristic of the compound in the cell, it is necessary that the value of G for the blank be lower than this value for a compound. Such is the case in Tables I and II. The data in Tables I and II are the results of two lines of eight pictures each. Since some 90 lines each containing as many and more pictures to the line were recorded, a more complete view of the average result is seen in Table III wherein are the averages of a few typical lines under various conditions.

The value G for a compound and the corresponding value for the water blank may be compared directly since the two sets of pictures were made and microphotometered at the same time. The value of G for one blank may not be compared with that for a different compound since the various pictures of compounds were taken at different times, on different plates, and were examined with the microphotometer at different sensitivities. A fair comparison may be made between the percentage by which the value of G differs from the value of the "off" reading for any water picture and this percentage for any compound. The sign of this percentage is purely conventional. It is taken as positive when the value of "on" is greater than the value of "off." This difference in percentage between water and compound was employed in a previous publication on this work[6] as the criterion of the minima having been photographed. Although it is an unsatisfactory measure and has no quantitative meaning, nevertheless it does indicate a density difference between "on" and "off" pictures of compounds and blanks which is sufficient proof of the reality of the minima.

The seeming discrepancy in the sign of the percentage between lines number 1 and 2 of the first group of Table III and the other lines of the group and a similar discrepancy in line number 6 of the second group is explained in Fig. 2. Considering the case of lines 1 and 2 let the rectangular figures represent the density curves of a pair of lines of a picture "off" a minimum. As represented A is somewhat brighter than B. These curves from the data of Table III will look as A′, B′ for the picture "on" a minimum. For such a case the percentage would have a positive value since A−B is smaller than A′−B′. Examples of this condition are lines numbered 3, 4 and 5. For lines 1 and 2 the direction of the intensity change in each beam is the same as that of lines 3, 4 and 5 but the initial intensity ratio of the two beams is reversed. For these two lines the density curves would be as in Fig. 6. The percentage in this case is negative. Many pictures were made at each of the two settings and the sign of the percentage was consistent for all pictures at each setting. The value of the percentage for water was found to be nearly zero and to vary with no regularity in sign as may be seen in Table III.

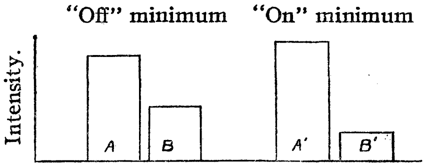

Fig. 6.—Percentage positive.

Duplicate exposures were made with the current in the coils B_1 and B_2 in Fig. 1 reversed to its original direction in order that any characteristic of the electrical circuit or optical system that might be giving these results should be detected.

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(6) Hughes and Goslin, *Phys. Rev.*, **47**, 317 (1935).

TABLE III

FIELDS ASSISTING, CURRENT IN REGULAR DIRECTION

		Compounds					Blanks				
No.	Material	On cm.	Off cm.	G cm.	%	No. of pairs	On cm.	Off cm.	G cm.	%	No. of pairs
1	H_3PO_4	5.61	6.37	0.76	−11.9	14	6.26	6.14	0.12	+1.9	14
2	$PbCl_2$	6.84	7.54	.70	− 9.2	12	5.76	6.08	.32	−5.2	14
3	Li_3PO_4	2.23	1.99	.24	+12.0	10	1.57	1.53	.04	+2.6	14
4	HBr	2.83	2.62	.21	+ 8.0	12	1.88	1.90	.02	−0.52	13
5	LiBr	1.93	1.77	.16	+ 9.0	13	1.41	1.37	.04	+0.21	13

FIELDS ASSISTING, CURRENT IN REVERSED DIRECTION

		Compounds					Blanks				
No.	Material	On	Off	G	%	No. of pairs	On	Off	G	%	No. of pairs
6	H_3PO_4	4.57	4.14	0.43	+10.5	14	2.19	2.17	0.02	+0.91	13
7	HBr	6.79	7.19	.40	− 5.5	14	4.49	4.50	.01	−2.2	14
8	LiBr	5.22	5.50	.28	− 5.2	14	4.08	4.13	.05	−1.2	14
9	H_3PO_4	1.12	1.25	.13	−10.4	20	0.61	0.61	.00	0.0	17
10	$CuCl_2$	0.87	0.95	.08	− 8.4	17	1.45	1.41	.04	+2.7	20

The two groups in Table III show the effect of reversing the direction of the current. Minima were photographed when the two magnetic fields were in the same direction, that is, when the two adjacent ends of B_1 and B_2 were N and S, respectively, and when the fields were in opposite directions. The results listed in Table III are for fields in the same direction. Pictures were made with the current in either direction when the fields were in opposite directions. No appreciable difference was noted in the quality of the minima for the different directions of the fields or current.

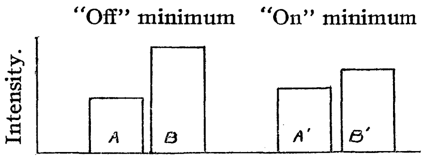


Fig. 7.—Percentage negative.

Since the purpose of this work was to show by a photographic test that minima are real it is necessary to consider the results of all the pictures which have been taken for this purpose, excluding only those which for valid reasons would not be expected to give positive results. The following reasons were considered valid for discarding pictures and the results of pictures taken under such conditions were not included in the means, percentages or totals given below.

1. Pictures taken with an unsteady spark were discarded. If the spark was unsteady for an entire plate the entire plate was discarded. If in a plate the spark was noticeably unsteady for a single line on the plate and with the proper adjustment became steady for the later pictures on the plate only the bad line was excluded. If for one picture in a line the spark was unsteady and that unsteadiness for the particular picture was recorded in the notes, the one picture affected was not included in the average for the line.

2. Plates were discarded which did not have the proper development or which showed slight scratches due to handling.

3. Plates which had an improper exposure as described above were discarded.

4. Plates were discarded which had an improper spacing between the lines. The lines on these plates were too close together due to an improper distance between camera and lens.

5. When it was found that positive results were never obtained when the resistance R_3 was omitted from the circuit those pictures taken without it were discarded.

6. This report does not carry the results of 200 pictures obtained before an automatic timing device was used. These results are positive but since the timing was uncertain they are not included.

7. A few lines of pictures taken when the concentration of material present was too low to give minima are not included.

8. Those pictures are not included for which visual observation showed the minima of an impurity present in the solution to be close to the "off" position of the minimum under consideration.

9. The pictures which were taken under conditions of high humidity are not included. Visual work has shown minima under such conditions to be very poor and with extreme humidity to disappear completely.

Table IV presents the average percentage difference for all pictures of compounds and water except those specified above with each of the four possible electrical connections. In determining the mean percentage for compounds the sign of the individual percentages is not considered since it must necessarily change with the electrical connection. In the case of water, however, an algebraic mean is given since the percentages appeared positive and negative in all connections.

TABLE IV

		Compounds		Blanks	
Fields	Current	%	No. of pictures	%	No. of pictures
Assist	Regular	+ 7.8	730	+1.46	208
Assist	Reversed	− 9.5	255	+1.0	109
Oppose	Regular	−11.5	265	−1.0	190
Oppose	Reversed	+12.3	246	+0.76	53

Mean per picture 9.4% Mean per picture +0.46%
Total pictures 1496 Total pictures 560

TABLE V

		Compounds		Blanks	
Fields	Current	%	No. of pictures	%	No. of pictures
Assist	Regular	+10.8	137	+0.45	89
Assist	Reversed	− 9.9	103	−1.44	54
Oppose	Regular	− 8.0	30	−0.82	46
Oppose	Reversed	+ 9.1	68	−0.11	36

Mean per picture 9.9% Mean per picture −0.35%
Total pictures 338 Total pictures 225

Table V is reproduced from a previous publication on this work.[6] The results presented have been incorporated in Table IV. It is of interest to note that the percentage for compounds varied only 0.5% with the addition of 1158 new pictures while the water, which shifted on either side of zero for the different connections, changed the sign of its earlier mean value with the addition of only 325 new pictures.

The water blanks tabulated above were made with samples of very pure water. The difference in conductivity between this water and a solution of an acid of a concentration of 1 part in 10^5 parts of water is large, and it has been suggested that the minima might be due to this change in conductivity. To investigate this point pictures were taken with the trolley on and off the position of the phosphoric acid minimum when only 1 part of cupric chloride in 10^5 parts of water was present in the tube. The percentage for 56 of these pictures was 0.91, showing conclusively that minima can be obtained for a particular substance only when the trolley is at the proper position regardless of the other materials present in the tube.

Since the differences in density to be measured in this procedure are small, it was found that the utmost care had to be exercised in the handling and development of plates and in their examination with the microphotometer. The plates were carefully inspected before placing in the microphotometer and any dirt or lint in the exposed area was gently brushed aside. In those cases where lint was found on the plate after the lines had been measured the line or lines in question were remeasured along with neighboring lines so that a proper comparison could be made. For example, in a particular strip of picture the "on" pictures were all larger than the "off" pictures except one pair. A bit of lint was found on one of the four lines of this pair of pictures and whereas the density differences read

	A	B	Diff.
on	14.43	14.10	0.33
off	14.50	14.10	.40

before cleaning, they read

on	13.70	13.39	0.31
off	13.58	13.34	.24

after cleaning, in accord with the other pictures in the strip.

The difference in actual galvanometer deflection recorded as A and B above for the two readings of the same lines may be due to a motion of the

TABLE VI

DIFFERENCES FOR PICTURES ON MINIMUM

	Trial 1 cm.	Trial 2 cm.	Trial 3 cm.	Trial 4 cm.
	1.08	1.10	1.10	1.10
	1.09	1.16	1.00	1.00
	1.08	1.10	1.10	1.00
	0.92	1.01	1.10	1.05
	1.17	1.19	0.90	0.90
	1.31	1.37	1.10	1.05
	1.07	1.17	1.35	1.45
	1.11	1.22	1.10	1.10
	1.20	1.38	1.30	1.30
	1.14	1.32	1.20	1.35
Mean	1.117	1.202	1.115	1.130

DIFFERENCES FOR PICTURES OFF MINIMUM

	Trial 1 cm.	Trial 2 cm.	Trial 3 cm.	Trial 4 cm.
	1.20	1.24	1.10	1.35
	1.26	1.29	1.15	1.30
	1.24	1.32	1.35	1.25
	1.15	1.25	1.10	1.00
	1.26	1.30	1.45	1.30
	1.35	1.44	1.40	1.35
	1.29	1.32	1.15	1.20
	1.25	1.35	1.28	1.20
	1.16	1.26	1.15	1.20
	1.32	1.41	1.35	1.35
Mean	1.248	1.318	1.248	1.250
Percentage	10.4	9.9	11.2	10.3

plate in its holder on the microphotometer causing a slightly different length of the line to have been measured. Many strips of pictures were examined along different sections on the length of the lines and although the lines varied in density along their length the density difference between the lines of a pair varied but little. Table VI presents the results of one strip measured four times.

Only the differences between the lines are recorded since it is these values that determine whether the minima have been photographed or not. Trials 1 and 3 were made on the top edge of the strip while 2 and 4 were made on the lower edge. To determine the constancy of the microphotometer Trials 3 and 4 were made several days after 1 and 2. Due to the removal of the plate from the microphotometer after each trial, a variation in the individual values recorded is to be expected. The percentages recorded in the table indicate in a measure the quality of the minima and from their values it will be observed that the minima vary but little along the length of the lines in a series of pictures. These percentages also indicate with what error a series of lines may be read over a period of time.

The means recorded in Tables I and II are simple arithmetic means. Such averages used in the course of this study gave results confirming visual work. It has been pointed out, however, by critics interested in this investigation that the simple averages used were obtained from data many of whose individual members deviated widely from the mean, and that this large deviation might be the major factor in giving the desired result. The author appreciated from the first of this study that the effect obtained was a small one and close to the experimental error. For this reason a very large number of photographs were taken with as many variations as possible. The fact that these many pictures gave the desired result was not considered sufficient evidence for the proof of this effect because all of the groups of pictures contained pictures which deviated widely from the mean. A recalculation of all the results was therefore made in which the extreme cases in the data were discarded in an effort to obtain a result free from such cases.

Using the average deviation of the individual pictures from their simple average it was found that 0.1% of all the pictures deviated from the average by more than three times the average deviation, 11.0% deviated by twice the average deviation and 34.0% by more than the average deviation. There was no appreciable difference in the number nor magnitude of the deviations for any group of pictures as compared to any other group.

The data presented in Table IV, recalculated, using only those pictures which are within twice the average deviation are presented in Table VII.

TABLE VII

SELECTED DATA FROM TABLE IV

		Compounds		Blanks	
Fields	Current	%	No. of pictures	%	No. of pictures
Assist	Regular	+ 9.9	662	+0.03	184
Assist	Reversed	−15.0	234	+1.1	101
Oppose	Regular	−12.3	245	−0.6	169
Oppose	Reversed	+13.1	219	+ .67	47
Mean per picture 10.5%				Mean per picture +0.09%	
Total 1320				Total 506	

On the basis of this calculation the minima appear better than before. The general effect on the individual strips was to raise the percentage. For some strips the percentage was lowered but in no case was there a change of sign of the percentage for compounds. In the strips for water there were many changes of sign and the direction of the change in percentage followed no general trend. This statistical treatment of results shows that the effect of the minima is superimposed on a changing background and that without this background the effect would appear larger and more pronounced than these results seem to indicate. A second recalculation using only those pictures within the average deviation gave results only slightly different from those in Table VII. Since one of the purposes of this investigation was to picture photographically that which the eye sees visually, one is hardly justified in discarding any data except the very extremes. It is the opinion of the writer that the truest picture of this effect is obtained when the result is calculated from data which come within twice the average deviation.

The Absolute Intensity Change for a Minimum

A study was made to determine the absolute value of the intensity change occurring when the trolley was moved to the position of a minimum from off this position. The measurement of the absolute value of this change was accomplished by imposing a 1% change on the intensity of each of the beams from the Wollaston prism by rotating the prism through an angle of 17′ which in accord with the cosine squared law gives the desired change. The mounting of the Wollaston was equipped with a divided circle with a vernier. Stops were placed on the vernier so that the Wollaston could be rotated readily through 17′ and a series of pictures was taken with the prism alternately at 45° and 45°17′. The 1% changes could be compared directly with pictures "on" and "off" minima. In setting up a plate in the microphotometer there is always some doubt as to the section along the length of the line that is being measured. For this reason it was thought that a proper comparison might not be made between the 1% changes and the minima pictures and a second series of pictures was made therefore in which the 1% changes were made in the same strip as the minima pictures. The sequence "on," "off" and 1% was repeated throughout the strip. The absolute value of the change thus determined was 0.7%. This value is the average of 168 pictures of compounds compared with 150 pictures of the 1% change. The maximum value of this change photographed for a series of two or more pictures was 1.0%. The value of the change when the data are treated as above using only those values which come within twice the average deviation is 0.8%. This is the average of 155 pictures compared with 145 pictures of the 1% change.

A small number of pictures were made on more dilute solutions to determine the manner in which the absolute change varied with concentration. To the average eye the apparatus as adjusted for photographing is sensitive to about 1 part of salt in 10^5 parts of water. When a dilution of 1 part in 10^7 parts of water was used a small positive effect of 0.3% was observed. A dilution of 1 part in 10^9 parts of water gave erratic results similar to a blank run.

Criticism has been made on the magnitude of this change in light intensity on the basis that such a small change could not be detected in visual work. The author appreciates that the small 0.7% change in light intensity is below the limit of a simple intensity change the normal eye can detect. A critical examination of this photographic measurement of the change in light intensity for a minimum shows however that such a measurement may be in error in itself and further that it may be in error when compared with the same effect measured by other means.

The several known facts about the minima themselves make it appear that the individual changes which over a long period of time cause the minima, must be in themselves very short lived. The very high resolving power of this apparatus is an indication of this short-timed effect. Minima which are separated by as little as 3 cm. on the trolley or 1×10^{-10} second are seen as separate minima. The photographs of the spark, plates 1 and 2, indicate that the light used in making the photographs comes in flashes of the order of 10^{-6} to 10^{-5} second duration. The composition of the light making up the minimum then must be a change in the intensity of the flash from the spark for a very small fraction of the total life of the flash.

The photographic effect of such a change is unknown but from the complicated effect of the flashes themselves it is probable that the change is not a simple one. Now in the above measurement the complex change of the minimum has been compared with the effect of flashes whose intensity has been changed by 1%. If the change for a minimum had been a simple change in the intensity of a continuous light then the procedure used would be valid but in view of the complex nature of the changes in the light in this experiment it is doubtful that a measurement in this manner gives the correct value.

The appearance of minima from the descriptions of many different observers indicates that any static measurement for the intensity change for a minimum over any appreciable period of time probably would not be an accurate measure of what the eye sees as a minimum. To one class of observers the minima appear as a gradually darkening field for a length of a few millimeters on the trolley. Minima appear best when observed with the trolley moving over them so that the change is seen by contrast. With the trolley moving in this manner the minima appear to shift slightly with the trolley. Now if a photograph is made with the trolley stationary at one point and the minima really do move slightly in their positions then the change for a minimum measured by such a photograph would show a change only for the time the minimum appeared at that setting of the trolley. This might be but a small fraction of the sudden change the eye would detect as the trolley passes over the proper position for a minimum.

A second class of observers sees the minimum as a shadow or dark band moving in the field of view as the trolley passes the position of a minimum. This change might be considered as a redistribution of the light in the field with little net change over the entire field. A photographic plate would record such a change as a very small one if the light from the entire field were focused to one point on the plate. Such a change would be easily discernible to the eye since vision would permit one to detect a darkening throughout different portions of the field.

There can be little doubt that the only valid way to measure the change the eye sees as a minimum is to use the eye to compare the minimum with a similar known change. Since the exact mechanism of the production of this effect is unknown at this time, it is impossible to produce a proper synthetic light change for comparison. Investigations are now under way to determine the mechanism of this effect.

Conclusion

The success of this photographic technique in detecting the small changes in light intensity due to minima over the other techniques which have been employed is due to the ability of the Wollaston prism to discriminate between the small changes in intensity due to minima and the changes in the incident light.

The observed photographic effect showed the following characteristics when tests were applied to prove the effects obtained were not due to changes in the electrical circuit or optical system:

1. No appreciable effect was obtained when blank solutions were used and the effect was only obtained for compounds when the trolley was placed at the proper position for one of the minima of a compound.
2. Minima were obtained when the setting of the trolley off the position of the minimum was taken on either side of the minimum position.
3. A decreasing absolute change in light intensity was found for decreasing concentrations of the compound.
4. The direction of the change in light intensity was found to change with the reversal of the direction of the current in the coils.
5. The direction of the light intensity change was found to reverse with the setting of the Wollaston prism on either side of the critical 45° position.

These five characteristics of the 2300-odd pictures taken in this investigation indicate that there is a small photographic effect in the magneto-optic apparatus which is characteristic of the compound present in the apparatus. This photographic effect was found to occur only at the positions of minima previously determined from repeated visual observation. The absence of minima in blank solutions; the absence of minima except at the proper trolley positions for a particular compound; and the reversal of the effect with the reversal of the direction of the current in the coils, have been observed in visual work. It is concluded therefore that the effect photographed is identical with the visual effect and that this effect is valid and characteristic of the compound present in the apparatus.

The author wishes to express his deep appreciation to Mr. Roy Goslin and Professor Fred Allison for their ready coöperation and many helpful suggestions in the course of this study. He wishes also to thank Mr. G. V. Waldo and Mr. H. Deer for their aid in the work and Dr. J. W. Beams for the use of his pneumatic top.

Summary

A photographic method has been developed to demonstrate the reality of minima in the magneto-optic apparatus. Microphotometer measurements of the difference in density of exposures taken on and off the positions of minima are attributed to variations in light intensity due to minima. The slight excess of the photographed effect over the experimental error necessitated a statistical study of the 2300 pictures taken in this investigation. This study showed only that the photographed effect was obscured by a background of changing light intensity. The measured change in intensity for a minimum was 0.7%. Water blanks showed approximately zero percentage change. The presence of foreign materials did not change the magnitude of the intensity change for a minimum. The direction of the effect was found to be dependent on the direction of the magnetic field in the coils.

AUBURN, ALABAMA

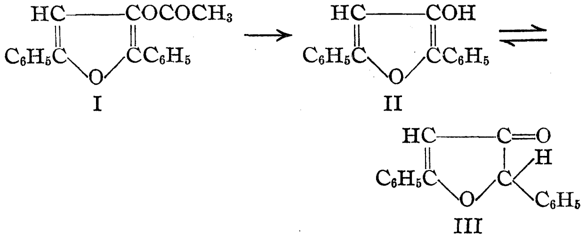
RECEIVED MAY 28, 1936

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Hydroxy Furans. II. Beta Hydroxy Diphenylfuran

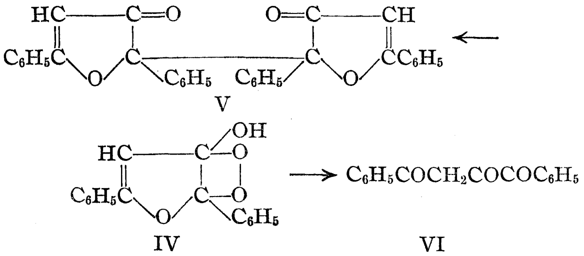
BY E. P. KOHLER AND D. W. WOODWARD

In accordance with the plan set forth in the first paper of this series[1] we have studied the properties of a β-hydroxy furan which has one phenyl group less than the one employed in the earlier work. Solutions of the new hydroxy compound were obtained by hydrolyzing the corresponding acetate[2] in the manner that was found to be best in the case of the triphenyl compound. The hydroxyl compound itself could not be isolated because it ketonizes rapidly and the less soluble ketonic modification crystallizes from the solutions.



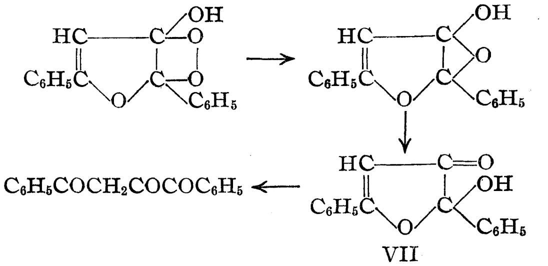
I II III

Solutions containing the enolic form, like those containing the corresponding triphenyl derivative, develop a color reaction with ferric chloride and absorb oxygen. The oxidation product is a crystalline peroxide which is unstable at the ordinary temperature and which explodes at about 100°. Like other peroxides that are formed from enols it readily gives up one atom of oxygen to mild reducing agents. Depending largely upon the medium in which it is reduced, the stable reduction product is either a dimolecular furan derivative or an open-chained triketone.



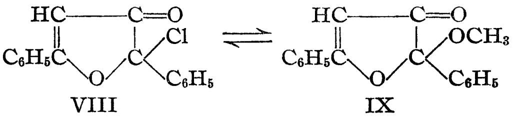
V IV VI

In accordance with the mechanism which has been established in more favorable cases in which all the intermediates were isolated, the triketone, doubtless, is the final product in a series of transformations which can be represented as follows



VII

The hydroxy furanone VII could not be isolated in this series but its ethers and esters were obtained without difficulty. Thus, when the acetate is treated either with chlorine or with phosphorus pentachloride, it is converted into a chloro furanone which passes into the ethers when it is dissolved in alcohols



VIII IX

For reasons which were enumerated in the discussion of the corresponding triphenyl derivatives, we had no doubt about the structure of these compounds, but inasmuch as others had previously obtained them by alkylating the triketone and had regarded them as open-chained compounds we decided to establish their formulas with certainty.

To this end we first prepared the two isomeric triketones, represented by formulas X and XI, and established their structure with alkaline hydrogen peroxide—the substance represented by X being oxidized to *p*-bromobenzoic acid and acetophenone while the isomer was oxidized to benzoic acid and *p*-bromoacetophenone.

$C_6H_5COCH_2COCOC_6H_4Br$ X

$BrC_6H_4COCH_2COCOC_6H_5$ XI

Each of these triketones was then methylated by means of methyl alcohol and hydrochloric acid and the structure of the resulting ethers was established by ozonization. The ozonization products of the ether derived from X were benzoic acid and methyl *p*-bromobenzoate, and those from XI were *p*-bromobenzoic acid and methyl benzoate. These are the degradation products to be expected from the cyclic ethers; they could not be formed from any open-chained ethers.

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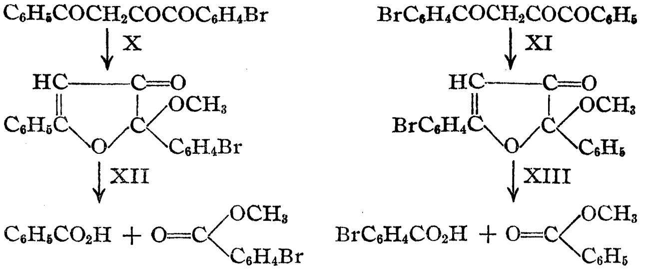
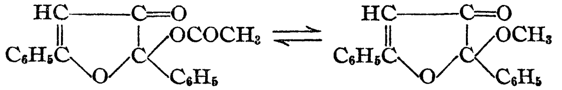
(1) Kohler, Westheimer and Tishler, THIS JOURNAL, **58**, 264 (1936).

(2) Lutz, *ibid.*, **48**, 2918 (1926).



With the cyclic character of the ethers established in this manner, the cyclic structure of substances related in origin and similar in properties can be accepted with confidence. Thus the acetate which is formed by the action of acetic anhydride on the triketone must be a furanone derivative because it passes into the ethers when it is dissolved in boiling alcohols.



XIV

This acetate was first obtained by Lutz and his collaborators who, misled by a faulty analysis, described it as the diacetate—"2,5-diphenyl-3,4-diacetoxy furan."[3] Both our analyses and our acetyl determination show that it is a monoacetate.

The chloro compound VIII which is related to the ethers in the same manner as the acetate must likewise have the cyclic structure with which we represent it. This chloro compound was first described by Lutz, Parrish and Wilder who obtained it by heating their supposed diacetate with acetyl chloride and sulfuric acid and therefore regarded it as a chloro acetate. It was later described again by Lutz and Wilder who obtained it from the triketone and the methyl ether and who, failing to recognize its identity with the previous preparation, now regarded it as the open-chained compound—$C_6H_5C(Cl){=}CHCOCOC_6H_5$. We repeated these reactions and found that the product in all cases is the cyclic chloro compound VIII. The simple and direct relations between the chloro compound, the ethers and the triketone nullify the elaborate mechanisms devised by Lutz and his collaborators.

A comparison of the reactions of β-hydroxy diphenylfuran with those of the triphenyl compound described in the earlier paper shows that the elimination of the phenyl group in the 4 position has virtually no effect on the chemical properties. Like the more highly phenylated analog, the new β-hydroxy furan behaves like an exceedingly reactive enolic form of a ketone.

Experimental

The acetate of β-hydroxy diphenylfuran[2] I was hydrolyzed by the same two methods that were employed with the triphenyl compound, namely, digestion with sulfuric acid in aqueous acetic acid and treatment with methylmagnesium iodide followed by acidification. The first method was employed for the purpose of isolating the keto furan and the second for preparing the peroxide.

Hydrolysis and Preparation of the Keto Furan.—A suspension of 10 g. of the acetate in a solution composed of 250 cc. of acetic acid, 250 cc. of water and 4 cc. of sulfuric acid was boiled in an atmosphere of nitrogen until all of the acetate had dissolved—about half an hour. The solution was made slightly alkaline with sodium carbonate and extracted with ether. The ethereal solution, washed and dried in the usual manner, was evaporated in a current of nitrogen. It deposited a solid product which after recrystallization from ether melted at 93°. The yield was 40–60%.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.3; H, 5.1. Found: C, 80.9; H, 5.3.

2,5-Diphenyl Furanone-3, III.—The furanone is unstable in the air both as solid and in solution. It is not extracted from its ethereal solutions by sodium carbonate but its solutions give a feeble color reaction with alcoholic ferric chloride.

Hydrolysis and Preparation of the Peroxide.—To a solution of methylmagnesium iodide containing three equivalents of the reagent was added 10 g. of the finely powdered acetate. The mixture was boiled for fifteen minutes and then decomposed with ice and acid in the usual manner. The ethereal layer, which gave a strong reaction with ferric chloride, was washed thoroughly with ice water and shaken with air. It soon deposited the peroxide in crystalline form. The yield was about 50%.

3-Hydroxy-2,5-diphenylfuran Peroxide, IV.—The peroxide crystallizes from ether with a molecule of ether. It can be obtained free from solvent by adding hexane to its ethereal solution and boiling off the ether. Both forms decompose in the air and explode at about 100°.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.6; H, 4.5. Found: C, 71.2; H, 4.7. Calcd. for $C_6H_{12}O_4\cdot(C_2H_5)_2O$: C, 70.2; H, 6.4. Found: C, 70.5; H, 6.3.

Reduction: The Dimolecular Product, V.—When the peroxide was reduced with potassium iodide and acetic acid it was in part converted into a dimolecular product which was also formed in variable quantities when the acetate was treated with halogens. It crystallized in minute needles and melted at 255°.

Anal. Calcd. for $C_{32}H_{22}O_4$: C, 81.7; H, 4.7. Found: C, 81.5; H, 4.9.

Reduction: β-Benzoyl Methylphenyl Diketone, VI.—Solutions of the peroxide in ethyl acetate or methyl alcohol rapidly absorbed one mole of hydrogen. The colorless solutions left after the removal of the catalyst, doubtless, contained the hydroxy furanone VII but they gradually

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[3] Lutz, Wilder and Parrish, THIS JOURNAL, **56**, 1986 (1934).

developed a yellow color and when they were concentrated they deposited oils. When the ethereal solutions were shaken with aqueous copper acetate they deposited a copper derivative from which acids liberated the triketone. Our examination of the two forms of the triketone which were reported by Lutz, Wilder and Parrish[3] (p. 1984) indicates that the yellow form is the triketone and the colorless form one of its enols. In the very pale yellow alcoholic solutions, equilibrated at the ordinary temperature, Kurt Meyer titrations showed 96.4% enol. In the distinctly yellow ethereal solutions the percentage of enol dropped to 71 and in bright yellow solutions in chloroform it is only 24. From these yellow solutions hexane precipitated the yellow form which has the characteristic color of α diketones.

2-Chloro-2,5-diphenyl Furanone-3, VIII.—A stream of chlorine was passed into a solution of 10 g. of the acetate of the hydroxy furan until the gain in weight was 3.2 g. The solution was washed with sodium bicarbonate, dried and evaporated. It deposited the chloro compound in colorless needles melting at 133°. The yield was 92%. The same chloro compound was formed when the acetate was treated with phosphorus pentachloride and also when the magnesium halide derivative of the hydroxy furan was treated with chlorine.

Anal. Calcd. for $C_{16}H_{11}O_2Cl$: C, 71.0; H, 4.1; Cl, 13.1. Found: C, 70.9; H, 4.3; Cl, 13.6.

2-Bromo-2,5-diphenyl Furanone-3.—The bromo compound was obtained in the same manner as the chloro compound. It crystallized in nearly colorless needles and melted at 135°.

Anal. Calcd. for $C_{16}H_{11}O_2Br$: C, 61.0; H, 3.5; Br, 25.4. Found: C, 61.0; H, 3.7; Br, 25.7.

These halogen compounds are active substances; in boiling alcohols they are transformed into ethers, methyl magnesium chloride reduces them to the magnesium derivative of the hydroxy furan, and when they are boiled with dioxane and water they are hydrolyzed to the triketone.

2-Methoxy-2,5-diphenyl furanone-3, IX, and the corresponding ethoxy compound are obtained when the halogen compounds are dissolved in boiling alcohols. They have been adequately described by Lutz, Wilder and Parrish who formulated them as open-chained compounds.

p-Bromobenzoyl Acrylic Acid, $BrC_6H_4COCH{=}CHCOOH$.—The acid, which was needed for the preparation of the bromo triketones, was made by dissolving one mole of bromobenzene in a liter of purified tetrabromoethane, adding 2.1 moles of aluminum bromide and then, with constant stirring and as rapidly as possible without raising the temperature above 50°, one mole of maleic anhydride. The mixture was stirred for three hours and then decomposed in the usual manner. A part of the acid separated from the acidified mixture, the remainder was recovered after distillation with steam. By recrystallization from acetone or benzene it was obtained in small, pale yellow prisms melting at 161°. The yield was 185 g.

Anal. Calcd. for $C_{10}H_7O_3Br$: C, 47.1; H, 2.8; Br, 31.4. Found: C, 47.1; H, 3.0; Br, 31.4.

The acid was converted into its chloride by heating it to 45° with an equivalent quantity of phosphorus pentachloride, removing the phosphorus oxychloride under diminished pressure and crystallizing the residue from benzene. The product crystallized in yellow needles which turned bright red on exposure to light and which melted at 103°.

p-Bromodibenzoyl Ethylene, $BrC_6H_4COCH{=}CHCOC_6H_5$.—To a solution of one mole of the acid chloride in 2 l. of benzene 1.2 moles of aluminum chloride was added while the solution was stirred and kept as free from hydrogen chloride as possible by sweeping it with a rapid current of nitrogen. The mixture was stirred and heated on a steam-bath for three hours, then decomposed in the usual manner. The product crystallized from benzene and chloroform in light yellow needles and melted at 127°. The yield was 62%. The same product was obtained in a yield of 50–60% by heating equivalent quantities of phenyl glyoxal and *p*-bromoacetophenone with two equivalents of acetic anhydride for an hour on a steam-bath.

Anal. Calcd. for $C_{16}H_{11}O_2Br$: C, 61.0; H, 3.5; Br, 25.4. Found: C, 60.9; H, 3.7; Br, 25.8.

Dibromides, $BrC_6H_4COCHBrCHBrCOC_6H_5$.—Addition of bromine to the unsaturated diketone in chloroform resulted, as usual, in the formation of two stereoisomeric dibromides. One of these dibromides separated from the chloroform in needles melting, with decomposition, at 170–175°; the other was obtained by evaporating the solution and recrystallizing the residue from ether. It melted at 116–119°.

Anal. Calcd. for $C_{16}H_{11}O_2Br_3$: Br, 50.6. Found: (I) Br, 50.5; (II) Br, 50.5.

2-Methoxy-2-phenyl-5-bromophenyl Furanone-3.—In order to convert the dibromide into the triketone a solution of 11 g. of potassium hydroxide in 100 cc. of methyl alcohol was gradually stirred into a solution of 27 g. of the dibromides in the same solvent. The solution was boiled for ten minutes, then acidified and boiled for fifteen minutes longer. The result was a mixture of triketones which were readily isolated by means of their copper derivatives but which were extremely difficult to separate by fractional crystallization. The mixture was therefore converted into ethers.

For this purpose a solution of 10 g. of the mixture in 30 cc. of methyl alcohol was saturated with gaseous hydrogen chloride. As the solution cooled it deposited 4.6 g. of an ether which separated in nearly colorless prisms and which melted at 158° after recrystallization from methyl alcohol.

Anal. Calcd. for $C_{17}H_{13}O_3Br$: C, 59.1; H, 3.8. Found: C, 59.1; H, 3.8.

Ozonization of the Ether.—A solution obtained by ozonizing 3 g. of the ether in carbon tetrachloride was evaporated under reduced pressure in a current of air. The residue was dissolved in ether and the solution was extracted with sodium bicarbonate. It removed *p*-bromo benzoic acid in 80% of the calculated quantity. The ethereal layer was evaporated and the residue was distilled under diminished pressure. The result was 0.8 g. of methyl benzoate boiling at 91° (15 mm.)—identified by the odor and hydrolysis to benzoic acid.

p-Bromobenzoyl Methylphenyl Diketone, XI.—The methyl ether melting at 158° was hydrolyzed in the usual way with methyl alcoholic potassium hydroxide and the product was isolated by means of the copper derivative. It crystallized from ether–petroleum ether in long yellow needles and it melted at 100–101°.

Anal. Calcd. for $C_{16}H_{11}O_3Br$: C, 58.0; H, 3.3. Found: C, 58.0; H, 3.7.

Proof of Structure.—A methyl alcoholic solution containing 4 g. of the triketone and 1.5 g. of 30% hydrogen peroxide was cooled to 0° and treated gradually with 1 g. of potassium hydroxide in the same solvent. The resulting red solution was left to itself until most of the color had disappeared, then acidified and extracted with ether. The oily residue left after the ether had been evaporated was digested for a short time on a steam-bath with sulfuric acid in order to decompose intermediate products, then subjected to the usual treatment for the separation of the acid and the neutral products. The neutral fraction contained only *p*-bromoacetophenone—identified as benzal *p*-bromoacetophenone. The acid fraction contained *p*-bromobenzoic acid and benzoic acid—separated by crystallization and identified by melting points. The yields were: 30% of the possible quantity of bromoacetophenone, 60% of bromobenzoic acid and 92% of benzoic acid.

2-Methoxy-2-*p*-bromophenyl-5-phenyl Furanone-3.—The second ether that was formed when the mixture of the triketones was alkylated, was obtained by concentrating the solution under diminished pressure. It crystallized from methyl alcohol in fine needles melting at 102°.

Anal. Calcd. for $C_{17}H_{13}O_3Br$: C, 59.1; H, 3.8. Found: C, 59.0; H, 4.0.

Ozonization.—The same procedure that was employed in the case of the isomeric ether resulted in methyl *p*-bromobenzoate melting at 80° and identified by comparison with a sample on hand—and benzoic acid. The yields were, respectively, 60 and 75%.

Benzoyl Methyl-*p*-bromophenyl Diketone, X.—The triketone was obtained without difficulty by hydrolyzing the ether and isolating the product by means of the copper derivative. It crystallized in yellow plates melting at 88–90°.

Anal. Calcd. for $C_{16}H_{11}O_3Br$: C, 58.0; H, 3.5. Found: C, 57.8; H, 3.5.

Proof of Structure.—Oxidation with alkaline hydrogen peroxide in the manner described under the isomeric triketone gave *p*-bromobenzoic acid—85% of the possible quantity—benzoic acid and acetophenone (50%) which was identified as *m*-nitrobenzal acetophenone.

2-Acetoxy-2,5-diphenyl Furanone-3.—All methods of preparation—from the chloro compound, the ether or the triketone—gave the same product melting at 140°.

Anal. Calcd. for $C_{16}H_{10}O_3(COCH_3)$: C, 73.5; H, 4.9; $COCH_3$, 14.6. Found: C, 73.4; H, 4.8; $COCH_3$, 14.3.

Summary

The properties of β-hydroxyl derivative of 2,5-diphenylfuran are compared with those of the hydroxyl derivative of 2,4,5-triphenylfuran. The removal of the phenyl group in the 4-position does not affect the properties of the hydroxyl compound but it diminishes the stability of the furanone into which the hydroxyl compound passes by spontaneous ketonization.

CAMBRIDGE, MASS.

RECEIVED AUGUST 5, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Researches on Pyrimidines. CLIV. Pyrimidine Side Chain Reactions Useful for the Synthesis of 1,3-Diazines Related Structurally to Vitamin B_1[1]

BY ANNE LITZINGER[2] AND TREAT B. JOHNSON

In two previous publications from this Laboratory,[3] the authors have emphasized the importance of increasing our present knowledge of aliphatic chemistry as applied to the pyrimidine cycle, and the bearing of such research developments on the determination of the correct constitution of vitamin B_1. In our preliminary paper entitled "Synthesis of Uracil-5-methylamine," we wrote as follows: "We believe that constructions of this type will prove to be of immediate interest in connection with the development of the newer chemistry of vitamin B_1."

The object of this paper is to present and describe a series of new reactions which have been applied successfully in our pyrimidine investigations, and which have opened up a practical method for synthesizing this interesting pyrimidine amine.[4] The chemistry of this amine will be discussed in the next paper of this series.[5]

The starting point of our new program of synthesis was the ethyl ester of 2-ethylmercapto-6-oxypyrimidine-5-acetic acid I which was first described by Johnson and Speh.[6] Applying suc-

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(1) This research was partially supported by a special grant from the Research Committee of the American Medical Association.

(2) This paper was constructed from a thesis presented by Dr. Anne Litzinger in June, 1936, to the Graduate Faculty of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(3) Pyrimidine paper CXLVI, Johnson and Litzinger, THIS JOURNAL, **57**, 1139 (1935); CLIII, Johnson and Litzinger, *Science*, **84**, 25 (1936).

(4) Nomenclature: Uracil-5-methylamine or thyminylamine. The last name is coined to emphasize its aliphatic nature and to indicate its relationship to the naturally occurring pyrimidine-*thymine*.

(5) CLV, THIS JOURNAL, **58**, 1940 (1936).

(6) Johnson and Speh, *Am. Chem. J.*, **38**, 602 (1907).

cessfully the different basic reactions of the Curtius technique[7] for conversion of a carboxyl into an amino group with this pyrimidine I, we have succeeded in isolating in crystalline form all the intermediate products characteristic of the series of reactions involved in the introduction of an amino group. These intermediates are recorded in Table I. A description of several other derivatives separated and identified in the course of the work is also given in the Experimental Part of this paper. We are extending this research to include the acetate derivatives of other types of pyrimidines, and characterized structurally by side chain substitutions in positions 2, 4 and 5 of the pyrimidine cycle.

TABLE I

INTERMEDIATES (PART ONE)

2-Ethylmercapto-6-oxypyrimidine-5-acetylhydrazide, II
2-Ethylmercapto-6-oxypyrimidine-5-acetylazide, III
2-Ethylmercapto-6-oxypyrimidine-5-methyl isocyanate, IV
Ethyl 2-ethylmercapto-6-oxypyrimidine-5-methylurethan IX
2-Ethylmercapto-6-oxypyrimidine-5-methylamine, VI

INTERMEDIATES (PART TWO)

Uracil-5-acetylhydrazide, XI
Uracil-5-acetylazide, XII
Uracil-5-methyl isocyanate or thyminyl isocyanate, XIII
Ethyl thyminyl-urethan, XV

Experimental Part

$\overline{\mathrm{NHC(SC_2H_5){=}NHC{=}C(CH_2COOC_2H_5)C}}\mathrm{O}$. **Ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate, I.**—The starting material of the series of reactions leading up to the final synthesis of thyminylamine was this ethyl ester of 2-ethylmercapto-6-oxypyrimidine-5-acetic acid. This pyrimidine was obtained in the form of its sodium salt by condensing diethyl formylsuccinate with ethyl pseudothiourea, in alkaline solution, according to the procedure previously described in a paper from this Laboratory by Johnson and Speh.[6] This pyrimidine is formed in excellent yield, is easily purified by crystallization from 50% ethyl alcohol, and crystallizes from hot solutions as a beautiful fibrous mass of colorless needles.

$\overline{\mathrm{NHC(SC_2H_5){=}NCH{=}C(CH_2CONHNH_2)C}}\mathrm{O}$. **2-Ethylmercapto-6-oxypyrimidine-5-acetylhydrazide. II.**—Thirty grams of the mercapto-pyrimidine acetate I (m. p. 146–147°) is dissolved in 300 ml. of absolute alcohol and to the hot solution is added 1.5 equivalents of 42% hydrazine hydrate (18 g.). The clear solution is then refluxed for two hours or until solid material begins to separate from the hot reaction mixture. Although the hydrazide is only moderately soluble in cold absolute alcohol, complete separation from solution is slow and, therefore, the reaction mixture is allowed to stand at room temperature for twenty-four hours before filtering off the crystalline hydrazide. This yields about 27 g. of the crude hydrazide melting at 198–200° with decomposition. On concentrating the alcohol filtrate more of the hydrazide is obtained contaminated with the unreacted pyrimidine acetate I. Such mixtures can be separated easily, however, by careful crystallization from absolute alcohol. Purification of the hydrazide is accomplished easily by recrystallization from 90% alcohol, and it crystallizes as sheaves of glistening plates which melt at 207–208° with decomposition. *Anal.* Calcd. for $C_8H_{12}O_2N_4S$: N, 24.54. Found: N, 24.46, 24.66.

This hydrazide is soluble in water (1 g. in 3 ml. hot and 10 ml. cold). Water is not recommended, however, as a solvent for purification as slight decomposition takes place in boiling solutions with evolution of ethyl mercaptan. Aqueous solutions of the hydrazide reduce Fehling's solution easily. The hydrazide is less soluble in absolute alcohol than in water (1 g. in 250 ml. hot and 450 ml. cold).

$\overline{\mathrm{NHC(SC_2H_5){=}NCH{=}C(CH_2CON_3)C}}\mathrm{O}$. **2-Ethylmercapto-6-oxypyrimidine-5-acetylazide. III.**—The mercapto-pyrimidine hydrazide II reacts smoothly with nitrous acid to form this azide, III. Twenty grams of the purified hydrazide is dissolved in 200 ml. of normal hydrochloric acid. To this clear solution, cooled in an ice-bath, is then added slowly, while stirring, an aqueous solution containing the required amount of sodium or potassium nitrite. An immediate precipitate of a fluffy solid is obtained which, after washing with water and drying, weighed 12 g. At ordinary temperatures this azide is stable, but on heating to 75–80° it evolves nitrogen vigorously, and then melts with decomposition at 175–180°. The compound responded to the characteristic reactions of an azide, and underwent quantitative transformations giving the corresponding ethyl and benzyl urethans and also the pyrimidine isocyanate derivative when treated with the proper reagents or solvents.

$\overline{\mathrm{NHC(SC_2H_5){=}NCH{=}C(CH_2NCO)C}}\mathrm{O}$. **2-Ethylmercapto-6-oxypyrimidine-6-methyl Isocyanate. IV.**—This interesting compound is easily prepared as follows: 2.4 g. of 2-ethylmercapto-6-oxypyrimidine-5-acetylazide is suspended in 20 ml. of dry toluene and the temperature of the heating bath slowly raised to about 80° when a vigorous evolution of nitrogen begins to take place. Too rapid heating leads to considerable decomposition and charring of the reaction product. When the violent evolution of nitrogen gas has ceased (twenty minutes) the toluene is then heated to its boiling point and the liquid finally refluxed for thirty minutes. At the end of this time, the toluene is cooled, and the insoluble isocyanate separated by filtration and washed with ether. The yield of crude material was 2.2 g. melting at 187–190° with decomposition. The isocyanate is purified by recrystallization from anhydrous dioxane, from which solvent it separates, on cooling, in the form of plates, which melt at 189–191° with decomposition. *Anal.* Calcd. for $C_8H_9O_2N_3S$: N, 19.90. Found: N, 19.74, 19.73.

This isocyanate is not appreciably soluble in the ordinary inert organic solvents and is unusually stable for an isocyanate compound. It underwent no detectable

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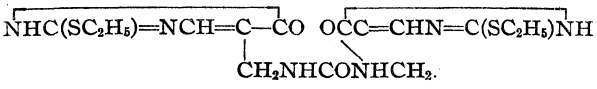
[7] Th. Curtius, *J. prakt. Chem.*, [2] **50**, 275 (1894); **58**, 190 (1898); **64**, 297, 401, 419 (1901); **91**, 1, 19 (1915); **94**, 85, 273 (1917); *Ber.*, **27**, 778 (1894).

change after preservation for five months in a tightly stoppered specimen tube. The compound responds to all the characteristic reactions of an isocyanate structure, and is a pyrimidine derivative which should prove very useful for future experimentation. It is the first mercapto-pyrimidine isocyanate derivative to be described.



$$\underset{CH_2NHCONHCH_2.}{NHC(SC_2H_5)=NCH=C\text{—}CO\quad OCC=CHN=C(SC_2H_5)NH}$$

V

Behavior toward Water: Formation of *sym.*-Di-(ethylmercapto-6-oxypyrimidine-5-methyl)-urea. V.—The rate of decomposition of the above isocyanate IV in cold water is very slow. When, however, the compound is warmed with water there is a rapid evolution of carbon dioxide, and during the time of heating there is a brief period of almost complete solution followed immediately by the precipitation of the symmetrical disubstituted urea V. While this urea constitutes the main reaction product, small quantities of the normal amine VI are also obtained when the mother liquor is concentrated to a small volume. For example: 1 g. of the isocyanate is boiled with 40 ml. of water until the evolution of carbon dioxide ceases and the solution is then cooled. We obtained 0.63 g. of the above urea crystallizing in the form of prisms and melting at 270–272° with decomposition. The compound is practically insoluble in water, and all the common organic solvents. *Anal.* Calcd. for $C_{15}H_{20}O_3N_6S_2$: N, 21.20. Found: N, 21.21, 21.16.

$NHC(SC_2H_5)=NCH=C(CH_2NH_2)CO$. **Isolation of 2-Ethylmercapto-6-oxypyrimidine-5-methylamine. VI.**—The combined filtrates and washings from the preceding experiment were concentrated to a volume of 10 ml. and the solution cooled, when 0.07 g. of this amine separated. It melted at 220–222° with decomposition. This pyrimidine is easily purified by crystallization from boiling water, and separates, on cooling, in the form of colorless needles, melting at 221–222° with decomposition. Aqueous solutions of the amine are strongly basic to the mixed indicator (methyl red and methylene blue). *Anal.* Calcd. for $C_7H_{11}ON_3S$: N, 22.70. Found: N, 23.00, 23.10.

Hydrolysis of the above pyrimidine isocyanate VI by boiling with strong hydrochloric acid leads to the formation of the hydrochloride of thyminylamine with evolution of ethyl mercaptan and carbon dioxide.

$NHC(SC_2H_5)=HCN=C(CH_2NHCONH_2)CO$. **2-Ethylmercapto-6-oxypyrimidine-5-methyl Urea. VII.**—This is formed quantitatively by action of aqueous ammonia on the pyrimidine isocyanate IV. The pyrimidine is very soluble in cold water and alcohol. It was purified by dissolving in 95% alcohol and allowing the solution to evaporate in a vacuum desiccator. In this way the urea was obtained in the form of colorless plates melting at 190–192° with decomposition. A mixture of this urea with the original isocyanate melted at 175–176°. *Anal.* Calcd. for $C_8H_{12}O_2N_4S$: N, 24.55. Found: N, 24.41, 24.64.

$NHC(SC_2H_5)=NCH=C(CH_2NHCONHC_6H_5)CO$. **2-Ethylmercapto - 6 - oxypyrimidine - 5 - methyl - phenylurea. VIII.**—This is formed by the action of aniline on the pyrimidine isocyanate IV in hot dioxane solution. The urea is easily purified by crystallization from 95% alcohol and crystallizes in plates melting at 223–224° with decomposition. The urea can be crystallized from both dioxane and water. *Anal.* Calcd. for $C_{14}H_{16}O_2N_4S$: N, 18.41. Found: N, 18.21, 18.31.

$NHC(SC_2H_5)=NCH=C(CH_2NHCOOC_2H_5)CO$. **Ethyl-2 - ethylmercapto - 6 - oxypyrimidine - 5 - methyl - urethan. IX.**—This urethan is formed by interaction of the pyrimidine isocyanate IV or the azide III with ethyl alcohol. Ten grams of the pyrimidine azide (described above) is suspended in 50 ml. of absolute alcohol and the temperature of the alcohol gradually raised by heating on a water-bath. Nitrogen is evolved vigorously and after heating one hour the azide is completely decomposed and a clear solution is obtained. The alcohol solution is now concentrated to a volume in 10 ml. and cooled when the desired urethan will separate. The yield was about 9.0 g. and the compound melted at 145–148°, to a clear liquid. The pyrimidine is purified by crystallization from 95% alcohol and separates, on cooling, in the form of plates melting at 148.5–149.5° to a clear liquid. *Anal.* Calcd. for $C_{10}H_{15}O_3N_3S$: N, 16.34. Found: N, 16.37, 16.39.

When warmed in an alcohol solution of hydrochloric acid the corresponding 2-oxypyrimidine-urethan XV is formed with evolution of ethyl mercaptan. On heating with strong sulfuric or hydrochloric acid (100–110°) the urethan is decomposed with formation of the corresponding salts of thyminylamine.

$NHC(SC_2H_5)=NCH=C(CH_2NHCOOC_7H_7)CO$. **Benzyl-2-ethyl-6-oxypyrimidine-5-methyl Urethan. X.**—The pyrimidine-azide III is decomposed smoothly, when warmed in benzyl alcohol, with evolution of nitrogen and formation of the above urethan. After thirty minutes of heating in a hot water-bath the volume of the benzyl alcohol solution is reduced to about 10 ml. and then diluted with cold water. The urethan is precipitated as an oil which finally solidifies. The yield is excellent. By recrystallization from 95% alcohol the urethan is obtained in the form of needles melting at 159–160° to a clear oil. *Anal.* Calcd. for $C_{15}H_{17}O_3N_3S$: N, 13.17. Found: N, 13.33, 13.27.

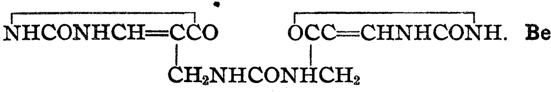
This pyrimidine is very soluble in cold benzyl alcohol (1 g. in 4 ml.), moderately soluble in 95% alcohol and insoluble in water.

Part Two

$NHCONHCH=C(CH_2CONHNH_2)CO$. **Uracil-5-acetyl Hydrazide. XI.**—The ethyl uracil-5-acetate which was used for the synthesis of this hydrazide was prepared by dissolving the ethyl ester of 2-ethylmercapto-6-oxypyrimidine-5-acetic acid I in absolute alcohol, saturating with hydrogen chloride gas and then refluxing the solution for two hours. The ester separated, on cooling, and agreed in all its properties with the pyrimidine ester previously described by Johnson and Speh.[6] To prepare the above hydrazide 2 g. of this ester, m. p. 202–204°, is dissolved in 30 ml. of 95% alcohol, and to the hot solution 1.5 g. of hydrazine hydrate is added. After refluxing for one hour and cooling for twelve hours 1.8 g. of the hydrazide separated. It is easily purified by recrystallization from boiling water and crystallizes in the form of plates which decompose without melting at about 326°, turning brown at 285°. The compound is insoluble in alcohol and the common organic solvents. Aqueous solutions of the hydrazide reduce Fehling's solution immediately. *Anal.* Calcd. for $C_6H_8O_3N_4$: C, 39.13; H, 4.40. Found: C, 39.15, 39.25; H, 4.41, 4.32.

$NHCONHCH{=}C(CH_2CON_3)CO$. **Uracil-5-acetylazide. XII.**—Four grams of the above hydrazide XI is dissolved in 100 ml. of *N* hydrochloric acid and 1.5 equivalents of sodium nitrite dissolved in the solution. There is an immediate reaction and the azide separates at once as a colorless powder. This is stable at room temperatures, but loses nitrogen when heated at 75–80° and then melts at 275–276° with decomposition. Although this pyrimidine was not analyzed, its structure was proved by its characteristic chemical behavior, yielding both urethan derivatives and the corresponding isocyanate, XIII.

$NHCONHCH{=}C(CH_2NCO)CO$. **Uracil-5-methyl Isocyanate (Thyminyl Isocyanate). XIII.**—This isocyanate was prepared according to the same technique as was used for the preparation of 2-ethylmercapto-6-oxypyrimidine-5-methyl isocyanate IV: 1.8 g. of uracil-5-acetyl azide XII yielded, when heated in toluene, 1.4 g. of the isocyanate as a colorless powder which melts at 273–275° with decomposition. *Anal.* Calcd. for $C_6H_5O_3N_3$: N, 25.15. Found: N, 25.15, 24.90.



$$\begin{array}{c} NHCONHCH{=}CCO \qquad OCC{=}CHNHCONH \\ CH_2NHCONHCH_2 \end{array}$$

XIV

Behavior toward Water: Formation of *sym.*-Di-thyminylurea. XIV.—Boiling water immediately decomposes thyminyl isocyanate XIII with vigorous evolution of carbon dioxide; 0.3 g. of this pyrimidine of m. p. 273–275°, after boiling for twenty minutes in 20 ml. of water, yielded 0.25 g. of this urea derivative. This is very insoluble in water and decomposes without further purification at 315°. *Anal.* Calcd. for $C_{11}H_{12}O_5N_6$: N, 27.26. Found: N, 27.09, 27.14.

$NHCONHCH{=}C(CH_2NHCOOC_2H_5)CO$. **Ethyl Thyminyl-urethan. XV.**—Five grams of ethyl 2-ethylmercapto-6-oxypyrimidine-5-methylurethan is dissolved in 50 ml. of 95% alcohol acidified with 5 ml. of concentrated hydrochloric acid. As soon as this solution is warmed, ethyl mercaptan is evolved, and within twenty-five minutes the urethan begins to crystallize from the hot solution, and the hydrolysis is practically complete. We obtained 3.4 g. of the above urethan melting at 254–258°. It is easily purified by crystallization from 95% alcohol and melts at 256–257° to a clear oil. The compound is more soluble in water than in alcohol. *Anal.* Calcd. for $C_8H_{11}O_4N_3$: N, 19.72. Found: N, 19.74.

This same urethan is also obtained in excellent yield by digesting uracil-5-acetylazide in absolute alcohol. When digested with either hydrochloric or sulfuric acid it is converted into the corresponding salts of thyminylamine.

$NHCONHCH{=}C(CH_2NHCOOC_7H_7)CO$. **Benzyl Thyminyl-urethan. XVI.**—When 0.8 g. of benzyl 2-ethylmercapto-6-oxypyrimidine-5-methylurethan was digested in alcohol acidified with hydrochloric acid for two hours, 0.5 g. of this urethan was formed. This is less soluble in alcohol than the corresponding mercapto compound X, and separates from this solvent in the form of microscopic plates which melt at 261–263° with decomposition. *Anal.* Calcd. for $C_{13}H_{13}O_4N_3$: N, 15.27. Found: N, 15.35, 15.55.

Summary

1. Starting with the known pyrimidine, ethyl-2-ethylmercapto-6-oxypyrimidine-5-acetate, several new derivatives have been synthesized by application of the Curtius reaction for replacement of the carbethoxy group by an amino radical.

2. Important new aliphatic derivatives of uracil have been described which will find use in developing new synthetic processes of biochemical interest.

3. A practical method is revealed for preparing uracil-5-methyl isocyanate or thyminyl isocyanate, the first isocyanate derivative to be described in the pyrimidine series.

4. Further applications of the Curtius reaction in the pyrimidine series will be made, and further synthetic work of biological interest is now in progress in this Laboratory.

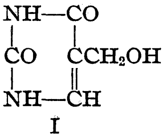
NEW HAVEN, CONNECTICUT RECEIVED JULY 25, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Researches on Pyrimidines. CLV. The Synthesis of Thyminylamine and its Conversion into Uracil[1]

BY TREAT B. JOHNSON AND ANNE LITZINGER[2]

It has previously been shown that the substitution of a carbinol radical $-CH_2OH$ in the 5-position of a 2,6-dioxypyrimidine is productive of an alcohol which easily undergoes a carbon–carbon cleavage, when subjected to hydrolysis, with formation of formaldehyde and the original pyrimidine. Such an instability was observed, for example, by Kircher[3] in 1911, who showed that the 5-carbinol derivative of 4-methyluracil II is quantitatively decomposed by digesting in boiling water with regeneration of 4-methyluracil and the liberation of formaldehyde.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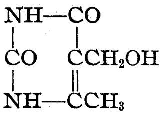
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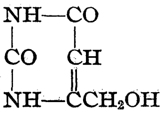
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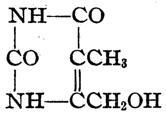
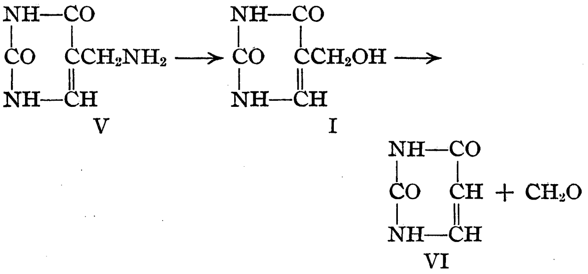

IV

A corresponding instability of a pyrimidine–carbinol linkage of this type was later found not to be the case when the carbinol radical is substituted in the 4-position of the pyrimidine cycle. Johnson and Chernoff,[4] in an investigation of synthetic pyrimidine nucleosides, prepared the thymine derivative IV which is isomeric with Kircher's pyrimidine II, and found that this compound can be heated with 10% sulfuric acid at 125° without alteration. There was no evidence of the formation of formaldehyde. Later these same investigators synthesized the corresponding carbinol derivative of uracil represented by formula III, and again made the discovery that the carbinol group could not be split off by hydrolysis,[5] with formation of uracil and formaldehyde.

These results revealed for the first time a fundamental difference in the stability of 4- and 5-carbinol substitutions in pyrimidines of the uracil type. It was, therefore, important to determine whether the fourth representative of the above series, thyminyl alcohol I, would conform to our prediction, and show the same behavior on hydrolysis as its higher homolog II.

As all attempts to produce thyminyl alcohol I by the action of formaldehyde on uracil have thus far proved unsuccessful, the authors decided to synthesize the corresponding and unknown primary base, *thyminyl-amine* V, and then convert this into the desired thyminyl alcohol I by the action of nitrous acid. A description of the preliminary reactions which have made possible the final synthesis of this interesting amine has already been given in the preceding paper of this series.[6] A complete description of the different procedures that the authors have finally applied successfully for the preparation of this interesting amine V is given in detail in the Experimental Part of this paper.



We now find that thyminylamine V, as well as thyminyl alcohol I, are both characterized by their instability when subjected to hydrolytic conditions. Both pyrimidines are decomposed by boiling with water with cleavage between two carbon atoms and regeneration of uracil VI. The primary aliphatic amine radical $-CH_2NH_2$ in the pyrimidine V is destroyed by hydrolysis with formation of uracil, ammonia and formaldehyde. The chemical evidence favors first the formation of thyminyl alcohol I as an inter-

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[1] For preliminary paper see Researches on Pyrimidines, CXLVI, THIS JOURNAL, **57**, 1139 (1935).

[2] This paper was constructed from a thesis presented by Dr. Anne Litzinger in June, 1936, to the Graduate Faculty of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy. This research was partially supported by a special grant from the Research Committee of the American Medical Association.

[3] Kircher, *Ann.*, **385**, 293 (1911).

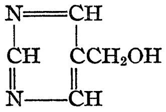
[4] Johnson and Chernoff, *J. Biol. Chem.*, **14**, 307 (1913).

[5] Johnson and Chernoff, THIS JOURNAL, **36**, 1742 (1914).

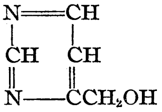
[6] Pyrimidine paper, CLIV, by Litzinger and Johnson, *ibid.*, **58**, 1936 (1936).

mediate, which being unstable then undergoes a normal hydrolysis like Kircher's pyrimidine-carbinol II, yielding uracil VI and formaldehyde. In fact, both transformations are practically quantitative. Because of the instability of thyminyl alcohol I in warm aqueous solutions, it has, thus far, been impossible for us to separate this pyrimidine from water solution after diazotization of the thyminylamine V without partial decomposition. Heretofore, we have discovered no pyrimidine constructions which reveal such characteristic differences in behavior between two carbon linkages attached to adjacent carbons in the pyrimidine ring.

It is the belief of the authors that these striking variations in chemical behavior will need to be considered carefully before corresponding constructions can be assigned to any pyrimidine compounds possessing the chemical properties of vitamin B_1.[7] Our next problem will be to determine whether the corresponding isomeric carbinol derivatives of a reduced pyrimidine substituted in positions 4 and 5, VII and VIII will show a corresponding difference in chemical stability. This study is now in progress in this Laboratory.



VII



VIII

Experimental Part

Thyminylamine or (Uracil-5-methylamine), V, $\overline{\text{NHCONHCH}{=}\text{C(CH}_2\text{NH}_2\text{)CO}}$.—This amino derivative of thymine can be prepared according to the following procedures:[1] (1) by hydrolysis of ethyl 2-ethylmercapto-6-oxypyrimidine-5-methylurethan with either hydrochloric or sulfuric acid leading to the formation of the corresponding salts of thyminylamine; (2) by hydrolysis of ethyl thyminyl-urethan with hydrochloric or sulfuric acid; (3) by hydrolysis of ethyl-2-ethylmercapto-6-oxypyrimidine-5-methyl isocyanate by action of hydrochloric or sulfuric acid; (4) by hydrolysis of thyminyl isocyanate with acids.[6]

Thyminylamine Sulfate, $(C_5H_7O_2N_3)_2{\cdot}H_2SO_4{\cdot}H_2O$.—This salt is formed by the action of concentrated sulfuric acid[8] on ethyl 2-ethylmercapto-6-oxypyrimidine-5-methylurethan according to procedure (1), but care must be taken in applying the reaction. It was found by experimentation that the best results are obtained by applying the hydrolysis reaction for two hours at a temperature of 110°. By lowering this temperature (90–100°) or reducing the time of heating, the desired change was incomplete. On the other hand, if the temperature of the sulfuric acid solution reached 120° and the heating was more prolonged, considerable charring and decomposition occurred. Five grams of the mercapto pyrimidine is stirred into 10 ml. of concentrated sulfuric acid. On heating this mixture, evolution of carbon dioxide begins at about 80°, and within a few minutes the pyrimidine-urethan dissolves completely and with no apparent evolution of ethyl mercaptan. A pale yellow solution is obtained. This is then cooled and poured into 200 ml. of water and the solution heated on a steam-bath until the evolution of mercaptan ceases. The solution is exactly neutralized with barium hydroxide to remove all sulfuric acid, and then a quantity of 0.2 *M* sulfuric acid is added, or the amount necessary to form the sulfate of the dissolved amine. The barium sulfate is then separated by filtration and the combined filtrates and washings are concentrated *in vacuo* to a volume of 15 ml. The addition of alcohol (25 ml.) leads to an immediate precipitation of the sulfate of the desired amine (3 g.) melting at 240–245°. This salt is finally purified by dissolving it in the least quantity of hot water and diluting with alcohol until the hot solution becomes turbid. On cooling, the sulfate separates in the form of glistening plates melting at 245–246° with decomposition. While the salt is insoluble in alcohol, 1 g. dissolves in 1.5 ml. of hot and 4 ml. of cold water. Ethyl thyminyl urethan is converted directly into thyminylamine by the action of concentrated sulfuric acid at 110°. The purified salt did not give Wheeler and Johnson's test for uracil.[9] *Anal.* Calcd. for $(C_5H_7O_2N_3)_2{\cdot}H_2SO_4{\cdot}H_2O$: N, 21.11; H_2O, 4.50. Found: N, 21.17, 21.10; H_2O, 3.90.

Thyminylamine Hydrochloride (Uracil-5-methylamine), $C_5H_7O_2N_3{\cdot}HCl{\cdot}0.5H_2O$.—This salt is formed by hydrolysis of ethyl 2-ethylmercapto-6-oxypyrimidine-5-methylurethan, or ethyl uracil-5-methylurethan with concentrated hydrochloric acid in a bomb tube. The degradation is complete after heating for two hours at 103–107°. The acid solution is then concentrated to a small volume and the hydrochloride precipitated by dilution with alcohol. On recrystallizing from dilute alcohol the salt separated in the form of glistening plates melting at 242–243° with decomposition. This salt is more soluble in water and alcohol than the sulfate. When 2-ethylmercapto-6-oxypyrimidine-5-methyl isocyanate or thyminyl isocyanate is digested on a steam-bath with concentrated hydrochloric acid, thyminylamine hydrochloride is formed.[10] *Anal.* Calcd. for $C_5H_7O_2N_3{\cdot}HCl{\cdot}0.5H_2O$: H_2O, 4.88; N, 23.66 (anhyd. salt). Found: H_2O, 4.82; N, 23.86.

Thyminylamine, V, $C_5H_7O_2N_3$.—An absolutely pure specimen of this amine has not been prepared. The purest product so far obtained was prepared as follows. One gram of the purified sulfate is dissolved in 10 ml. of water and the sulfuric acid removed by precipitation as barium sulfate in a hot solution. After filtering and cooling, the free thyminylamine (0.5 g.) deposits as a colorless amorphous powder melting at 260–270° with decomposition. The amine is insoluble in the ordinary organic solvents and moderately soluble in water. Warm aqueous solutions of the base were invariably characterized by a

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(7) Johnson and Litzinger, *Science*, **84**, 25 (1936).

(8) Jeffreys, *Ber.*, **30**, 900 (1897).

(9) Wheeler and Johnson, *J. Biol. Chem.*, **3**, 183 (1907).

(10) *Cf.* Naegeli and Lendorff, *Helv. Chim. Acta.*, **12**, 227 (1929).

distinct odor of ammonia resulting from a slow hydrolysis of the pyrimidine. The amine was purified for analysis by recrystallization from hot water, and separated on cooling as a colorless semi-crystalline powder melting at 265°. *Anal.* Calcd. for $C_5H_7O_2N_3$: N, 29.79. Found: N, 27.99, 27.93.

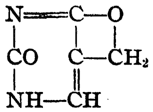
Behavior of Thyminylamine in Boiling Aqueous Solution.—An aqueous solution of 0.6 g. of thyminylamine in 40 ml. of water was boiled vigorously for twenty-five minutes, and the vapor condensed and conducted into 10 ml. of 4.5% boric acid solution. At the end of this time the borate solution was titrated with 0.02 *N* hydrochloric acid; 17.13 ml. of this standard acid was neutralized, being equivalent to 0.005824 g. of ammonia. Therefore, under these conditions, approximately 8.0% of the thyminylamine was decomposed. The acid distillate gave a positive aldehyde test with Schiff's reagent, indicating the presence of formaldehyde, and also a strong Wheeler and Johnson test for uracil.[9] It was our observation, as stated above, that thyminylamine could not be purified by crystallization from hot water without undergoing partial decomposition. The aqueous filtrates in every case responded to the characteristic color test for uracil and ammonia could be detected easily.

Behavior when Digested with Hydrochloric Acid.—0.35 g. of thyminylamine was refluxed with 15 ml. of strong hydrochloric acid for five hours, and the solution was then heated on a steam-bath for one and one-half hours longer or to complete dryness. We obtained a colorless solid residue of 0.25 g. which was recrystallized from hot water. It separated, on cooling, in the form of round, corpuscular crystals characteristic of the pyrimidine uracil and decomposed without melting at 308–312°. This solid gave a voluminous purple precipitate when it was tested according to the Wheeler and Johnson technique. It was apparent from the intensity of the color test that uracil represented the major proportion of the solid residue left after evaporation. However, the melting point is low for uracil (335°) and a nitrogen determination indicated some form of contamination. The question whether this is due to traces of thymine as a second product of hydrolysis has not been decided. In an equimolecular mixture of uracil and thymine the theoretical percentage of nitrogen would be 23.6. *Anal.* Calcd. for $C_4H_4O_2N_2$: N, 25.00. Found: N, 23.17, 23.16.

Action of Nitrous Acid on Thyminylamine

The Formation of Uracil-5-carbinol or Thyminyl Alcohol, $\mathrm{NHCONHCH{=}C(CH_2OH)CO}$.—Thyminylamine sulfate was dissolved in water and the sulfate ion removed by adding the required quantity of barium hydroxide to form barium sulfate. In the boiling solution were then dissolved two equivalents of barium nitrite, followed by the gradual addition of the required amount of 0.2 *M* sulfuric acid. The solution was then freed from barium sulfate by filtration and finally concentrated *in vacuo* to a volume of 1 cc. On adding absolute alcohol, a mixture of products was precipitated which melted from 240 to 300°. This gave a strong color test for uracil. By fractional crystallization from alcohol and ether we finally succeeded in separating a substance which melted from 190–200°, and which was probably an impure sample of the unknown thyminyl alcohol. All attempts to synthesize this alcohol by the action of formaldehyde on uracil have thus far proved unsuccessful. The carbinol radical is apparently not firmly bound at the 5-position of the uracil molecule. *Anal.* Calcd. for thyminylcarbinol, $C_5H_6O_3N_2$: N, 19.72. Found: N, 18.87, 19.01.

In a second experiment the oxides of nitrogen were conducted into an aqueous solution of thyminylamine for fifteen minutes. After concentrating the resulting solution by heating on a steam-bath, we obtained a product which decomposed at 270–295° and which also gave a good color test for uracil. Further purification finally led to a colorless substance melting at 195–200°. This material was very soluble in both cold and hot water, and was insoluble in alcohol. It was purified by crystallization from dilute alcohol. The structure of this substance was not established, but it is an interesting fact that a nitrogen determination agreed with the calculated for an inner anhydride derivative of thyminyl alcohol. *Anal.* Calcd. for $C_5H_4O_2N_2$: N, 22.57. Found: N, 22.69.



X

$\mathrm{NHCO{\cdot}NHCH{=}C(CH_2NHCSNH_2)CO}$, **Thyminyl-thiourea,** was prepared by the action of ammonium thiocyanate on thyminylamine sulfate in hot aqueous solution. It was purified by crystallization from dilute alcohol and separated in the form of glistening plates melting at 204–205° to an oil. The yield was quantitative. *Anal.* Calcd. for $C_6H_8O_2N_4S$: N, 28.00. Found: N, 27.96.

Summary

1. Methods of synthesizing the pyrimidine—*thyminylamine*—have been described in this paper.

2. A study of this amine has revealed the fact that it is very susceptible to hydrolysis and is easily converted into uracil, formaldehyde and ammonia.

3. By diazotization of thyminylamine, the corresponding thyminyl alcohol is formed. This carbinol is likewise unstable and undergoes hydrolysis with formation of uracil and formaldehyde.

4. This discovery that the substitution of hydrogen in the methyl group of thymine by an hydroxyl or amino radical weakens the carbon linkage of this side chain, is a result of biochemical significance.

NEW HAVEN, CONN.

RECEIVED JULY 25, 1936

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Reaction of Sodium with Triphenylchloromethane and with Triphenylmethyl in Organic Solvents

BY W. E. BACHMANN AND F. Y. WISELOGLE

From the results that have been reported by a number of investigators,[1] it has been concluded that sodium does not react with triphenylchloromethane or triphenylbromomethane in ether or in benzene solution. This result is strange in view of the ease with which the halogen atom of triphenylchloromethane can be removed by other metals as silver, mercury and copper and especially by sodium amalgam. In order to account for the formation of triphenylmethyl from sodium and triphenylchloromethane in the presence of bromobenzene, Morton and Stevens[1d] postulated the intermediate formation of an active "metal halyl" from sodium and bromobenzene, followed by interaction of this "sodium carrier" and the triphenylchloromethane.

During the past four years a number of us in this Laboratory, including Professor M. Gomberg, have utilized the reaction between sodium and triphenylchloromethane in ether to prepare triphenylmethyl, for we found that the reaction proceeds *rapidly* provided that fresh surfaces of the metal are exposed throughout the reaction. Indeed, the reaction is so rapid under certain conditions that it is necessary to cool the mixture. Thus, 5 g. of triphenylchloromethane can be converted completely to triphenylmethyl in ten minutes. In our opinion the reaction is ordinarily prevented or retarded by the formation of an insoluble coating of sodium chloride on the surface of the metallic sodium. If the coating is continually scraped off or if fresh surfaces of the metal are exposed in some other manner as by pressing the metal with a glass rod, then the reaction is able to proceed at a rapid rate. It is easy to understand why liquid sodium amalgam (1 or 40%) is capable of reacting rapidly with triphenylchloromethane.

It is not unlikely that as soon as some triphenylmethyl is formed part of the reaction leading to the further formation of triphenylmethyl takes place through the intermediate formation of triphenylmethyl-sodium, which then reacts with the triphenylchloromethane.

$$(C_6H_5)_3C + Na \longrightarrow (C_6H_5)_3CNa$$
$$(C_6H_5)_3CNa + ClC(C_6H_5)_3 \longrightarrow (2C_6H_5)_3C + NaCl$$

In this way a direct reaction between the sodium and the triphenylchloromethane is not involved. Whatever the mechanism, the reaction between sodium and triphenylchloromethane in ether can be made to proceed rapidly.

According to Schlenk and Marcus[1c] sodium does not add to triphenylmethyl in ether except in the form of sodium amalgam; instead, the radical is polymerized to *p*-benzohydryltetraphenylmethane under the influence of the sodium metal. Under the conditions employed by us triphenylmethyl and sodium powder reacted rapidly in ether to give triphenylmethyl-sodium in practically quantitative yield, only traces of the dimer being formed. The same authors reported that triphenylmethyl-sodium reacts with air to form triphenylmethyl, which oxidizes further to triphenylmethyl peroxide, but they give no experimental details. Inasmuch as interaction of triphenylmethyl-magnesium bromide and air gives triphenylcarbinol (in the form of its bromomagnesium salt) as the chief product,[2] we have investigated the behavior of the corresponding sodium derivative. Here, too, by passing air through a solution of triphenylmethyl-sodium we obtained triphenylcarbinol as the principal product and only a small amount of triphenylmethyl peroxide.

Although Morton and Stevens observed no reaction between sodium and triphenylchloromethane in benzene in sixty days, the reaction can be made to take place in this solvent also. The rate of the reaction in benzene is very much slower than the rate in ether and for this reason the reagents must be extremely pure if by-products are to be avoided. Thus, in two hours, by pressing the sodium with a glass rod, a 10% yield of triphenylmethyl was obtained. Triphenylmethyl-sodium can also be prepared in benzene from triphenylchloromethane and sodium provided the mixture is shaken with glass beads.

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[1] (a) Elbs, *Ber.*, **17**, 700 (1884); (b) Gomberg, *ibid.*, **33**, 3150 (1900); (c) Schlenk and Marcus, *ibid.*, **47**, 1664 (1914); (d) Morton and Stevens, THIS JOURNAL, **54**, 1919 (1932).

[2] Bachmann and Cockerill, *ibid.*, **55**, 2932 (1933).

Experimental

Formation of Triphenylmethyl.—To a mixture of 2 g. of sodium powder in 80 cc. of anhydrous ether (or 40 cc. of ether and 40 cc. of benzene) in an Erlenmeyer flask was added 5 g. of triphenylchloromethane. Frequently the sodium immediately became colored with red triphenylmethyl-sodium and the solution became yellow. The flask was fitted with a stopper bearing a movable glass rod flattened at one end. By pressing the sodium against the bottom of the flask a rapid reaction was initiated and the solution became orange-yellow as the radical was formed. After ten minutes the color began to change to the red color of triphenylmethyl-sodium, an indication that all of the triphenylchloromethane had reacted. Oxidation of the triphenylmethyl gave an 80% yield of triphenylmethyl peroxide, m. p. 185–186°. A similar result was obtained by vigorously shaking a mixture of the metal and triphenylchloromethane in ether with sharp particles of glass for twenty minutes.

p-Benzohydryltetraphenylmethane is formed to a slight extent when the complete reaction between the sodium and triphenylchloromethane is slow. This is the case when only the theoretical amount of sodium (1 atom) is employed and the mixture is shaken for a day or two in order to allow time for the last traces of sodium to react. When the reaction proceeds rapidly as is the case when the sodium is pressed with a glass rod, the formation of the dimer is practically entirely suppressed.

Preparation of Triphenylmethyl-sodium.—After pressing the sodium (2 g.) contained in a solution of 5 g. of triphenylchloromethane in 40 cc. of anhydrous ether and 40 cc. of benzene with a glass rod for ten minutes, the rod was removed and the mixture was shaken for two hours. Hydrolysis of the deep-red triphenylmethyl-sodium solution gave a 96% yield of triphenylmethane and only a trace of *p*-benzohydryltetraphenylmethane. The excellent yield of triphenylmethane is an indication of the completeness of the two reactions: the reaction of sodium with triphenylchloromethane and the addition of sodium to triphenylmethyl. Even after one-half hour of shaking the solution contained only 2% of triphenylmethyl that had not been converted to triphenylmethyl-sodium. Similar results were obtained by simply shaking a mixture of triphenylchloromethane and sodium powder in ether–benzene with sharp particles of glass for several hours. In addition to hydrolysis the triphenylmethyl-sodium was also treated with benzyl chloride to give *unsym*-tetraphenylethane and with carbon dioxide to form triphenylacetic acid in excellent yields.

By shaking a mixture of 2.78 g. of triphenylchloromethane, 2 g. of sodium powder and two dozen glass beads in 40 cc. of benzene for one month, triphenylmethyl-sodium was formed as a red precipitate. Hydrolysis gave a 70% yield of triphenylmethane.

Oxidation of Triphenylmethyl-sodium.—Dry air was passed through a solution of triphenylmethyl-sodium that had been prepared from 5 g. of triphenylchloromethane for one hour. From the products of hydrolysis there were isolated 3.15 g. (67%) of triphenylcarbinol and 0.2 g. (4%) of triphenylmethyl peroxide. Although the oily residue liberated iodine from hydrogen iodide, a search for triphenylmethyl hydrogen peroxide was unsuccessful.

Summary

Sodium reacts rapidly with triphenylchloromethane in ether provided fresh surfaces of the metal are exposed throughout the reaction.

Sodium adds to triphenylmethyl in ether and in benzene to form triphenylmethyl-sodium.

Triphenylcarbinol is the principal product of the oxidation of triphenylmethyl-sodium.

ANN ARBOR, MICHIGAN RECEIVED JULY 6, 1936

[CONTRIBUTION FROM THE GENERAL MOTORS CORPORATION, RESEARCH LABORATORIES SECTION]

The Action of Aluminum Halides on *n*-Pentane

BY A. L. GLASEBROOK, N. E. PHILLIPS AND W. G. LOVELL

Recently, Nenitzescu[1] investigated the reactions of *n*-hexane and *n*-heptane in the presence of aluminum chloride and found isomerization to the 2- or 3-methyl isomer to be the main reaction. Dehydrogenation, condensation to higher paraffins, cyclization to mono and bicyclic cycloparaffins, hydrogenation and splitting of the chain to lower paraffins also occurred. Calingaert[2] repeated the work of Nenitzescu and found that only about 6% of the reacting *n*-heptane was isomerized.

We attempted to study the reported isomerization of *n*-heptane; however, preliminary experiments gave reaction products which were very difficult to analyze and we decided to use *n*-pentane as the starting material. The use of this hydrocarbon was expected substantially to reduce the number and complexity of reaction products, and, since Nenitzescu[3] had shown the reaction between *n*-pentane, acetyl chloride and aluminum chloride to lead to the formation of *unsym*-methyl isopropyl acetone, a result which can best be explained by the preliminary isomerization of *n*-

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[1] Nenitzescu and Dragan, *Ber.*, **66**, 1892 (1933).

[2] Calingaert and Beatty, THIS JOURNAL, **58**, 51 (1936).

[3] Nenitzescu and Chicos, *Ber.*, **68**, 1584 (1935).

pentane to isopentane, we did not expect the isomerization reaction to be affected by the change in starting materials.

Using freshly sublimed aluminum chloride and dry pentane no reaction occurred even after refluxing for several days. When small amounts of water, alkyl chlorides (but not aromatic chlorides), or hydrated aluminum chloride were added to the reaction mixture, the pentane commenced to undergo decomposition almost immediately. The products did not appear to vary, regardless of the method used to start the reaction, and only the butanes and isopentane could be identified, the latter being the chief product. During the reaction, the aluminum chloride surface became coated with a layer of brown tar, which, after hydrolysis of the aluminum chloride residue, was found to consist of a mixture of highly unsaturated, halogen-containing compounds. Substances boiling higher than *n*-pentane and soluble in the reaction mixture were also formed, but, owing to the small amounts present, could not be identified.

Since water and hydrated aluminum chloride react with aluminum chloride to give aluminum oxide and hydrochloric acid, these substances were investigated for their ability to induce the decomposition of pentane in the presence of aluminum chloride. Anhydrous aluminum oxide had no effect, but when dry hydrogen chloride was bubbled through the reaction mixture, the usual reaction commenced, and, apparently, this is the substance which is responsible for the increased activity of the aluminum chloride. This fact was also observed by Ipatieff and Grosse.[4] The same explanation can also be used in the case of the alkyl chlorides, since these substances react with aluminum chloride to give hydrogen chloride.[5] In addition, we found anhydrous hydrogen bromide to be exceptionally effective in activating aluminum chloride.

Aluminum bromide was next investigated. This compound is quite soluble in *n*-pentane. The bromide proved much more effective in causing the decomposition of pentane, and it was unnecessary knowingly to add other substances to the reaction mixture to induce reaction. In one day a reaction mixture containing only 1.52 mole % aluminum bromide undergoes as much change as a reaction mixture containing 17.4 mole % aluminum chloride, and, promoted by 0.2 mole of water per mole of aluminum chloride, undergoes in two days' reaction time. Qualitatively the products obtained using the bromide catalyst were the same as those obtained using the chloride. The amount of pentane reacting increased with the reaction time and the aluminum bromide concentration. Table I gives the results obtained in a study of these variables. The amount of butanes formed is shown to increase practically linearly with the extent of the reaction, whereas the amount of isopentane formed reaches a maximum from which it slowly declines as the extent of the reaction is further increased.

The addition of such substances as anhydrous hydrobromic acid or water increases the reaction velocity. The effects caused by the addition of these substances to the reaction mixture are shown in Table II.

When gaseous *n*-pentane carried by a stream of dry nitrogen was passed over aluminum chloride at temperatures from 40 to 133°, no reaction could be detected outside of a slight discoloration of the aluminum chloride. The addition of promoter substances to the gas stream readily caused the decomposition of *n*-pentane, and it was unnecessary to use temperatures higher than 40°. Anhydrous hydrobromic acid was the most effective substance investigated for activating the aluminum chloride. Using gaseous *n*-pentane the amount of butanes formed was greatly increased and only insignificant amounts of isopentane formed. Traces of hydrogen were also formed in these experiments. Most of the higher boiling substances remained behind on the aluminum chloride and caused the latter to slowly liquefy with continued use.

The aluminum chloride became decreasingly active when the addition of hydrogen halides or halogen halide forming substances was discontinued. Aluminum chloride which had been activated by mixing anhydrous hydrobromic acid to the gas stream lost its activity more slowly than the other substances investigated, and it was also possible to activate the aluminum chloride by treatment with anhydrous hydrobromic acid prior to the introduction of the *n*-pentane vapor. This procedure was ineffective with water vapor and anhydrous hydrochloric acid. Using aluminum chloride which had been activated by treatment with anhydrous hydrobromic acid before use, we were able to test the gases leaving the

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[4] Ipatieff and Grosse, *Ind. Eng. Chem.*, **28**, 461 (1936).

[5] See, for example, Mouneyrat, *Compt. rend.*, **127**, 109 (1898).

Table I

The Effect of Reaction Time and Catalyst Concentration on the Decomposition of *n*-Pentane in the Presence of Aluminum Bromide

n-Pentane used, g.	105	105	105	105	110	110	110	110
Aluminum bromide used, g.	11.3	11.3	11.3	11.3	6.2	21.5	36.4	57.2[b]
Mole % aluminum bromide	2.82	2.82	2.82	2.82	1.52	5.28	8.94	14.05
Reaction time, hrs.	22	51	95	169	26.2	26.2	26.2	26.2
Reaction loss, % by wt.	1.0	1.4	1.0	4.3[a]	1.5	0.9	3.2[c]	6.8[c]
Butanes, % by vol.	1.5	2.8	5.0	8.8	1.5	6.1	10.2	14.1
Isopentane, % by vol.	40.8	51.0	55.9	44.2	27.2	53.5	46.8	40.4
Material boiling higher than *n*-pentane, % by vol.	2.5	3.4	3.4	5.9	2.8	3.1	5.4	5.9
Insoluble tar, % by wt.	Neg.	Neg.	0.5	1.0	Neg.	Neg.		

[a] The capacity of the gas receiver was exceeded in this experiment, and some of the gas is known to have escaped
[b] All of the aluminum bromide did not dissolve in this experiment. [c] These figures include the insoluble tar.

Table II

The Effect of Promoters in the Reaction of *n*-Pentane in the Presence of Aluminum Bromide

	Reaction with 2 cc. water added	Reaction without water	Reaction in presence of HBr	Reaction in absence of HBr
n-Pentane used, g.	200	200	202	202
Aluminum bromide used, g.	27	29	18	18
Mole % aluminum bromide	3.52	3.77	2.36	2.36
Reaction time	about 3 days		about 38 hours	
Reaction loss and tar, % by wt.	3.0	1.5	2.5	neg.
Butanes, % by vol.	10.7	5.9	7.0	3.0
Isopentane, % by vol.	58.6	51.0	51.5	42.8
Material boiling higher than *n*-pentane, % by vol.	6.0	2.7	2.5	3.6

aluminum chloride for bromine content, and found that the amount of decomposition decreased as the bromine content of the exit gases dropped.

Experimental

Reagents.—The *n*-pentane used was a commercial product derived from petroleum. Before use the material was shaken with concentrated sulfuric acid until the acid remained colorless on further treatment, then washed, dried and distilled from sodium. The distilled material had a practically constant boiling point and the constants: n^{20}_{D} 1.3579; d^{20}_{4} 0.6264. The anhydrous aluminum chloride was a c. p. grade and was resublimed in a current of dry nitrogen at 200 to 230° before use. The aluminum bromide was prepared by the action of bromine on the hot metal and purified by distillation. Before use the aluminum bromide was redistilled over aluminum.

Aluminum Bromide Dissolved in *n*-Pentane.—*n*-Pentane (usually between 100 to 200 g.) was placed in a round-bottomed flask and aluminum bromide added. The flask was fitted with a reflux condenser cooled with refrigerated water at 5 to 10°. The top of the condenser was attached to a drying tube filled with dehydrite. The drying tube in turn, connected to a gas receiver. At all times the system was kept under a slight vacuum. The aluminum bromide did not dissolve immediately, and, after the closed system had been established, the flask was shaken and heated to hasten the process of solution.[6] After solution of the aluminum bromide had occurred, the heat was removed and the flask allowed to stand undisturbed at room temperature.

Before stopping the experiment, the flask containing the reaction mixture was cooled with ice water. In practically every case, this cooling sufficed to condense all the gas (usually 200–400 cc.) which had formed during the experiment. The flask was then disconnected and the flask contents slowly poured into a cooled separatory funnel containing crushed ice which hydrolyzed the dissolved aluminum bromide. The aluminum bromide–tar compounds which formed were separately hydrolyzed and extracted with ether because after hydrolysis they were slightly soluble in *n*-pentane and readily so in higher hydrocarbons.

Identification of the Reaction Products.—The analyses were obtained by distillation of 100 cc. of the reaction product. The column used for isobutane was a 91-cm., 5 mm. inside diameter Podbielniak-type column with a partial condensation head, which was cooled with a dry-ice–acetone bath. The isopentane was separated from *n*-pentane in a 28-plate vacuum jacketted column with a partial condensation head. The holdup of this column was 6 cc. A number of known mixtures were analyzed in these columns and excellent results obtained. The total distillation loss from the two distillations was usually between 0.5 and 1.5 cc. Figure 1 shows a typical distillation curve obtained.

Although the distillation curve shows only the presence of isobutane, a small amount of *n*-butane could probably

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(6) If the pentane contains even traces of olefins the process of solution will be characterized by the formation of a yellow cloudiness in the solution. This gradually clears, and, after an hour or so, the solution becomes entirely clear and colorless. The clearing of the solution is accompanied by the precipitation of small droplets of brown polymer on the sides of the flask. These coalesce on further standing and sink to the bottom of the flask. When pure pentane is used, usually two days elapse before any tar precipitates. Outside of this, however, no differences could be detected.

be found by a redistillation of the break material between isobutane and isopentane. The isopentane fractions were always checked by their critical solution temperatures[7] and frequently the refractive index and density were measured. The average values for the refractive index and density of the isopentane fractions reported in Table I were n^{20}_D 1.3548 and d^{20}_4 0.6203.

The substances boiling higher than *n*-pentane were not present in sufficient quantities to allow purification and identification.[8] By distilling the residues from several experiments a single plateau occurred in the distillation curve at 58 to 60°, but insufficient material was obtained to allow its identification. The fractions were all saturated and measurement of the refractive index suggested the material to be largely paraffinic. Usually the analysis for the higher boiling material was obtained by measurement of the critical solution temperature of the residue from the isopentane distillation.

Likewise, the insoluble tars which formed were not present in sufficient quantities to be identified. The tars from a series of experiments were saved and distilled. The material distilled over the range 100 to 240° without the appearance of a constant boiling substance. All of the fractions were strongly unsaturated and gave tests for halogens. The tars gave an intense purple color when bromine and *m*-cresol were added to their dilute solutions in *n*-heptane or other higher paraffins. The same color reaction is also given by the tars obtained from the reactions of other hydrocarbons with aluminum halides.

Aluminum Chloride and Liquid *n*-Pentane.—In general, the same experimental procedure was used as with aluminum bromide. However, the aluminum chloride reaction mixtures were always kept at the boiling point instead of room temperature. Usually 30 to 40 g. of aluminum chloride was used for each 100 g. of pentane and 0.2 mole of water (or its equivalent when other substances were used) added per mole of aluminum chloride used. With aluminum chloride the reaction velocities were slower, and even after five to ten days' reaction only 30 to 40% of the pentane could be decomposed. In several experiments a large butane fraction was obtained by starting with quantities of *n*-pentane as much as 1000 g. In these cases up to 10% *n*-butane was found in the butane fraction.

Experiments with Gaseous *n*-Pentane.—In the usual experiment a charge of 250 to 300 g. of aluminum chloride was placed in the middle of a 91-cm. long Pyrex tube of 3.8-cm. inside diameter. The reaction tube was heated in a horizontal electric furnace. The mixture of *n*-pentane vapor and nitrogen was produced by bubbling a stream of dry nitrogen through a wash bottle containing the hydrocarbon. The amount of pentane introduced was controlled by regulation of the temperature of the liquid pentane. In experiments in which water was added to the vapor entering the reaction tube, an additional wash bottle containing water was placed in the line just previous to entrance into the reaction tube. In certain experiments anhydrous hydrogen bromide or chloride replaced nitrogen as the carrier gas. A carrier gas flow of 50 cc. per min. was used to introduce 0.2 g. per minute of *n*-pentane into the reaction tube. When water vapor was used, it was added to the gas stream at the rate of 0.005 g. per minute. Varying the rate of flow of the pentane changed only the amount of decomposition. The gases leaving the reaction tube passed through a trap cooled to −60 to −70°. The gas which did not condense in this trap was collected in a gas receiver.

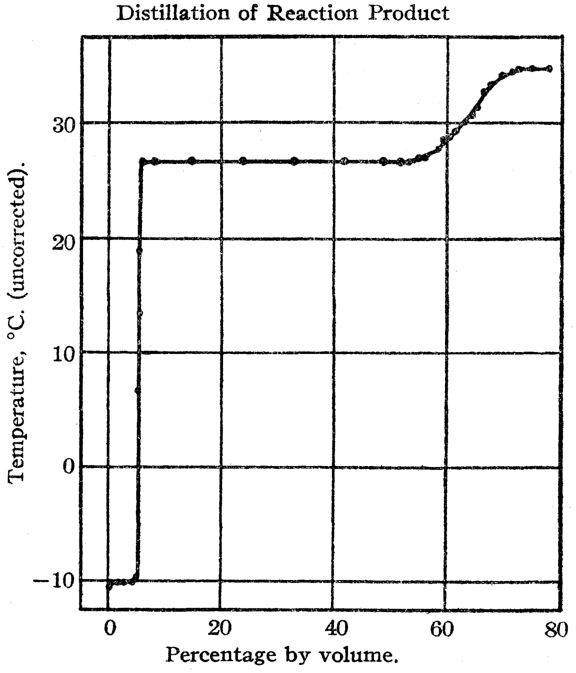

Fig. 1.—Sample used, 100.0 cc.; isobutane distillation loss, 0.4 cc.; isopentane distillation loss, 1.0 cc.

When nitrogen was used as the carrier, 85 to 95% of the pentane sent through was recovered as liquid, the tarry deposit on the aluminum chloride and the gas accounting for the balance. When the gas collected in the gas receiver was slowly passed through a trap at −30 to −40° practically the entire hydrocarbon content was condensed. Traces of hydrogen were found in the gas remaining, and its hydrocarbon content had carbon numbers between 3.9 and 4.6. When the halogen acids were used as carriers, they were removed, after leaving the reaction tube, by treatment with dilute caustic solution, and in these cases the gas loss was negligible.

In a typical experiment a product was obtained containing 33.7% butanes and 13.4% isopentane. Reducing the amount of decomposition did not materially change the relative amounts of products formed. Redistillation of the butane fractions in a Podbielniak low temperature column showed these fractions to contain from 4 to 11% *n*-butane, the balance being isobutane.

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[7] In order to avoid the use of sealed tubes, Eastman Kodak practical *m*-cresol was used instead of aniline for the critical solution temperature measurements. This material lowered the critical solution temperature of isopentane to about 12° depending upon the water content of the cresol. The solution temperature of *n*-pentane was 10° lower. The cresol was kept protected from the atmosphere and was measured out with a mercury sealed buret. The solution temperatures so determined remained constant as long as a given sample of cresol was in use.

[8] Insoluble tars and substances boiling higher than the starting material are produced in greater abundance with *n*-heptane and are being more thoroughly investigated in the study of this substance.

Summary

1. Dry *n*-pentane, either in the form of vapor or liquid, undergoes little, if any, decomposition in the presence of freshly sublimed aluminum chloride. If, however, anhydrous hydrogen bromide or chloride, water, hydrated aluminum chloride, or alkyl chlorides are added, reaction immediately commences. In the liquid phase reaction, the butanes and isopentane have been identified as reaction products. The latter is the chief product. Undefined saturated higher boiling products and an insoluble unsaturated polymer are also produced. In the vapor phase reaction the amount of isobutane formed is greatly increased and with extensive reaction becomes the chief product. For the vapor phase reaction aluminum chloride and anhydrous hydrobromic acid provide the most active catalyst.

2. In moderate concentration, aluminum bromide is soluble in *n*-pentane. It is a much more active substance than aluminum chloride and does not require the addition of other substances to cause the decomposition of *n*-pentane. The extent of reaction has been found to depend on the aluminum bromide concentration as well as the reaction time. The reaction products were the same, qualitatively, as those obtained with the chloride catalyst. As the extent of reaction was increased, the amount of butanes formed increased linearly, whereas the amount of isopentane formed reached a maximum value and then slowly declined. As much as 55.9% isopentane was obtained from *n*-pentane. When water is added to the reaction mixture, or anhydrous hydrogen bromide bubbled through it, the reaction velocity is increased.

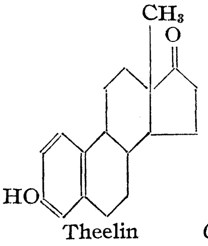
Detroit, Michigan Received July 21, 1936

[Contribution from the School of Chemistry and Physics of the Pennsylvania State College, and the Parke, Davis and Co. Research Laboratories]

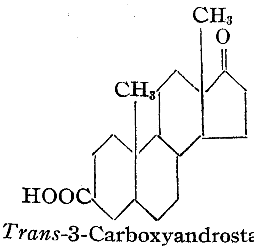
Sterols. VII. *Cis* and *Trans* 3-Carboxyandrostanone, An Oestrus-Producing Male Hormone Derivative, and *epi*-Cholesterol

By Russell E. Marker, Oliver Kamm, Thomas S. Oakwood and Joseph F. Laucius

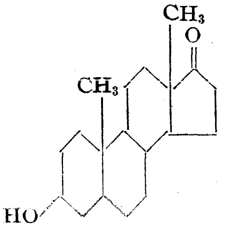
Because of the acidic nature of theelin, we prepared an androsterone derivative having a carboxyl group in the 3-position to see whether this compound would have female hormone properties in addition to male activity. The product was the mixture of *cis*- and *trans*-3-carboxyandrostanone. We made no attempt to separate the two stereoisomers. We found that the ethyl ester of this compound gave an oestrus response in rats when given in quantities of from 5–10 γ. The ethyl ester is much more active than the free acid. These compounds, however, were inactive when tested for male hormone properties by the cock's comb test in doses of 2 mg. Thus it is not necessary to have unsaturation in the molecule to have an oestrus-producing compound.



Theelin



Cis and Trans-3-Carboxyandrostanone



Androsterone

Because of the importance of obtaining *epi*-cholesterol in large quantities for research purposes avoiding the expensive digitonin process for the separation of the *cis* and *trans* isomers, we have looked for other means of separating these isomers, and found that by crystallizing the acetates from ethyl alcohol, a partial separation can be accomplished giving a product containing 80–90% of *epi*-cholesterol. The remaining cholesterol can then be removed completely by recrystallizing the benzoates from ethyl alcohol. We previously separated the two isomers by digitonin.[1]

We found that *epi*-cholesterol behaves very similarly in instability to *epi*-allocholesterol pre-

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[1] Marker, Oakwood and Crooks, This Journal, **58**, 481 (1936).

pared by Evans and Schoenheimer.[2] In an attempt to convert *epi*-cholesterol into *epi*-allocholesterol through its hydrochloride, we obtained cholesterylene almost quantitatively by dehydration and no *epi*-cholesterol hydrochloride. The same is true when *epi*-cholesterol is warmed with a small amount of hydrogen chloride in alcohol, dehydrating to cholesterylene. Evans and Schoenheimer found the same thing to happen when *epi*-allocholesterol was warmed with alcoholic hydrogen chloride. On attempting to prepare dibromo-*epi*-cholesteryl acetate by the addition of bromine in acetic acid to *epi*-cholesteryl acetate, there was a similar splitting giving a tetrabromocholestane. This product is a different isomer from that obtained by the addition of bromine to cholesterylene.

epi-Cholesterol does not irradiate with ultraviolet light to give products of antirachitic value.

Experimental

***Cis* and *Trans*-3-Carboxyandrostanone.**—The methyl ester of *cis*- and *trans*-3-carboxycholestane was prepared according to the method of Marker, Oakwood and Crooks.[1]

A solution of 100 g. of the methyl ester in 3700 cc. of glacial acetic acid was placed in a 5-liter flask equipped with a stirrer and dropping funnel. The temperature of the flask was kept at 45–50° during the addition of a solution of 115 g. of chromic anhydride in 350 cc. of 90% acetic acid. After addition was complete (three hours) stirring and warming was continued for seven hours. At the end of this time 200 cc. of methyl alcohol was added to destroy any excess chromic acid. The acetic acid was distilled from the reaction mixture under reduced pressure, keeping the temperature of the bath below 50°. After most of the acetic acid was distilled, 500 cc. of water was added and the distillation continued for an additional two hours. The residue was extracted with five 500-cc. portions of ether and the ether extract was successively washed once with 200 cc. of 10% hydrochloric acid, once with 100 cc. of a saturated solution of sodium bicarbonate, and then twice with 100-cc. portions of a 5% sodium hydroxide solution. The extract was dried with sodium sulfate and the ether distilled. The oil was dissolved in 1500 cc. of 95% alcohol to which was added 5 g. of semicarbazide hydrochloride and 5 g. of sodium acetate. The alcohol was distilled and the residue digested with 1500 cc. of dry ether for three hours. The insoluble crystalline residue was filtered, washed with dry ether, then boiled two hours with 50 cc. of distilled water. The semicarbazone was filtered, washed with ether, then extracted with acetone in a Soxhlet extractor; yield 2.5 g.; m. p. 250–260° (dec.).

A mixture of 1.0 g. of the semicarbazone, 115 cc. of alcohol, 15 cc. of concd. sulfuric acid and 24 cc. of water was boiled for one hour. The solution was poured into 1500 cc. of distilled water and extracted with three 300-cc. portions of dry ether. The ether extract was washed twice with water and then the ether was distilled. The residue was treated overnight with a solution of 5 g. of potassium hydroxide in 50 cc. of methyl alcohol. The alcoholic solution was poured into a liter of distilled water. This was concentrated *in vacuo* until 300 cc. was distilled to remove the alcohol. The solution was extracted with alcohol-free ether to remove neutral organic material. The aqueous portion was acidified with 5 *N* sulfuric acid, and then was extracted three times with 300-cc. portions of ether. On evaporation of the ether a solid remained. This was crystallized from acetone; yield 300 mg.; m. p. 253°.

Anal. Calcd. for $C_{20}H_{30}O_3$: C, 75.5; H, 9.5. Found: C, 75.7; H, 9.5.

The ether solution which was obtained from the filtration of the semicarbazone was evaporated to dryness. On recrystallization from methyl alcohol–ether, 35 g. of unoxidized methyl ester of *cis*- and *trans*-3-carboxycholestane, m. p. 69°, was obtained.

Ethyl Ester of *cis*- and *trans*-3-Carboxyandrostanone.—These acids esterify very readily in a small amount of alcohol. When ordinary ether containing ethyl alcohol was used to extract the *cis*- and *trans*-3-carboxyandrostanone from the hydrolysis in the above experiment, the resulting product was the ethyl ester of *cis*- and *trans*-3-carboxyandrostanone. It was crystallized from dilute alcohol; m. p. 108–110°.

Anal. Calcd. for $C_{22}H_{34}O_3$: C, 76.2; H, 9.9. Found: C, 75.8; H, 10.2.

Separation of *epi*-Cholesterol from the mixture of *epi*-Cholesterol and Cholesterol.—A mixture of *epi*-cholesterol and cholesterol was obtained by passing oxygen into cholesterylmagnesium chloride. 10.2 g. of magnesium turnings was covered with 50 cc. of dry ether. To this was added 1 cc. of ethyl bromide. After the Grignard had started a solution of 170 g. of well purified cholesteryl chloride dissolved in 1 liter of dry ether was added dropwise with vigorous stirring over a period of six hours. The ether solution was kept at a reflux temperature during the addition. It was then stirred vigorously for twelve hours. At the end of this time practically all of the magnesium was in solution. The product was cooled to 0° and oxygen passed into the reaction mixture for four hours. The oxygen was under a slight pressure during addition. The mixture was poured into dilute sulfuric acid and the mixture of cholesterols was extracted with ether. After washing with water, the ether layer was filtered from a small amount of insoluble white solid. The ether was then distilled leaving a white product. From 1360 g. of cholesteryl chloride was obtained 950 g. of the crude mixture of cholesterols.

A mixture of 50 g. of the above cholesterols, 20 g. of succinic anhydride and 40 cc. of dry pyridine was heated over steam for two hours. After cooling to room temperature, the product was dissolved in 300 cc. of ether, and 200 cc. of water containing 60 cc. of concd. hydrochloric acid was added. After extraction of the pyridine 300 cc. more ether was added and the half-succinic ester extracted with a solution of 25 g. of sodium carbonate in one liter of water at 33°. The alkaline extract was extracted twice with ether, then acidified with hydrochloric acid. The succinate was extracted with ether. After distilling the ether, the residue was refluxed with 25 g. of sodium hydroxide in one liter of water with stirring. The purified

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(2) Evans and Schoenheimer, This Journal, **58**, 182 (1936).

cholesterols were extracted with ether; 820 g. was obtained from 1150 g. of crude material. This was converted into the acetate by boiling for one hour with three times excess of acetic anhydride. The excess acetic anhydride was removed by vacuum distillation. The acetates were boiled with 6 liters of 95% ethyl alcohol and the solution cooled to 5°. The precipitate was filtered and recrystallized, m. p. 101–104°. One more crystallization of the product gave pure cholesteryl acetate, m. p. 114°, which gave no depression in melting point when mixed with cholesteryl acetate prepared from pure cholesterol. The alcoholic mother liquors from the above crystallization were evaporated to dryness and hydrolyzed by means of alcoholic sodium hydroxide, giving a product consisting of approximately 90% of *epi*-cholesterol and 10% cholesterol. This mixture was then converted into the benzoate, and freed of cholesterol benzoate by crystallization from alcohol. The benzoate was then hydrolyzed and the *epi*-cholesterol crystallized from alcohol, m. p. 141.5°. Mixed with pure *epi*-cholesterol, m. p. 141.5°, it gave no depression in melting point, whereas when mixed with cholesterol, m. p. 147°, a depression of 19° was observed; $[\alpha]^{30}\text{D}$ $-35.0°$ in 1% alcohol.

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.9; H, 12.0. Found: C, 83.9; H, 12.1.

Action of Bromine on *epi*-Cholesteryl Acetate.—To a solution of 100 mg. of *epi*-cholesteryl acetate in 3 cc. of ether was added a solution of 40 mg. of bromine in 5 cc. of acetic acid. A solid crystallized out. This was filtered and recrystallized from acetic acid, m. p. 110°. It gave a tetrabromocholestane.

Anal. Calcd. for $C_{27}H_{43}Br_4$: C, 47.2; H, 6.3. Found: C, 47.4; H, 6.7.

This bromide is different from the tetrabromide formed from cholesterylene and bromine, giving a depression in melting point when mixed.

Action of Hydrochloric Acid on *epi*-Cholesterol.—A solution of 1 g. of *epi*-cholesterol in 30 cc. of alcohol containing 1 g. of hydrochloric acid was refluxed for sixteen hours. The insoluble oil was sublimed under high vacuum, then crystallized from alcohol, m. p. 76–77°, uncorr. Mixed with cholesterylene, m. p. 74–76°, prepared by the action of quinoline on cholesteryl chloride it gave no depression in melting point; $[\alpha]^{30}\text{D}$ $-78.3°$ compared to $[\alpha]^{30}\text{D}$ $-80.0°$ for authentic cholesterylene, concentration 1% in benzene.

When an attempt was made to prepare *epi*-allocholesterol by the addition of hydrochloric acid in the cold to an alcoholic solution of *epi*-cholesterol the same dehydration occurred, giving cholesterylene.

Summary

A mixture of *cis*- and *trans*-3-carboxyandrostanone and its ethyl ester was prepared and found to produce oestrogenic activity in rats, but lacked male activity in the cock's comb test.

epi-Cholesterol and cholesterol can be separated into their components by crystallization of their acetates followed by crystallization of their benzoates. *epi*-Cholesterol on treatment with alcoholic hydrogen chloride forms cholesterylene. *epi*-Cholesterol acetate on treatment with bromine gives a tetrabromocholestane which is a different isomer from the product obtained by the action of bromine on cholesterylene.

STATE COLLEGE, PA.
DETROIT, MICH.
RECEIVED JULY 10, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Mechanism of Carbohydrate Oxidation. XXII.[1] The Preparation and Reactions of Glyceraldehyde Diethyl Mercaptal

BY HAROLD W. ARNOLD AND WILLIAM LLOYD EVANS

During the course of our work on the synthesis of *β-d*-glucosidoglyceraldehyde derivatives[2] it seemed desirable to have available a monomeric glyceraldehyde derivative containing an unblocked hydroxyl group only on the third carbon atom. The following scheme was used in attempting to prepare such a derivative:

Glyceraldehyde diethyl mercaptal was prepared as a distillable oil by the usual procedure employed in preparing sugar mercaptals. It readily reacted with triphenylmethyl (trityl) chloride to form a crystalline trityl ether. From the work of Helferich and his students[3] it appears probable that the compound prepared was 3-trityl glyceraldehyde diethyl mercaptal. A few exceptions to Helferich's rule concerning the preferential reaction of trityl chloride with primary alcohol groups have been found[4] but they do not invalidate the rule because of the vigorous reaction conditions employed in discovering them.

The 3-trityl glyceraldehyde diethyl mercaptal could be easily acetylated or benzoylated to give

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(1) No. XXI of this series, THIS JOURNAL, **58**, 1890 (1936).

(2) H. W. Arnold and W. L. Evans, *ibid.*, **58**, 1890 (1936).

(3) B. Helferich, P. S. Speidel and W. Toeldte, *Ber.*, **56**, 766 (1923); B. Helferich, L. Moog and A. Jünger, *ibid.*, **58**, 872 (1925); B. Helferich, W. Klein and W. Schäfer, *Ann.*, **447**, 19 (1926).

(4) R. C. Hockett and C. S. Hudson, THIS JOURNAL, **53**, 4456 (1931); *ibid.*, **56**, 945 (1934).

crystalline products. All attempts to detritylate these compounds failed to give derivatives containing the free hydroxyl group on the third carbon atom. Various detritylation procedures were used. In each case the trityl ether was quantitatively cleaved, but the reaction product was a dark, gummy mass from which no definite compound could be isolated. Detritylation by catalytic hydrogenation[5] was not attempted since work by Dr. M. L. Wolfrom in this Laboratory had shown that this procedure fails when applied to diethyl mercaptal derivatives, presumably because the catalyst becomes poisoned.

To show the analogy between the reactions of glyceraldehyde diethyl mercaptal and *d*-glucose diethyl mercaptal,[6] the glyceraldehyde diethyl mercaptal was acetylated. The product was subjected without purification to the hydrolytic action of mercuric chloride and cadmium carbonate in moist acetone to give a distillable oil whose properties corresponded to those reported by Fischer and Baer[7] for a monomeric glyceraldehyde diacetate which they prepared by a different procedure. Deacetylation of the oil gave a sirup which reacted with 2,4-dinitrophenylhydrazine in acid solution to yield the known 2,4-dinitrophenylhydrazone of glyceraldehyde. The oil likewise reacted with an acid solution of *p*-nitrophenylhydrazine under more drastic conditions to give a crystalline product which was apparently glyceraldehyde *p*-nitrophenylosazone acetate.

Experimental Part

Glyceraldehyde Diethyl Mercaptal.—Fifteen grams of glyceraldehyde was placed in a glass-stoppered bottle; 13 cc. of ice-cold concentrated hydrochloric acid and 30 cc. of ice-cold diethyl mercaptan were added in rapid succession, and the stopper tightly closed. The mixture was shaken vigorously, the stopper being lifted occasionally to release pressure. A light yellow solution resulted after twenty-five minutes. The mixture was again cooled in an ice–salt bath and 100 cc. of ice water added. A heavy oil settled to the bottom of the bottle. This showed no tendency to crystallize after standing in ice for two hours. It was then separated from the remainder of the liquid, the aqueous layer being extracted twice with small volumes of chloroform. The oil and the combined extracts were dried over anhydrous sodium sulfate. Removal of the chloroform under reduced pressure left 22.5 g. of the oil. This was distilled *in vacuo*. After a small forerun, the bulk of the liquid distilled smoothly at 155–160° (bath, 185°) under a pressure of 3 mm. The fraction distilling at this temperature weighed 15.0 g. The residue in the flask was a dark brown oil. Redistillation of the main fraction under 3 mm. pressure gave 13.2 g. of a light yellow oil boiling at 156–158° (bath, 180–185°). This corresponded to a yield of 40%. The oil is immiscible with water, but miscible with all common organic solvents.

Anal. Calcd. for $C_7H_{16}O_2S_2$: S, 32.66; mol. wt., 196. Found: S, 32.38; mol. wt. (ebullioscopic in benzene), 188.

The dark brown oil which remained from distillation deposited a small quantity of crystals (0.2 g.) after standing in the ice chest for several days. Recrystallization from ethyl alcohol gave small needles melting at 126–127.5° (corr.). The molecular weight as determined by the Rast method was 295. The analysis indicated a sulfur content of 10.6%. It seems probable that this compound is formed by the condensation of several molecules of the diethyl mercaptal.

3-Trityl Glyceraldehyde Diethyl Mercaptal.—A mixture of 5 g. of glyceraldehyde diethyl mercaptal, 8 g. of trityl chloride, and 50 cc. of anhydrous pyridine was allowed to stand in a stoppered flask at room temperature for forty-eight hours. At the end of this time it was filtered to remove a small quantity of trityl carbinol that had precipitated. The filtrate was then slowly dropped into one liter of rapidly stirred ice water. The product first separated as a thick sirup which crystallized entirely within an hour. The solid was filtered off and dried on porous porcelain. The weight of the crude product was 9.0 g. and the melting point was 96.5–98°. After three crystallizations from 80% alcohol, the melting point was constant at 100–101° (corr.). The weight was 5.2 g. corresponding to a yield of 55%. The compound is insoluble in water and petroleum ether, soluble in ethyl and methyl alcohol at the boiling point, and soluble in the common organic solvents at ordinary temperatures. If it is allowed to crystallize slowly from alcoholic solution, it forms large prismatic needles.

Anal. Calcd. for $C_{26}H_{30}O_2S_2$: S, 14.69. Found: S, 14.54.

3-Trityl 2-Acetyl Glyceraldehyde Diethyl Mercaptal.—A mixture of 1.72 g. of the trityl ether, 10 cc. of anhydrous pyridine and 10 cc. of purified acetic anhydride was allowed to stand in a stoppered flask at room temperature for twenty-four hours. The solution was then slowly dropped into 500 cc. of rapidly stirred ice water. After an hour, the product had become almost entirely crystalline. It was filtered off, washed with water, and dried on porcelain. After three recrystallizations from 95% ethyl alcohol, the melting point was constant at 93–94° (corr.). The weight of pure product was 1.50 g., corresponding to a yield of 80%. When the hot alcoholic solution was rapidly cooled, the compound crystallized in tiny needles.

Anal. Calcd. for $C_{26}H_{29}O_2S_2(COCH_3)$: acetyl, 2.08 cc. of 0.1 *N* NaOH per 100 mg.; S, 13.34. Found: acetyl, 2.03 cc., 2.05 cc.; S, 13.40. *Mol. wt.* Calcd. for $C_{28}H_{32}O_3S_2$: 480, Found: (cryoscopic in benzene), 458.

3-Trityl 2-Benzoyl Glyceraldehyde Diethyl Mercaptal.—1.42 g. of the trityl ether was dissolved in 10 cc. of anhydrous pyridine. The solution was cooled in ice and 4 cc. of ice-cold benzoyl chloride added. The mixture was allowed to stand in a stoppered flask at room temperature

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(5) F. Micheel, *Ber.*, **65**, 262 (1932).

(6) M. L. Wolfrom, THIS JOURNAL, **51**, 2188 (1929); **52**, 2464 (1930).

(7) H. O. L. Fischer and Erich Baer, *Ber.*, **65**, 345 (1932).

for twenty-four hours. It was then slowly dropped into 400 cc. of rapidly stirred ice water. After the mixture had stirred for one hour it was extracted with three successive 50-cc. volumes of chloroform. The chloroform solution was washed successively with water, dilute sulfuric acid, sodium bicarbonate solution and water. After drying over calcium chloride the solvent was removed by a warm air stream. The residue was recrystallized five times from absolute alcohol. The melting point had then become constant at 90–91° (corr.). The weight of the crystalline product was 1.70 g., corresponding to a yield of 97%. The solubility relationships are approximately the same as those of the corresponding acetyl compound. If allowed to crystallize slowly from alcohol, it forms long (1–2 cm.) prismatic needles.

Anal. Calcd. for $C_{33}H_{34}O_3S_2$: S, 11.82. Found: S, 12.01.

Monomeric Glyceraldehyde Diacetate.—8.94 g. of glyceraldehyde diethyl mercaptal and a mixture of 25 cc. of purified acetic anhydride and 25 cc. of anhydrous pyridine were allowed to stand in a stoppered flask for twenty-four hours at room temperature. The mixture was then poured into 500 cc. of ice water. After standing for several hours, this was extracted with five 50-cc. portions of chloroform. The chloroform solution was washed successively with water, dilute sulfuric acid, sodium bicarbonate solution and water. It was dried over calcium chloride. Removal of the solvent left a viscous yellow oil which could not be distilled under the conditions used (2 mm. pressure and bath temp. of 230°). No apparent decomposition took place at this temperature. The weight of the oil was 11.6 g., approaching the weight required if the theoretical quantity of mercaptal diacetate (12.7 g.) were formed. No analytical data were obtained for this compound. It was used directly in the attempt to prepare aldehydoglyceraldehyde diacetate.

After the manner of Wolfrom[6] the above oil and a mixture of 40.4 g. of mercuric chloride in 70 cc. of acetone, 45 g. of cadmium carbonate and 40 cc. of water were vigorously stirred, under mercury seal, for seventy-two hours at room temperature, small amounts of fresh cadmium carbonate being added at intervals. The solution was filtered over cadmium carbonate into a flask containing the same reagent. The solution was evaporated to complete dryness without removing the cadmium carbonate. The residue was repeatedly extracted with chloroform. Concentration of the chloroform solution *in vacuo* left a viscous yellow oil. This was vacuum distilled at a pressure of 3 mm. With a bath temperature of 180–190° a fraction weighing 4 g. distilled at 154–156°. The properties of this oil corresponded to those recorded by Fischer and Baer[7] for monomeric glyceraldehyde diacetate. It rapidly reduced Fehling's solution in the cold. A molecular weight determination (cryoscopic in benzene) gave a value of 168 (calcd., 174).

The following experiments were carried out to establish the identity of the compound. (1) One and one-half grams of the oil was allowed to stand overnight at 0° with 15 cc. of a saturated solution of ammonia in methyl alcohol. The alcohol was removed *in vacuo* and the remaining sirup dissolved in 50 cc. of water. The solution was cooled in ice and a cooled solution of 1.5 g. of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid was added. Precipitation of a yellow crystalline solid began almost immediately, being complete within an hour. The precipitate was washed with water and dried. Recrystallization from 50% alcohol gave 1.0 g. of yellow needles melting at 155° (corr.). This corresponds to the melting point of glyceraldehyde-2,4-dinitrophenylhydrazone as recorded by Fischer and Baer.[8] The mixed melting point with an authentic sample prepared from glyceraldehyde according to the procedure of Fischer and Baer was likewise 155°.

(2) One and seven-tenths grams of *p*-nitrophenylhydrazine and 1.2 g. of the supposed aldehydo-glyceraldehyde diacetate in a mixture of 20 cc. of alcohol and 30 cc. of 3 *N* hydrochloric acid were heated on the water-bath for an hour and a half. Within a few minutes after beginning the heating a dark red precipitate began to form. Precipitation was complete within an hour. The precipitate was washed repeatedly with water and dried on porcelain. It weighed 1.2 g. Recrystallization from ethyl alcohol containing about 10% by volume of pyridine gave blood red needles which melted at 282–286° (block) with previous darkening at 235–240°. This compound is thought to be monoacetyl glyceraldehyde *p*-nitrophenylosazone.

Anal. Calcd. for $C_{17}H_{16}O_6N_6$: N, 21.0. Found: N, 20.8. Calcd. for $C_{15}H_{13}O_5N_6(COCH_3)$: acetyl, 2.50 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 2.60 cc.

Summary

1. The diethyl mercaptal of glyceraldehyde has been prepared. It forms a crystalline trityl ether on reaction with trityl chloride. The trityl ether yields crystalline acetyl and benzoyl derivatives. Attempts to remove the trityl group from these compounds have been unsuccessful.

2. Acetylation of the glyceraldehyde diethyl mercaptal yields an oil which is apparently the diacetate. Treatment of this oil with mercuric chloride and cadmium carbonate in the presence of aqueous acetone yields a compound whose properties correspond to those of a monomeric glyceraldehyde diacetate. The compound reacts with *p*-nitrophenylhydrazine in acid solution to yield what is apparently monoacetyl glyceraldehyde *p*-nitrophenylosazone. This view is supported by our analytical data. Deacetylation of the diacetate yields a sirup which reacts with 2,4-dinitrophenylhydrazine to form glyceraldehyde 2,4-dinitrophenylhydrazone.

COLUMBUS, OHIO RECEIVED JULY 13, 1936

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(8) H. O. L. Fischer and Erich Baer, *Helv. Chim. Acta*, **17**, 622 (1934).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 146]

Raman Spectra. I. Benzoyl Chloride and Certain of its Substitution Products

BY DOROTHY D. THOMPSON[1] AND JAMES F. NORRIS

For a number of years the relative reactivities of certain bonds in organic compounds have been studied in this Laboratory. The determination of the rates at which a type substance and certain of its substitution products react with a definite compound under fixed conditions led to results that showed the effect of the nature of the substituent and its position on the reactivity of the bond under investigation. In certain cases the relative reactivities determined by rate measurements were compared, with striking results, with the temperatures at which the members of a series containing the same radicals first gave indication of the breaking of the bonds studied.

Among the series of reaction rate measurements was that of benzoyl chloride and its derivatives with methyl alcohol,[2] with ethyl alcohol[3] and with water in the presence of acetone.[4] Although interesting conclusions and comparisons were drawn from these data, no satisfactory interpretation of the results was reached since the mechanism of the reaction was not clearly understood. The differences in rate can be traced to the carbon–chlorine bond if the reaction is either one of simple substitution or one in which an unstable addition compound of the oxonium type is involved. If, however, an unstable compound is formed by the addition of alcohol across the carbonyl, the change in the carbon–oxygen bond is being measured. Or, if the intermediate compound of any type is formed rapidly and decomposed very slowly, the rates would be a measure of the relative reactivities of a bond in the intermediate.[3] Substitution of an atom in benzoyl chloride would alter both the carbon–chlorine and carbonyl bonds. It appeared, therefore, that an examination of the lines in the Raman spectra produced by these groups would add valuable information to this problem because of the following facts.

(1) Harkins and Haun[5] determined the Raman spectra of certain alkyl chlorides. When the positions of the intense lines which give the frequency of longitudinal vibration of the halogen atom with the adjacent $-CH_2-$ group are compared with the rates of hydrolysis of the corresponding halides, a striking relationship appears. In methyl chloride, which is hydrolyzed with difficulty, this line has a displacement of 712 $cm.^{-1}$; the other primary chlorides which hydrolyze more easily have a smaller displacement (around 650 $cm.^{-1}$), which corresponds to a smaller force of binding. The more easily hydrolyzed secondary chlorides have Raman frequencies around 610 $cm.^{-1}$, and the tertiary chlorides which hydrolyze still more readily have a still smaller displacement (560 $cm.^{-1}$). It seemed probable that a similar relationship would be found for the acyl chlorides.

(2) Bourguel[6] compared the effect of different groups in olefins on the strength of the double bonds by a comparison of the displacements of the lines characteristic of the carbon–carbon double bond. This bond is similar to the carbonyl in acyl chloride.

For these reasons measurements of the Raman spectra of a series of acyl chlorides were made and examined. In attempts to determine which lines were associated with the carbon–chlorine bond, the spectra were compared with each other and, in certain cases, with the corresponding ester and aldehyde. On account of the complexity of the problem we are not able, at this time, to identify with any certainty the lines sought.

It was possible to identify the lines produced by the carbonyl linking on account of their isolated position (around 1750 $cm.^{-1}$). There appeared to be no relation between the relative reactivities of the acyl chlorides and the position of these lines.

In order to find out more about any intermediate compound formed, the spectrum of a mixture of benzoyl chloride and ethyl alcohol was photographed as soon as possible after mixing and, later, after the reaction was complete. The first spectrum contained the lines due to the substances present—ethyl alcohol, benzoyl chloride and

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[1] From the thesis presented by Dorothy D. Thompson in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1935.

[2] James F. Norris and H. H. Young, Jr., THIS JOURNAL, **57**, 1420 (1935).

[3] Norris, Fasce and Staud, *ibid.*, **57**, 1415 (1935).

[4] Berger and Olivier, *Rec. trav. chim.*, **46**, 516 (1927).

[5] Harkins and Haun, THIS JOURNAL, **54**, 3920 (1932).

[6] Bourguel, *Compt. rend.*, **194**, 1736 (1932).

ethyl benzoate; the second, the lines of ethyl benzoate and ethyl alcohol. If an intermediate compound had been formed in appreciable quantities as the result of an addition to the carbonyl group, the intensities of the lines corresponding to this group would have changed. This was found not to be the case. An experiment with a mixture of chloral and alcohol gave a spectrum in which lines due to the carbonyl in the aldehyde were not present—a fact which is optical evidence of the absence of a carbonyl linking in chloral alcoholate.

After the work described in this paper was completed, a paper was published by Kohlrausch, Pongratz and Stockmair[7] in which are reported the Raman spectra of a number of derivatives of benzoyl chloride. We had determined some of these and others not reported. In certain cases we found lines not observed by Kohlrausch and in other cases lines are missing in our spectra. It seems advisable to publish all our results so that the data will be available for future interpretation when Raman spectra are better understood.

Experimental

Apparatus.—A Hilger E-439 glass spectrograph was used for these determinations. Although the dispersion is small, the resolution is good and preliminary experiments with a Hilger "Constant Deviation" spectrograph of much higher dispersion showed that the use of fine-grained plates made possible by the large aperture of the former spectrograph gave greater precision than the coarse grained plates made necessary by the slower instrument. The time of exposure varied from one to four hours. Usually both long and short exposures were taken to give the best conditions for reading both the strong and weak lines.

In order to make certain the correct assignment of exciting line to a given Raman line, an efficient system of filters was worked out. Since benzoyl chloride and some of its derivatives are decomposed by ultraviolet light, the compound being investigated was always protected by either Corning "Greenish Nultra" glass (4 mm.) or by a saturated solution of sodium nitrite (2 mm.). These filters also, of course, prevented any Raman lines from being excited by the mercury lines in the ultraviolet. For every compound at least one plate was taken with radiation by both blue and violet mercury light, another with blue light only—the violet light being removed by a solution of quinine sulfate in dilute sulfuric acid. Although this filter was protected from ultraviolet light, there was some yellowing, so the solution was changed every hour. A third plate was taken with light filtered by Corning "Red Purple Ultra" glass (2 mm.) to weaken the blue light.[8] It was found much more efficient for this purpose than iodine in carbon tetrachloride usually recommended.

The photographs were made with Eastman Spectrographic plates—"III-O" for excitation by both blue and violet light, "III-G" for blue radiation alone, "I-O" (because of the density of the filter) for excitation by violet light, and "I-G" for photographs of the nitro compounds.

A Wood's type Raman tube was used with a cooling jacket and an extra jacket for liquid filters. The light source consisted of three Pyrex mercury arcs constructed according to High and Pool running vertically on 110 d. c. at a steady current of 3.5 to 4 amperes, and cooled by an electric fan.

Accuracy.—The accuracy of measuring the plates depends on the intensity and on the sharpness of the lines. The sharp, relatively strong lines were measured with an error of less than ± 1 cm.$^{-1}$, while the error in reading the weak, diffuse lines was sometimes as great as ± 3 cm.$^{-1}$. The values in the tables are weighted averages of at least three values (usually five or six) with the following exceptions: (1) the very weak lines which are not strong enough to appear on the plate when excited by the 4047 Å. line; (2) those in the region 1650–1800 cm.$^{-1}$, which when excited by the 4047 Å. line fall on the plate on top of the very much over-exposed mercury line (4358 Å. group); and (3) those of high frequency, above 2000 cm.$^{-1}$, which when excited by 4358 Å. fall below 4916 Å. where the dispersion is very poor.

The lines on the plate were measured to 0.001 mm. by a Hilger comparator. The wave lengths were determined by reference to three dispersion curves made from the spectrum of an iron arc and the wave numbers were determined (corrected to vacuum) by reference to Kayser's "Tabelle der Schwingungszahlen."[9]

Purification of Compounds.—With the exception of benzoyl chloride, *m*-chloro, *m*-nitro and *p*-nitrobenzoyl chloride which were purchased from Eastman Kodak Company and then highly purified, all of the compounds were prepared by the action of thionyl chloride on the purified acid according to the method previously described.[2] They were distilled under reduced pressure at least three times using a still-head provided with ground-glass joints, and large quantities were prepared, so that only constant boiling middle fractions need be used, thus avoiding the possibility of contamination by thionyl chloride or polymerization compounds.

Explanation of Tables.—The values of the Raman spectra have been summarized in the usual way. The value of the Raman shift in cm.$^{-1}$ is followed by a number in parentheses indicating the relative intensity (estimated)—the large numbers indicating greater intensity and the letter "b" for broad. This is followed by letters indicating the exciting lines as follows: a = 4047 Å., b = 4078 Å., c = 4339 Å., d = 4348 Å. and e = 4358 Å., the symbols ± before a letter indicate that the line appeared both as Stokes and anti-Stokes line.

Preceding the summary of Raman values is a summary of experimental detail. The first

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(7) Kohlrausch, Pongratz and Stockmair, *Monatsh.*, **67**, 104 (1935–1936).

(8) Murray and Andrews, *J. Chem. Phys.*, **1**, 406 (1933).

(9) Kayser, "Tabelle der Schwingungszahlen," Verlag S. Hirzel, Leipzig, 1925.

column gives the number of the plate which was measured. Roman numerals refer to earlier work. The second column gives the type of filter used: (G. N., Corning "Greenish Nultra" glass; Q. S., a saturated solution of quinine sulfate in dilute sulfuric acid; R. P. U., Corning "Red Purple Ultra" glass). The type of plate listed in the third column refers to those of Eastman Kodak Company. The fourth column gives the exposure time in hours. The strength of the continuous background was greatest between 4358 and 4916 Å. Column 5 refers to this region. "Very weak" indicates practically no background, and "very strong" that the plate had to be illuminated by a very strong light to see the Raman lines. The spectrograph used was, unless otherwise stated, the Hilger E-439 described above. Some of the earlier investigations, however, were carried out on a Zeiss of low dispersion and on a Hilger Constant Deviation all glass spectrograph having a dispersion two to three times that of the Hilger E-439. The employment of these instruments is indicated in the last column.

BENZOYL CHLORIDE

Previous investigators: Kohlrausch and Pongratz,[10] *Monatsh.*, **64,** 361 (1934), Thatte and Ganesan,[11] *Phil. Mag.*, **12,** 823 (1931), Matsuno-Han,[12] *Bull. Chem. Soc. Japan*, **9,** 88 (1935). Eastman White Label, distilled 4 times *in vacuo;* b. p. 67.6–67.8° at 7.5 mm.

Plate	Filter	Type	Time	Background	Spectrograph
97	G. N.	III-O	3	Weak	Hilger E-439
98	G. N.	III-O	5	Weak	Hilger E-439
5	Q. S.	I-G	21	Strong	Hilger C. D.
99	Q. S.	III-G	3	Medium	Hilger E-439

$\Delta\nu$ = 164(1b)(e); 313(3)(a, e); 415(2b)(a, e);[a] 507(3)(a, e); 672[a](3)(a, e); 775(00)(e); (840)(00)(e); (873)[a](00)(e); 1002[a](5)(a, b, e); 1026(1)(a, e); 1164(2)(a, e); 1175(4)(a, b, e); 1205(4)(a, b, e); 1450(2)(a, e); 1490(0)(a, e); 1595(8)(a, c, e); 1738[a](2b)(b, c, e); 1780[a](4b)(b, c, e); 3074(6b)(a).

[a] Differ from Kohlrausch and Pongratz by more than 2 cm.$^{-1}$. None differ by more than 6 cm.$^{-1}$.

Lines reported by Kohlrausch and Pongratz not found here 1317($^1/_2$); 2610(3b); 2649(2b); 3012(1b). Lines not reported by Kohlrausch and Pongratz and found here 840(00); two lines at 1164(2) and 1175(4), where Kohlrausch and Pongratz report only one 1170(11b).

o-METHYLBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair,[7] *Monatsh.*, **67,** 104 (1935–1936). Prepared from synthetic *o*-methylbenzoic acid and thionyl chloride. Distilled 3 times; b. p. 75.6 ± 0.05° at 5.5 mm.

Plate	Filter	Type plate	Time	Background
38	G. N.	III-O	3.5 hrs.	Weak
39	G. N.	III-O	3.5	Very weak
35	Q. S.	III-G	3	Weak
57	R. P. U.	I-O	4	Weak
42	R. P. U. (Satd. $NaNO_2$)	I-O	4	Medium

$\Delta\nu$ = 126[a](6b)(a, ±e); 220[a](2)(a, e); 286[b](4)(a, b, e); 382(2)(a, ±e); 436[b](2)(a, d, e); 477(2b)(a, c, e); 568(7)(a, e); 648(0)(a, e); 665(4)(a, e); 714(00)(a, e); 768(2)(a, e); 864(1)(a, e); 1053[b](6)(a, b, e); 1121(1)(a, e); 1164(3)(a, b, e); 1186(2)(a, e); 1204(6)(a, b, e); 1296[b](0)(a, e); 1382(2)(a, e); 1436(00)(a, e); 1476[b](4)(a, e); 1567[b](6)(a, e); 1599(6)(a, e); 1770(7b)(b, e); 2936[b](3)(a, b); 3070[b](5b)(a).

[a] Differ by more than ±6 cm.$^{-1}$. [b] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$. Av. dev. of at least 7 readings < ±1 cm.$^{-1}$.

Kohlrausch, Pongratz and Stockmair report, also, 89(4); 1725(2b); 2975(5). Not reported by Kohlrausch, Pongratz and Stockmair 714(00) (found 5 times); 1436(00).

m-METHYLBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair.[7] Prepared from synthetic *m*-methylbenzoic acid by $SOCl_2$. Distilled 2 times *in vacuo;* b. p. 71.2 ± 0.05° at 4 mm.

Plate	Filter	Type plate	Time	Background
80	G. N.	III-O	2.75	Weak
81	Q. S.	III-G	3	Dark
82	Q. S.	III-G	1.75	Medium
83	R. P. U.	I-O	2	Weak

$\Delta\nu$ = 155(7b)(±a, e); 222(4)(±e); 270(3)(a, ±e); 304(1)(a, ±e); 350(1)(a, ±e); 375(00)(e); 421(3b)(a, e); 505[a](2)(a, e); 524(1)(a, e); 537[a](2)(a, e); 668(5)(a, b, e); 768(1)(a, e); 948(0)(a, e); 1003(5)(a, b, e); 1094[b](00)(a, e); 1152(2)(a, b, e); 1174(1)(a, e); 1244(5)(a, b, e); 1380(1)(a, e); 1586[a](7)(a, e); 1606[b](7)(a, e); 1769[b](7b)(e); 2925(2b)(a); 3066[a](4b)(a).

[a] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$. [b] Differ by more than 6 cm.$^{-1}$.

Reported by Kohlrausch, Pongratz and Stockmair and not found; 480($^1/_2$); 802(1); 892(2); 927(2); 1410($^1/_2$); 1481(0); 1719($^1/_2$); 2964(1). Not reported by Kohlrausch, Pongratz and Stockmair 375(0).

p-METHYLBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair.[7] Prepared from synthetic *p*-methylbenzoic acid + $SOCl_2$. Distilled 8 times *in vacuo;* b. p. 72.8–73.0° at 4.5 mm.

Plate	Filter	Type plate	Time	Background
70	G. N.	III-O	3	Dark
71	G. N.	III-O	1	Medium
72	Q. S.	III-G	1	Dark
74	R. P. U.	I-O	1	Weak
75	Q. S.	III-G	2	Medium

$\Delta\nu$ = 170(2)(+b, e); 264(4)(a, ±e); 290(4)(a, ±e); 413(5b)(a, d, e); 484(4)(a, ±e); 614(3)(a, e); 640(3)(a, b, e); 715(00)(a, e); 781[a](6)(a, b, e); 827(0)(a, e); 875(0)(a, e); 1122(0)(a, e); 1173[a](8)(a, b, c, e); 1207[a](4)(a, b, e); 1306(3)(a, e); 1380[a](1)(a, b, e); 1503(1)(a, d, e); 1606[a](10b)(a, e); 1744[b](5b)(b, e); 1777[b](6b)(b, e); 2927[a](4)(a); 3072(3)(a).

[a] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$. [b] By more than 6 cm.$^{-1}$.

Lines reported by Kohlrausch, Pongratz and Stockmair not found: 355(2); 1027$(^1/_2)$; 1443(1); 2873(2). Lines not reported by Kohlrausch, Pongratz and Stockmair but found: 1122(0)(a, e).

o-METHOXYBENZOYL CHLORIDE

Previous investigators: None. Prepared from methylsalicylic acid + $SOCl_2$. Distilled 4 times *in vacuo;* b. p. 119.6 ± 0.05° at 1 mm.

Plate	Filter	Type plate	Time	Background	Spectrograph
115	G. N.	III-O	4	Weak	Hilger E-439
116	Q. S.	III-G	4	Weak	Hilger E-439
116(a)	R. P. U.	I-O	1.5	Weak	Hilger E-439
12	Q. S.	I-G	14	Medium	Hilger C. D.

$\Delta\nu$ = 125(4b)(a, ±e); 249(00)(e); 377(1)(d, e); 426(0)(e); 449(a, e); 535(0)(e); 574(3)(a, e); 651(1b)(e); 743(1)(e); 776(1)(e); 857(00)(e); 1052(6)(a, e); 1126(1)(a, c, e); 1166(7)(a, e); 1189(6)(a, e); 1258(6)(a, e); 1284(0)(a, e); 1481(6)(a, e); 1574(6)(a, e); 1600(6)(a, e); 1778(7b)(b, e); 2841(0)(a); 2943(00)(a); 3080(2)(a).

m-METHOXYBENZOYL CHLORIDE

Previous investigators: None. Prepared from *m*-methoxybenzoic acid (Eastman White Label) + $SOCl_2$. Distilled 3 times *in vacuo;* b. p. 110.8–111.0° at 8.5 mm.

Plate	Filter	Type plate	Time	Background
109	G. N.	III-O	4	Medium
110	G. N.	III-O	2	Weak
118	G. N.	III-O	6	Medium
111	Q. S.	III-G	3	Weak
112	R. P. U.	I-O	2	Weak

$\Delta\nu$ = 155(3b)(±e); 260(0b)(e); 327(2)(e); 369(1)(e); 415(1b)(e); 452(2)(a, e); 502(2)(a, e); 567(1)(a, e); 667(8)(a, b, e); 770(0)(a, e); 996(10)(a, e); 1154(2)(a, b, e); 1190(2)(a, e); 1261(10)(a, b, e); 1289(2)(a, b, e); 1319(0b)(a, e); 1341(1)(a, e); 1587(8)(a, e); 1602(5)(a, e); 1736(1)(b, e); 1771(8)(e); 2839(1)(a); 2922(1)(a); 3085(4)(a).

p-METHOXYBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair.[7] Prepared from *p*-methoxybenzoyl chloride (Eastman White Label) + $SOCl_2$. Distilled 5 times *in vacuo;* b. p. 90.8 ± 0.05° at 1 mm.; $d^{20}{}_4$ 1.2609; n^{20} 1.5802.

Plate	Filter	Type plate	Time	Background	Spectrograph
XV	None	50	1	Medium	Zeiss
3	G. N.	Hyperpress	30	Strong	Hilger C. D.
8	Q. S.	I-G	21.5	Strong	Hilger C. D.
119	G. N.	III-O	4.5	Medium	Hilger E-439
120	R. P. U.	I-O	2	Weak	Hilger E-439

$\Delta\nu$ = 247(2)(d, e); 288(4b)(a, ±e); 410^a(2)(a, e); 454^b(3)(a, d, e); 470^a(2)(a, e); 612^b(6)(a, c, e); 635(1)(a, e); 650^b(5)(a, b, e); 735^b(0)(a, e); 783^b(b)(a, b, e); 879^b(2b)(a, e); 1007^b(2)(a, e); 1123(1)(a, b, e); 1165^b(20b)(a, b, e); 1212(4)(a, b, e); 1230(0)(a, e); 1270^b(2)(a, b, e); 1322^a(2)(a, e); 1423(1)(a, b, e); 1444(0)(a, e); 1465^b(0)(a, e); 1506^b(1)(a, e); 1579^b(4)(a, e); 1599(20b)(a, e); 1736^b(4b)(a, b, e); 1770^b(5b)(b, e); 2844(2)(a); 2938(0)(a); 3083(3b)(a).

[a] By more than 6 cm.$^{-1}$. [b] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$.

Reported by Kohlrausch, Pongratz and Stockmair, not found: 148(6); 223(3); 1022$(^1/_2)$; 1059$(^1/_2)$; 1104(3). Not reported by Kohlrausch, Pongratz and Stockmair: 247(2); 635(1); 1123(1); 1230(0); 1444(0); 2844(2); 2938(0); 3083(3b).

o-CHLOROBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair.[7] Prepared from *o*-chlorobenzoic acid + $SOCl_2$. Distilled 3 times *in vacuo;* b. p. 78.9–79.2° at 2 mm.

Plate	Filter	Type plate	Time	Background
87	G. N.	II-O	4	Weak
89	Q. S.	III-G	2	Weak
91	R. P. U.	I-O	2	Weak

$\Delta\nu$ = 125(4)(±a, ±e); 201^a(1)(a, ±e); 252^a(2b)(a, ±e); 356(1)(e); 423^a(1)(a, e); 447^a(4)(a, d, e); 482^a(1)(a, e); 540^a(4)(a, b, e); 643^a(3)(a, e); 659^a(3)(a, e); 727^a(0)(a, e); 767^b(00)(a, e); 1044^b(5)(a, b, e); 1138^b(1)(a, e); 1168^b(2)(a, b, e); 1194^b(4)(a, b, c, e); 1266(1)(a, b, e); 1287^a(0)(a, e); 1406(00)(a, e); 1437(00)(a); 1464^a(1)(a, c, e); 1569(0)(a); 1589^b(6)(a, e); 1790^b(4b)(b, d, e); 3074(5)(a).

[a] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$. [b] By more than 6 cm.$^{-1}$.

Lines reported by Kohlrausch, Pongratz and Stockmair not found: 176(4); 860(1b); 1725(1). Lines not reported by Kohlrausch, Pongratz and Stockmair but found: 1406(00); 1437(00); 1569(0).

m-CHLOROBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair.[7] Eastman White Label, distilled 4 times *in vacuo;* b. p. 103.4 ± 0.05° at 12.5 mm.

Plate	Filter	Type plate	Time	Background
46	G. N.	III-G	6	Weak
45	Q. S.	III-G	6	Medium
84	R. P. U.	I-O	2	Very weak
117	G. N.	III-O	8	Weak

$\Delta\nu$ = 149^a(8)(±a, ±e); 205(3)(±a, ±e); 241^a(3)(±e); 289(2)(a, ±e); 328(2)(a, e); 352(2)(a, e); 443^b(4)(a, d, e); 479^a(0)(e); 515^b(4)(a, c, e); 555(0)(a); 657(8)(a, b, e); 718^b(1)(a, e); 798(0)(a, e); 1000(12)(a, e); 1039(1)(a, e); 1086(2)(a, e); 1164^a(3)(a, e); 1191(15)(a, b, e); 1415^b(2)(a, e); 1588^a(10)(a, e); 1754^a(8)(e); 3074(8)(a).

[a] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$. [b] By more than 6 cm.$^{-1}$.

Lines reported by Kohlrausch, Pongratz and Stockmair not found: 312(2); 387(2); 406(2); 613(1); 1385(0). Lines not reported by Kohlrausch, Pongratz and Stockmair but found: 555(0); 1039(1).

p-CHLOROBENZOYL CHLORIDE

Previous investigators: Kohlrausch, Pongratz and Stockmair.[7] Prepared from *p*-chlorobenzoic acid + $SOCl_2$. Distilled 3 times *in vacuo;* b. p. 93.6–93.9° at 9 mm.

Plate	Filter	Type plate	Time	Background
92	G. N.	III-O	4	Medium
93	G. N.	III-O	2	Medium
94	Q. S.	III-G	4	Very strong
95	Q. S.	III-G	2	Medium
96	R. P. U.	I-O	1	Medium

$\Delta\nu$ = 115(0b)(±a); 150^a(3b)(+a, ±e); 262^a(8b)(a, ±e); 311^a(2)(a, e); 402(4)(a, b, e); 455^a(4)(a, ±e); 562(4)(a, b, e); 628(3)(a, b, e); 723^a(10)(a, b, ±e); 875^a-

(0b)(a, e); 1015[a](0)(a, e); 1091(15)(a, b, e); 1172(15)(a, b, e); 1203(15)(a, b, e); 1398(1)(a, e); 1589[a](20)(a, c, e); 1739[b](8b)(b, e); 1780[b](6b)(b, e); 3075[a](12)(a).

[a] Differ from Kohlrausch, Pongratz and Stockmair by more than 2 cm.$^{-1}$. [b] By more than 6 cm.$^{-1}$.

Lines reported by Kohlrausch, Pongratz and Stockmair not found: 1295($^1/_2$). Lines not reported by Kohlrausch, Pongratz and Stockmair but found: 115(0b).

o-NITROBENZOYL CHLORIDE

Previous investigators: None. Prepared from *o*-nitrobenzoic acid + $SOCl_2$. Distilled 4 times *in vacuo;* b. p. 128.2 ± 0.05° at 5 mm. [Excitation by blue light only. Violet light completely absorbed. No Raman lines of longer wave length than 4916 Å. measured because of low dispersion and large number of weak Hg lines there.]

Plate	Filter	Type plate	Time	Continuous Background	Spectrograph
14	Q. S.	I-G	20	Weak	Hilger C.D.
XXI	None	"Gaevaert Sensima"	4	Strong	Zeiss
77	Q. S.	I-G	2	Strong	Hilger E-439
85	Q. S.	I-G	1.25	Medium	Hilger E-439
126	Satd. $NaNO_2$	I-G	4	Faint	Hilger E-439

$\Delta\nu$ = 49(1)(e); 98(1)(e); 125(0)(e); 168(1)(e); 474(2)(e); 552(0)(e); 646(2b)(e); 854(2)(e); 1043(5)(e); 1085(1)(e); 1152(1)(e); 1170(2)(e); 1205(4)(e); 1352(20b)(e); 1449(1)(e); 1540(2)(d, e); 1581(5)(c, e); 1608(1)(e); 1800(1)(e).

m-NITROBENZOYL CHLORIDE

Previous investigators: None. Eastman "White Label," crystallized from carbon tetrachloride and petroleum ether. Distilled *in vacuo* 4 times; b. p. 120.2–120.4° at 2.5 mm. [Absorbed violet light completely treated as *o*-nitro-.]

Plate	Filter	Type plate	Time	Background
78	Q. S.	I-G	1	Dark
79	Q. S.	I-G	2	Very dark
124	Satd. $NaNO_2$	I-G	4	Weak

$\Delta\nu$ = 48(1)(e); 192(0)(d, e); 387(1)(e); 437(1)(e); 491(0)(e); 518(0)(e); 656(2)(e); 700(0)(e); 843(0)(e); 928(00)(e); 1005(5)(e); 1091(1)(e); 1203(6)(e); 1284(0)(e); 1352(10)(e); 1437(1)(e); 1540(2)(e); 1586(2)(e); 1618(1)(e); 1760(3)(e); 2500(0)(e).

p-NITROBENZOYL CHLORIDE

Previous investigators: None. Eastman "White Label," crystallized from carbon tetrachloride 4 times, but still yellow. [Dissolved in acetone. Absorbed all Raman light of shorter wave length than 4579 Å.]

$\Delta\nu$ = 1109(1)(e); 1353(6)(e); 1534(0)(e); 1601(6)(e); 1772(1)(d, e).

Summary

The Raman spectra of the monomethoxy and mononitro (incomplete) substitution products of benzoyl chloride have been determined for the first time. The spectra of benzoyl chloride, its monomethyl and monochloro derivatives have been determined and compared with the data of Kohlrausch, Pongratz and Stockmair.

CAMBRIDGE, MASS. RECEIVED JULY 17, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, THE UPJOHN COMPANY]

Alkyl Phenols. I. The 4-*n*-Alkylpyrogallols[1]

BY MERRILL C. HART AND E. H. WOODRUFF

Since Johnson and Lane[2] demonstrated that the introduction of an alkyl group into resorcinol increased its germicidal activity, a vast amount of work has been done on the alkyl mono- and dihydroxy phenols and their derivatives. The literature of the past fifteen years is so voluminous in this respect that no attempt will be made to list it here.

However, during this time the alkylated trihydroxyphenols have received only a haphazard attention. Hurd and Parrish[3] recently reported the phenol coefficients of dihexenyl (2 forms), heptenyl and diheptenylpyrogallol, using *S. Aureus* as the test organism, to be 20 and 250, 120 and 20, respectively. Niederl, Natelson and Beekman[4] prepared diisobutylpyrogallol but have not reported its phenol coefficient. Klarmann[5] gives the phenol coefficients of *n*-hexyl, phenylmethyl, phenethyl and phenylpropyl phloroglucinol as 8 by the Hygienic Laboratory test.

In view of the wide divergence of the phenol coefficients as well as the lack of definite information concerning the variation of activity with structure in the trihydroxy phenols, it was thought to be of interest to prepare a homologous series of alkylpyrogallols and determine their activity as germicides. As is readily seen from Fig. 1, the phenol coefficients vary regularly with increasing length of the alkyl group attached in a manner quite similar to those series already investigated.

Since the maximum germicidal activity against

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(1) Presented at the Pittsburgh meeting of The American Chemical Society, September, 1936.

(2) Johnson and Lane, THIS JOURNAL, **43**, 348 (1921).

(3) Hurd and Parrish, *ibid.*, **57**, 1731 (1935).

(4) Niederl, Natelson and Beekman, *ibid.*, **55**, 2571 (1933).

(5) Klarmann, *ibid.*, **48**, 2359 (1926).

gram negative organisms reaches a maximum with a side chain of five carbon atoms in the monohydroxy phenols and with six carbon atoms in the dihydroxy phenols, it might be expected that the maximum would not occur until a side chain of seven carbons in the trihydroxy phenols. This is not the case, the maximum occurring with a six carbon side chain as in the dihydroxy phenols. In the case of gram positive organisms as indicated by the tests with *S. Aureus* the phenol coefficient continues to rise with the length of the side chain as in the case of other alkylated phenols. The reversal of effectiveness against gram positive and gram negative bacteria occurs with the *n*-hexyl derivative. Thus the "quasi specific" effect as noted by Klarmann[6] in other series is evidenced by the alkylpyrogallols.

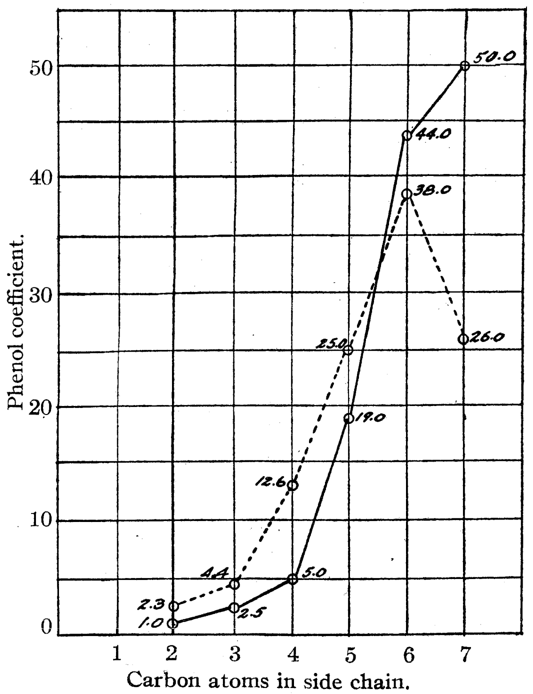

Fig. 1.– – – – –, *B. Coli;* ———, *S. Aureus.*

While the alkylpyrogallols are effective germicides they are not as effective as the alkyl mono- or dihydroxy phenols. The comparison is easily seen in Fig. 2,[7] the comparison being against gram negative organisms. Just why the phenol coefficient should diminish with the increase in number of phenolic hydroxyls, the group presumably responsible for the germicidal property of the molecule, is not clear, and in view of the conflicting theories as to the mode of action of the phenolic germicides, no attempt will be made to elucidate this point.

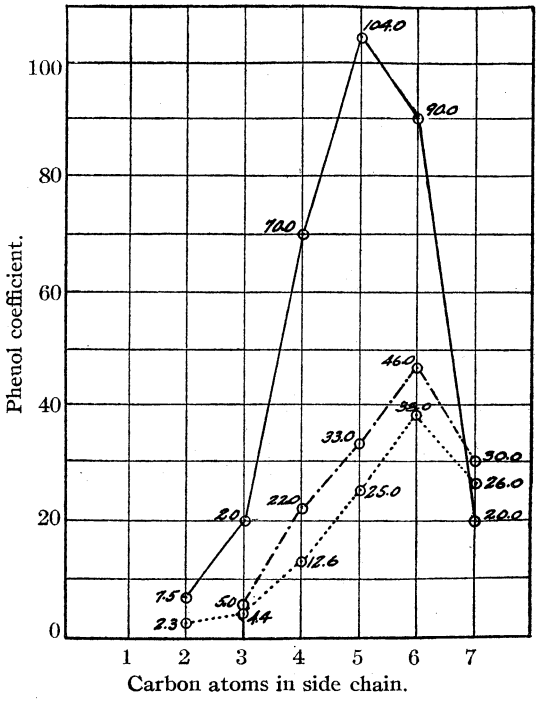

Fig. 2.———, Alkyl phenols, Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280, (1930); —·—·, alkyl resorcinols [Ref. 8]; ······, alkyl pyrogallols.

None of the alkylpyrogallols are stable in alkaline solution although the rate of oxidation is diminished as the length of the alkyl group attached is increased.

The 4-*n*-alkylpyrogallols were prepared by the reduction of the corresponding ketone by the method of Clemmensen.[8] The ketones were prepared by the method of Nencki, as given by Johnson and Lane[2] and Dohme, Cox and Miller.[9] Difficulty was encountered in the preparation of the C_5 and C_7 ketones and alkylpyrogallols, the yields being appreciably lower than the other members of the series. A similar lowering of the yield was noted by Stoughton, Baltzly and Bass[10] in the case of *n*-amylhydroquinone. Whether the lower yield was due to experimental conditions or a peculiarity of the odd numbered side chain was not investigated.

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(6) Klarmann, Shternov and Gates, THIS JOURNAL, **55**, 2576 (1933).

(7) The bacteriological data from the literature, as recorded in Fig. 2, were obtained by the Hygienic Laboratory method. This is a somewhat different test than the F.D.A. method used here for the alkylpyrogallols. It is not believed that this difference would change the relative order of effectiveness of the alkylpyrogallols with respect to the other two series.

(8) Clemmensen, *Ber.*, **47**, 51–63 (1914).

(9) Dohme, Cox and Miller, THIS JOURNAL, **48**, 1688 (1926).

(10) Stoughton, Baltzly and Bass, *ibid.*, **56**, 2007 (1934).

TABLE I

Compound	Cryst. form	Solvent	M. p.,[d] uncorr., °C.	Yield, %	Calcd., % C	Calcd., % H	Found, % C	Found, % H
Gallacetophenone		[a]	170	58		[e]		
Gallpropiophenone		[a]	128–129	35		[f]		
Gallbutyrophenone		[a]	101–102	36		[g]		
Gallvalerophenone	Yellow needles	[b,c]	84–84.5	14	62.82	6.71	62.89	6.60
Gallcaprophenone	White needles	[b,c]	86.5–87	32	64.25	7.19	64.19	7.59
Gallheptophenone	Small lemon-yellow needles	[b,c]	78–78.5	11	65.52	7.62	65.39	7.65

[a] Chloroform. [b] Benzene. [c] Petroleum ether (b. p. 30–60°). [d] All melting points are on air-dried material. [e] "Organic Syntheses," Vol. XIV, p. 40. [f] Beilstein, Erganzungsband III, p. 115. [g] *Ibid.*, p. 119.

TABLE II

4-*n*-Alkyl-pyrogallol	Cryst. form	Solvent	Yield, %	M. p., °C.	Analyses (micro) Calcd., % C	Calcd., % H	Found, % C	Found, % H
Ethyl		[a]	48	108.5		(8)		
Propyl	White rods	[a]	45	110–111	64.25	7.14	64.07	6.96
Butyl	Light tan needles	[b]	56	88–89	65.89	7.75	65.97	7.55
Amyl	White rods	[b]	25	90–91	67.30	8.33	66.94	7.95
Hexyl	White needles	[b]	54	104–105	65.52	8.64	65.39	8.75
Heptyl	Silvery needles	[c]	30	116–117	69.55	8.99	69.33	8.80

[a] Chloroform. [b] Benzene. [c] Petroleum ether (b. p. 30–60°).

Experimental

2,3,4-Trihydroxyphenyl *n*-Amyl Ketone (Gallcaprophenone).—One hundred and thirty-six grams (1.0 mole) of anhydrous zinc chloride was dissolved in 250 g. (2.1 moles) of caproic acid with the aid of heat, whereupon 126 g. (1.0 mole) of pyrogallol was added. The mixture was heated at 130–140° for one and one-half hours. The unreacted caproic acid was removed by vacuum distillation. The heavy oil was washed several times with water and recrystallized from a mixture of toluene and petroleum ether; yield 68 g. or 32.1%, m. p. 83–85°. Further recrystallizations from the same mixed solvents gave white needles, m. p. 86.5–87°.

4-*n*-Hexylpyrogallol.—Fifty grams of gallcaprophenone was reduced by the method of Clemmensen[8] using 200 g. of amalgamated zinc and 500 cc. of dilute hydrochloric acid (1:1 concd. hydrochloric acid and water). After reduction the cooled solution was extracted with ether, the ether solution dried with anhydrous magnesium sulfate, filtered and the ether removed by distillation. The residual oil was poured into 1 liter of petroleum ether (b. p. 30–60°). The solid obtained melted at 102–103° and weighed 25 g. or 53.4% of the theoretical. After several recrystallizations from a mixture of benzene and petroleum ether (b. p. 30–60°) white needles, m. p. 104–105°, were obtained.

The phenol coefficients were determined by the F. D. A. technique at 37.5° using *S. Aureus* and *B. Coli* as test organisms. The authors wish to thank Dr. John F. Norton and Mr. E. A. Gibson of the Bacteriological Laboratory of The Upjohn Company for the determination of the phenol coefficients, and Mr. C. H. Emerson for the micro analyses given.

Summary

1. The 4-*n*-alkylpyrogallols from C_2H_5 through C_7H_{15} have been prepared and their phenol coefficients determined.

2. The phenol coefficients varied with increasing size of the attached alkyl group in a similar manner to the alkyl mono and dihydroxyphenols.

3. The "quasi specific" effect was found to exist in the alkyl pyrogallols.

4. The phenol coefficient of compounds having the same alkyl group tends to diminish as the number of phenolic hydroxyl groups in the molecule increases.

KALAMAZOO, MICH.

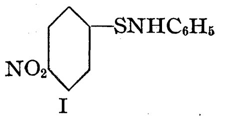
RECEIVED AUGUST 8, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Molecular Rearrangement of Sulfenanilides in Alkaline Solution. IV

BY MAURICE L. MOORE[1] AND TREAT B. JOHNSON

In extending our study of the molecular rearrangement of sulfenanilides in alcoholic alkaline solution, it was interesting to find that the *p*-nitro substituted derivatives of these compounds, I, do not undergo rearrangement to give mercapto-diphenylamine compounds when heated in alcoholic sodium hydroxide solution. This is all the more interesting in view of the fact that Smiles[2] has not, thus far, reported the molecular rearrangement of similar derivatives in the *o*-amino sulfide series, whereas he has done so in the *o*-hydroxysulfones.[3] Thus, 4-nitrophenylsulfen-*o*-chloroanilide, 4-nitrophenylsulfen-*o*-toluidide and 4-nitrophenylsulfenanilide did not undergo structural changes when digested in alcoholic sodium hydroxide solution for three hours. A small amount of the corresponding disulfide was isolated from the reaction mixture, but by far the chief proportion of the recovered product was the unaltered sulfenanilide used as the starting material. Thus, it appears from our results that the substitution of a nitro group in the *p*-position does not give enough activity to the carbon atom at the sulfur linkage to produce a rearrangement as is the case when the nitro group occupies an *o*-position. The latter type of compounds undergo rearrangement upon heating to give the corresponding amino sulfides.



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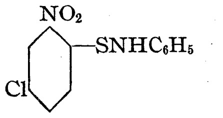

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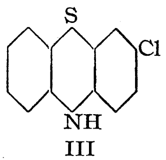

III

A rearrangement of the 2,4-nitrochlorophenyl derivatives II was observed to occur in the usual manner to give the respective mercaptodiphenylamines. Thus, 2,4-nitrochlorophenylsulfenanilide gave the sodium salt of 2-mercaptophenyl-2′,4′-nitrochlorophenylamine when refluxed in alcoholic sodium hydroxide solution for three hours. This compound was isolated and identified by conversion into its thiomethyl ether. 2-Nitrophenylsulfen-*o*-chloroanilide, 2,4-nitrochlorophenylsulfen-*o*-toluidide and 2,4-nitrochlorophenylsulfen-*o*-chloroanilide underwent a corresponding rearrangement when treated in like manner. In each case the sodium salt of the mercapto compound was isolated as a brilliant red crystalline solid, which was converted into the corresponding thiomethyl ether for characterization by the action of methyl iodide.

This isolation of the sodium salt and the thiomethyl ether by the rearrangement of the 2,4-nitrochlorophenyl derivatives is somewhat in contradiction to the results of Smiles[2c] with the 2,4-nitrochlorophenyl derivatives of the *o*-aminosulfides, as he was unable to isolate the free mercapto-diphenylamine or the thiomethyl ether because of the rapid formation of a thiazine compound III. The latter formation involves the splitting out of nitrous acid.

Experimental Part

2,4 - Nitrochlorophenylsulfen - *o* - chloroanilide.—2,4-Nitrochlorophenylsulfur chloride (25 g.) gave 20 g. of an orange-red glistening crystalline material when treated with *o*-chloroaniline (28 g.) under the usual conditions. It was easily crystallized from boiling alcohol, m. p. 112°.

Anal. Calcd. for $C_{12}H_1O_2N_2SCl_2$: N, 8.89; S, 10.16; Cl, 22.54. Found: N, 8.89, 8.76; S, 10.41, 10.18; Cl, 22.21, 22.40.

Procedure for Rearrangement.—The necessary sulfenanilide (5 g.) was placed in alcohol (25 ml.) containing 20% sodium hydroxide (5 ml.) according to the procedure previously reported[4] and refluxed for three hours. The reaction product was isolated and purified as the sodium salt.

Methylation of the Mercaptan.—The sodium salt from the above operation (5 g.) was dissolved in alcohol (15–25 ml.), refluxed for a short time (fifteen to sixty minutes) with an excess of methyl iodide (3 ml.) and worked up in the usual manner. In certain instances it was found that the thiomethyl ether would separate out of the hot alcohol after refluxing for varying lengths of time (fifteen to sixty minutes).

In Table I are recorded the results of the rearrangement of different sulfenanilides under the influence of alkali.

Summary

Digestion of *p*-nitrophenyl derivatives of sulfenanilides in alcoholic sodium hydroxide solution

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[1] A. Homer Smith Research Fellow, 1935–1936.

[2] (a) Evans and Smiles, *J. Chem. Soc.*, 181 (1935); (b) Wight and Smiles, *ibid.*, 340 (1935); (c) Evans and Smiles, *ibid.*, 1263 (1935).

[3] Kent and Smiles, *ibid.*, 422 (1934).

[4] Moore and Johnson, THIS JOURNAL, **57**, 1517, 2234 (1935).

TABLE I

Compounds			Yield, %	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found		Sulfur, % Calcd.	Sulfur, % Found		Chlorine, % Calcd.	Chlorine, % Found	
4-Nitrophenylsulfen-		Anilide[a]						No rearrangement					
		p-Toluidide[a]						No rearrangement					
		o-Chloroanilide[a]						No rearrangement					
2,4-Nitrochlorophenylsulfen-	Na salt of mercapto-diphenylamine derivative	Anilide[a]	85					10.58	10.53		11.73	11.64	
		o-Toluidide[a]	95					10.11	10.19	10.03	11.22	11.23	
		o-Chloroanilide[a]	90					9.50	9.27	9.42	21.07	21.41	21.30
	Thiomethyl ether of mercapto-diphenylamine derivative	Anilide[a]	85	135–136	9.51	9.33	9.20	10.87	10.56	10.67	12.06	12.34	12.21
		o-Toluidide[a]	80	164–165	9.08	9.13	9.04	10.37	10.10	10.25	11.51	11.70	11.62
		o-Chloroanilide[a]	80	158–158.5	8.51	8.30	8.44	9.73	9.88	9.82	21.58	21.77	21.65
2-Nitrophenylsulfen-*o*-chloranilide[a]	Sodium salt of mercapto-diphenylamine derivative		90					10.58	10.60	10.42	11.73	11.61	11.55
	Thiomethyl ether of diphenylamine derivative		84	144.5–145	9.51	9.61	9.59	10.87	10.90	10.96	12.06	12.05	12.12

[a] For the preparation of these compounds, see THIS JOURNAL, **58**, 1091 (1936).

failed to bring about a rearrangement to their corresponding *o*-mercaptodiphenyl amines. The 2,4-nitrochlorophenyl derivatives, however, undergo a rearrangement to *o*-mercaptodiphenylamines when so treated, and it was possible to isolate the sodium salt as well as the thiomethyl ether without cyclization to thiazine compounds. The study of sulfenanilides will be continued in this Laboratory.

NEW HAVEN, CONN.

RECEIVED JULY 13, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Natural and Synthetic Rubber. XVI. The Structure of Polystyrene

BY THOMAS MIDGLEY, JR., ALBERT L. HENNE AND HENRY M. LEICESTER

Polystyrene[1] is a friable solid which exhibits rubber-like properties at temperatures above 65°; it is obtained by heat polymerization of styrene.

Staudinger and his co-workers[2] have stated that polystyrene can be decomposed by heat into a mono-, di- and tristyrene; that the latter two compounds can be decomposed to monostyrene; and that 2,4-diphenyl-1-butene and 1,3-diphenylpropane can be detected among the heat decomposition products. They have therefore reached the conclusion that polystyrene is a long chain of styrene units bound together by ordinary valences, with a phenyl group linked to every second carbon. They have advocated formula I and rejected formula II.

$$\text{—CH}_2\text{CHPhCH}_2\text{CHPhCH}_2\text{CHPh—} \qquad \text{(I)}$$

$$\text{—CH}_2\text{CHPhCHPhCH}_2\text{CH}_2\text{CHPhCHPhCH}_2\text{—} \qquad \text{(II)}$$

Staudinger's experiments were repeated and found to be correct but the following additional facts were noted: (1) heat decomposition of polystyrene does not yield monostyrene exclusively; (2) rapid decomposition yields large amounts of monostyrene, while slow decomposition yields "di-styrene," "tri-styrene" and other intermediate products; (3) the partially decomposed products are complicated mixtures, and their further decomposition gives a poor yield of monostyrene; (4) diphenylbutene and diphenylpropane are present in very small quantities, and only in products obtained from incomplete decomposition; (5) all efforts to analyze the dimeric fraction by oxidation, reduction, nitration, bromination, etc., gave indifferent results. These additional experimental data cast strong doubts on the significance of the decomposition products in establishing the formula of polystyrene.

An explanation of dependence of the elasticity of natural and synthetic rubbers on their structural formula has been offered by Mack.[3] The application of his ideas to the case of polystyrene leads directly to the conclusion that the elastic properties of this substance are consistent with formula II, and not at all with the heretofore accepted formula I, for the following reasons.

In the case of formula I, the 1,3-placement of the phenyl groups results in optimum packing of the phenyl groups, optimum contacting of the hydrogen atoms, and good satisfaction of the van der Waals forces *when the chain molecule is extended;* consequently there is no tendency to fold

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(1) Whitby, *Rubber Chem. Tech.*, 465 (1931).

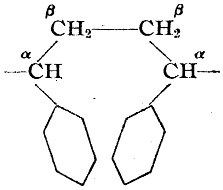
(2) Staudinger, *et. al.*, *Ber.*, **59**, 3019 (1926); **62**, 241–63 (1929); **62**, 2406 (1929); *Ann.*, **517**, 35–53 (1935).

(3) Mack, THIS JOURNAL, **56**, 2757 (1934).

or shorten the chain. But in the case of formula II, the 1,4-placement throws the phenyl groups together into pairs on adjacent carbon atoms, with two chain carbon atoms separating these pairs. Not only do the two phenyl groups within a pair turn into one another to establish better contacting, but van der Waals forces draw together into contact the various separate pairs, thus folding the extended chain and giving automatic retraction, hence elastic, rubber-like behavior. The motion of the bulky phenyl groups is sluggish at room temperature, but becomes more free and more swift with increasing thermal agitation, *i. e.*, at higher temperature.

Since Staudinger's reasons for discriminating against the formula required by Mack's theory were not found convincing, it was decided to apply to styrene the experimental procedure previously used with isoprene and dimethylbutadiene to establish the course of their transformation into synthetic rubber and methyl rubber, respectively.[4] This procedure consists in stopping the polymerization at the dimeric stage by addition of nascent hydrogen generated by the interaction of sodium and ethanol. Sodium chips are added to styrene and alcohol is fed at a rate sufficient to produce a lively evolution of hydrogen; the reaction liberates a considerable amount of heat, but the boiling of the alcohol automatically regulates the temperature. The reaction products consist of about 75% of ethylbenzene and 25% of 1,4-diphenylbutane. Significant is the fact that the reaction products are pure and entirely free from isomers or by-products.

The course of the polymerization is interpreted as follows. If the thermal agitation of the liquid styrene molecules consisted only of Dulong and Petit motions, back and forth, polymerization could take place by the random linking of two carbon atoms in α-position (with regard to the phenyl group), two carbon atoms in β-position, or one α- and one β-atom, and consequently the two phenyl groups of the dimeric compounds would be located in 1,4-, 2,4- or 2,3-position. The molecules are, however, in a liquid, and therefore crowded; they are thus compelled to rotate about the center of their own volume, that is, close to the center of the phenyl group. Then, no matter how the rotation occurs, the β-carbon atoms, at the end of the side-chain, are the only ones which can eventually come close enough to link. The chances of an α-carbon coming close enough to a β-carbon of another molecule to link are very remote, and its chances of coming close enough to another α-carbon are nil, because in addition to being shielded by the bulky phenyl group, it is most effectively buried within the sphere of revolution established by the outlying CH_2 group. As soon as two molecules have linked together the dimeric compound assumes a shape such as:[5]



where the free bonds of the α-carbon atoms are now at the surface and ready to join with the bonds of another dimer. From this stage the process of polymerization takes place by mere repetition.

It is therefore concluded that formula II is the correct representation of polystyrene and that Mack's explanation of its elasticity is consistent with the facts. This conclusion has been obtained in private discussion with Dr. Mack, whom we wish to thank.

Experimental

Preparation of Diphenylbutane with Sodium and EtOH.—Alcohol was added dropwise to 17 g. (20 cc.) of freshly distilled styrene and 5.3 g. of sodium chips at such a rate that hydrogen was steadily evolved. During the first part of the reaction, it was necessary to cool the mixture occasionally. As the reaction proceeded the solution became brown and sodium alcoholate separated, so that when all the sodium had been used up, the reaction mixture was almost solid. Ether was then added and the solution washed three times with water and dried over calcium chloride. The combined ether extracts from three runs (totaling 62 g. of styrene) were fractionated. Two fractions were obtained, one boiling at 135–150°, the other at 304–308°. The latter solidified in the receiver. The first fraction weighed 46 g. (74%) and consisted of ethylbenzene containing almost no styrene, as shown by the facts that no polymerization occurred when sulfuric acid was added to the liquid, or when it was heated for a prolonged period of time. The solid material, which weighed 11.5 g. (18.5%) after crystallization from alcohol, melted sharply at 52–52.5°, and the melting point showed no depression when the crystals were mixed with 1,4-diphenylbutane prepared by the catalytic reduction of 1,4-diphenylbutadiene.[6] The mother liquors from the crystallization were di-

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[4] Midgley and Henne, THIS JOURNAL, **51**, 1294 (1929); **52**, 2077 (1930).

[5] This is more easily seen on a three dimension scale model.

[6] *Org. Syntheses*, **16**, 28 (1936).

luted with water and extracted with ether. From the extract was obtained 2 g. (4.3%) of a semi-solid yellow oil from which more 1,4-diphenylbutane separated.

Summary

Styrene treated with sodium and alcohol gives 75% of ethylbenzene and 25% of 1,4-diphenylbutane. This shows that polystyrene should be represented by formula II, in opposition to the heretofore accepted formula I. Only formula II is consistent with Mack's explanation of the rubber-like elastic properties of polystyrene.

COLUMBUS, OHIO RECEIVED JULY 15, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEW HAMPSHIRE]

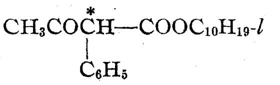
A Comparison of the Rate of Racemization with the Rate of Enolization

BY R. H. KIMBALL

It has long been assumed that optically active ketones, esters and acids can undergo racemization through formation of the inactive enol, which reverts to the racemic mixture. General acceptance of this mechanism has followed recognition of the fact that such substances can only be racemized when they are capable of enolization. This has been confirmed recently by Conant and Carlson,[1] who conclude that the rate of racemization can be considered as the rate of enolization, and point out the significant fact that whatever mechanism is assumed the rate of enolization cannot be faster than that of racemization, since the enol is necessarily inactive.

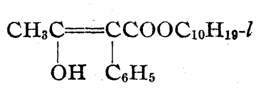
Whether enolization can be *slower* than racemization can only be determined by measuring the loss of optical activity and the development of enol simultaneously by independent methods. The familiar Kurt Meyer method of bromine titration has been applied in the past to measurement of the rate of enolization of acetoacetic ester and related substances.[2] An unsuccessful attempt to combine this method with polarimetric measurements has been described by Wren,[3] who tried to follow the development of enol during the racemization of methyl phenyl succinate by bromine titration, but failed because no detectable amount of enol was present. The difficulty has been that substances appreciably enolized racemize so easily that they cannot be obtained optically active; while substances which can be obtained optically active are not perceptibly enolized.

The substance employed in the present attack on the problem is the menthyl ester of α-phenylacetoacetic acid[4] I.



$CH_3CO\underset{C_6H_5}{\overset{*}{C}H}{-}COOC_{10}H_{19}\text{-}l$

I



$CH_3\underset{OH}{C}{=}\underset{C_6H_5}{C}COOC_{10}H_{19}\text{-}l$

II

The form of this substance obtained by crystallization from methyl alcohol is the ketonic modification, as demonstrated by the fact that the fresh solution gives no color with ferric chloride and does not absorb bromine.

Freshly dissolved in benzene or alcohol the substance is dextrorotatory. The rotation at once starts to decrease, passing through zero and finally reaching a constant strongly levo value. This takes weeks without a catalyst, but addition of a small amount of piperidine or barium hydroxide brings it to equilibrium in a few minutes.

Rupe[4] interpreted this to mean that the active menthol has brought about resolution of the α-phenylacetoacetic acid, the form crystallizing from methyl alcohol being the dextro-keto modification I because of its dextro rotation—a long series of similar menthyl esters in which resolution is not possible being strongly levorotatory like menthol itself. He ascribed the mutarotation to formation of the enol II in which the optical activity of the alpha carbon atom is lost. Since only one of the three asymmetric carbon atoms is affected, this is not a true but a partial racemization, and at equilibrium the solution will contain the enol mixed with the diameric dextro-keto and levo-keto modifications.

In the usual true or partial racemization the proportion of enol is always negligible. Here on the contrary the enol steadily increases during the mutarotation until it constitutes the major part of the equilibrium mixture. The most significant comparison between the rate of this development of enol and the rate of racemization of the carbon atom involved will be made during

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[1] Conant and Carlson, THIS JOURNAL, **54**, 4048 (1932).

[2] K. H. Meyer, *Ann.*, **380**, 233 (1911); *Ber.*, **44**, 2725, 2729 (1911); Grossman, *Z. physik. Chem.*, **109**, 305 (1924).

[3] Wren, *J. Chem. Soc.*, **113**, 210 (1918).

[4] Rupe, *Ann.*, **395**, 91 (1913); **398**, 372 (1913).

the early stages of the reaction, when the reverse processes are not yet apparent and the change of *d*-keto to enol is the only thing taking place.

With this in view the solvent chosen was cyclohexane, in which enolization is 71% complete at equilibrium. About 10 g. of pure crystalline *d*-keto form was weighed into a volumetric flask and made up to 100 cc. with pure cyclohexane containing a few parts per million of piperidine as the catalyst. The solution was quickly transferred to an all-glass polarimeter tube with an attached chamber, water-jacketed to maintain constant temperature and designed to permit frequent and thorough mixing of the solution (Fig. 1). Polarimeter readings were taken at intervals through the first half of the racemization.

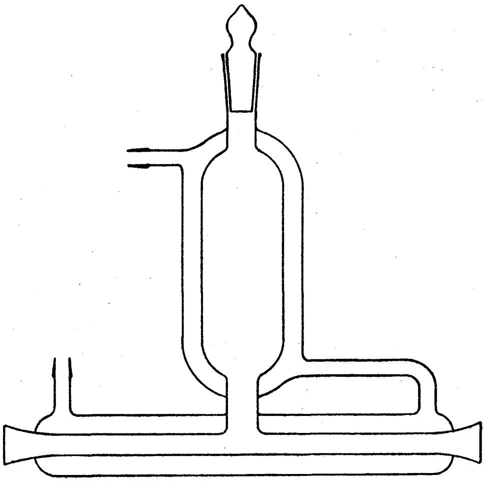

Fig. 1.—Polarimeter tube.

The development of enol was followed by pipetting out samples of the solution and titrating them with dilute alcoholic bromine to the first bromine color, the "direct" method of Kurt Meyer. Here it proved very satisfactory since the bromine was absorbed rapidly in the cold, and the sharp end-point persisted for five minutes. Finally more catalyst was added and the reaction was allowed to run to equilibrium, to obtain the values for the rotation and for the concentration of enol.

The pseudo-unimolecular velocity constant $k_1 + k_2$ for the racemization was obtained in the ordinary way by plotting the values of log $(\alpha_t - \alpha_{eq.})$ against t, where α_t and $\alpha_{eq.}$ represent the polarimeter readings at time t and at equilibrium. For the enolization the volume of thiosulfate used by each sample is proportional to the concentration of enol, so that log $(V_{eq.} - V_t)$ was plotted against t. The best straight lines were run through these points and $k_1 + k_2$ calculated from the slope in the usual manner. For both the racemization and the enolization the points fell closely along straight lines (Fig. 2, A and B) and the reactions therefore follow the unimolecular law. Measurements normally extended over a period covering the first half of the racemization and the first quarter of the enolization, in one case the racemization being followed to 80% completion and the enolization to 50% completion without the appearance of a trend.

The data for three runs with varying amounts of catalyst are summarized in Table I.

TABLE I

VELOCITY CONSTANTS × 10^4 TIME IN MINUTES FOR THE RACEMIZATION AND ENOLIZATION OF MENTHYL α-PHENYLACETOACETATE I

Run no.	I	II	III
Approx. concn. piperidine in parts per million	8	10	12
$k_1 + k_2$ for racemization	12.8	17.8	24.8
$k_1 + k_2$ for enolization	3.72	6.64	8.02
k_1 for enol. (graphically)	2.51	4.48	6.17
k_1 for enol. (calculated)	2.59	4.71	6.34
k_1 polarimetrically using α_{enol}	14.5	20.1	28.5
k_r (total racemization)	8.22	16.3	21.6
k_{dl} (racem. through ion)	5.47	10.5	14.3
k_e (racem. through enol)	2.75	5.80	7.32
Ratio k_{dl}/k_e	1.99	1.82	1.95

It is evident that racemization as measured by $k_1 + k_2$ proceeds several times as fast as enolization. However, a much more significant comparison can be made. If the *d*-keto form loses its activity through changing directly to the enol, the rate of this change k_1 can be obtained from data taken in the early stages of the reaction, and it should have the same value by both methods of measurement.

For the enolization k_1 is easily determined by plotting the log of the concentration of keto against t in the usual way. The points still fall on a straight line through the measured range (Fig. 2, D) and the slope of this line gives the values of k_1 for enolization shown in Table I.

It is also possible to calculate k_1 from the two equations for $k_1 + k_2$ and for the equilibrium constant in the usual way, and the values are in satisfactory agreement.

To measure the rate of change of *d*-keto to enol polarimetrically, it is necessary to know the rotatory power of the pure enol. Attempts to isolate the enol by chemical methods failed, shift to the equilibrium mixture taking place too easily.

Distillation under a high vacuum from a Hickman molecular still was finally successfully employed. The crystalline keto form was catalyzed with a little barium hydroxide and distilled slowly, yielding a uniform distillate containing 64% of enol, which probably represents the equilibrium in the vapor phase.[5] This mixture was repeatedly fractionated in the absence of catalyst, the distillate becoming progressively richer in enol until the concentration reached 93.8%, which apparently represents a constant boiling mixture. This is a colorless viscous oil, hardening to a glass at low temperatures without crystallization; it has the same composition as the ketonic form, gives an immediate deep purple color with ferric chloride, and absorbs bromine rapidly in the cold. Alone or in solution it is very stable in the absence of catalyst, but with a trace of piperidine it undergoes mutarotation to the same equilibrium mixture reached by the *d*-keto form.

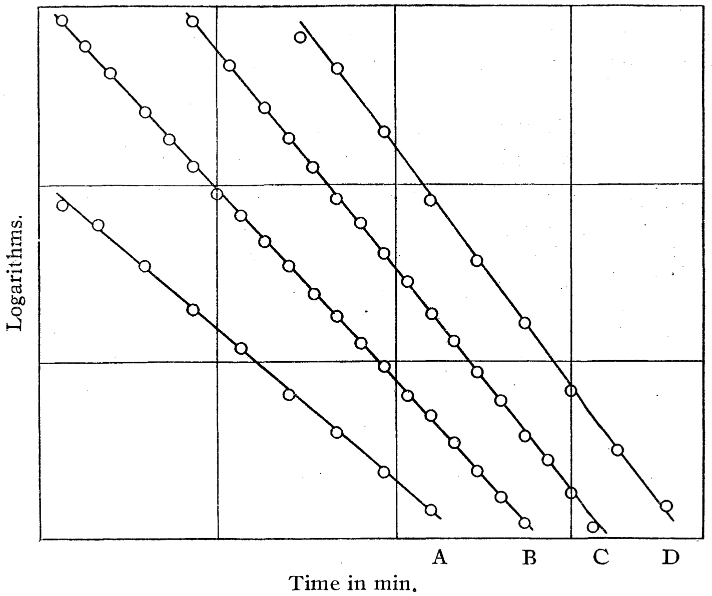

Fig. 2.—Graph of run III: A, $k_1 + k_2$ for enolization ($\times 10^4$) = 8.02; B, $k_1 + k_2$ for racemization = 24.8; C, k_1 polarimetrically using α_{enol} = 28.5; D, k_1 for enolization (titrimetrically) = 6.17. Range of measurement: A and D 3–18% enol; B and C 7–65% racemization. Time scale: unit square = 150 min. Logarithm scale: unit square for A = 0.0600; for B and C = 0.1500; for D = 0.0300.

The value for the rotation of pure enol was obtained by following this mutarotation in cyclohexane by the polarimeter and by titration in the usual way. On plotting this series of values for decreasing enol content against the rotation, a nearly straight line was obtained and extrapolated to the rotation of pure enol as shown in Fig. 3. The accuracy of this extrapolation is favored by the small change in rotation, and the value obtained $[\alpha]^{25}\text{D}$ −56.5° should be close to the true rotation of the enol.

The rate of change of *d*-keto to enol can now be determined polarimetrically by substituting α_{enol} for $\alpha_{eq.}$ and plotting log ($\alpha_t - \alpha_{enol}$) against t (Fig. 2, C). The points still fall along a straight line through the first half of the racemization, and the slope of this line gives values for k_1 (Table I) which are four or five times as large as the values of k_1 for the same change of *d*-keto to enol obtained by titration.

There seems to be no doubt therefore that in this substance the alpha carbon atom loses its optical activity much faster than the enol is produced. This can hardly be explained by some means of racemization operating independently of the enolization, in view of the almost inseparable connection between the two processes.[6] As the only alternative it is evident that *enolization cannot consist of a simple reversible change of keto to enol, but must proceed through some intermediate step.* In this intermediate step the configuration of the alpha carbon atom is destroyed, and since only part of the active substance changing to the intermediate in a given time goes on to form enol, and part reverts to *inactive* keto, the rate of racemization will be faster than the rate of enolization.

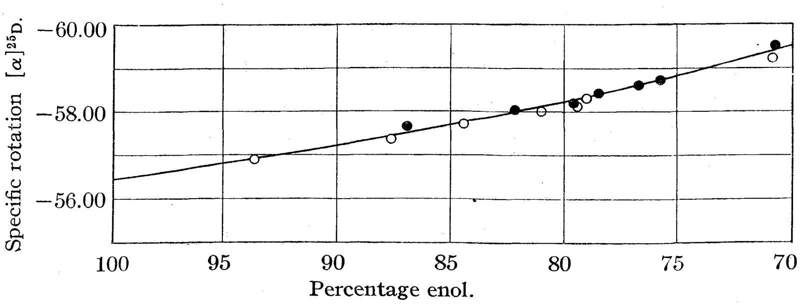

Fig. 3.—Mutarotation of constant boiling mixture extrapolated to 100% enol to obtain $[\alpha]^{25}\text{D}$ − 56.5°: ○, run I; ●, run II.

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(5) Conant and Thompson, THIS JOURNAL, **54**, 4039 (1932).

(6) Conant and Carlson, THIS JOURNAL, **54**, 4048 (1932); discussion by Wagner-Jauregg in "Stereochemie," ed. Freudenberg, Franz Deuticke, Vienna, 1933, p. 858.

The relationship between racemization and enolization from the standpoint of the ionic theory of prototropic change has been discussed recently by Ingold and collaborators[7] in several papers which appeared during the course of this work. They formulate the mechanism of keto-enol tautomerism under the influence of a basic catalyst in the usual way[8]

$$B + H{-}C{-}C{=}O \rightleftarrows BH + [C{-}C{=}O]^- \rightleftarrows B + C{=}C{-}OH$$

and point out that if the configuration of the alpha carbon atom is retained in the common ion, the rate of enolization and of racemization should be equal; on the other hand, if the asymmetry is lost in the common ion, the rate of racemization must exceed that of enolization.

They tested the question in the methyleneazomethine system

$$C(H){-}N{=}C \rightleftarrows C{=}N{-}C(H)$$

by comparing the rate of racemization of an active tautomeride under the influence of sodium ethoxide with the rate of its isomerization as determined by chemical analysis. In three cases the rates were identical within the experimental error, and the authors conclude that in this system the intermediate anion does not attain kinetic freedom and therefore retains its optical activity up to the instant of transformation into the inactive isomer.

In the base-catalyzed keto–enol system now under consideration the racemization takes place much faster than the formation of enol; and some intermediate stage in the process unavoidably must be recognized. If the ionic mechanism is adopted it follows that contrary to the situation in the methyleneazomethine system the intermediate anion does not retain its asymmetry, so that recombination with the proton gives both enol and *racemized* keto forms and accounts for the higher rate of racemization.

The existence of some supplementary means of racemization apart from conversion to the enol makes it obvious that the values of k_1 so far obtained do not express the true rate of racemization nor its relationship to the rate of enolization. Both can be calculated, however, from the data at hand as follows.

Adopting some form of intermediate as necessary to acount for the results, the racemization of the menthyl ester is represented by scheme (1), where D, L, E and B represent, respectively, the *d*-keto form, the *l*-keto form, the enol and the intermediate, presumably the common anion. In the ordinary partial racemization such as the inversion of menthone where the amount of E is always imperceptible, the measured "rate of racemization" is simply the rate at which the original rotation of D changes to the rotation of the equilibrium mixture DL. As each molecule of D reacts it becomes part of the equilibrium mixture, so we can consider the *original* active substance D* as changing *irreversibly* to DL at a rate k_r equal to the measured rate of racemization.

$$\begin{tikzcd} D \arrow[r, shift left, "k_1"] & B \arrow[l, shift left, "k_3"] \arrow[r, shift right, "k_4"'] \arrow[d, shift right, "k_5"'] & L \arrow[l, shift right, "k_2"'] \\ & E \arrow[u, shift right, "k_6"'] & \end{tikzcd} \qquad (1)$$

$$\begin{tikzcd} D^* \arrow[r, "k_r"] & B \arrow[r, "k_3 + k_4"] \arrow[d, "k_5"'] & DL \\ & E & \end{tikzcd} \qquad (2)$$

$$\begin{tikzcd} & DL \\ D^* \arrow[ur, "k_{dl}"] \arrow[dr, "k_e"'] & \\ & E \end{tikzcd} \qquad (3)$$

$$k_{dl} + k_e = \frac{2.3}{t} \log \frac{C_{0D^*}}{C_{D^*}} \qquad (4)$$

$$\frac{k_{dl}}{k_e} = \frac{C_{DL}}{C_E} \qquad (5)$$

Representing the case at hand in the same way reduces (1) to (2), for early stages of the reaction where k_6 can be neglected. And since B changes immediately to DL and to E as fast as it is produced from D*, the effect is that of a direct change of D* simultaneously to DL and to E as shown in (3), where $k_{dl} + k_e = k_r$ the total rate of racemization, and $k_{dl}/k_e = (k_3 + k_4)/k_5$. The individual rates can now be obtained from equations (4) and (5), where C_{0D^*}, is the concentration of D* at t_0 and C_{D^*}, C_{DL} and C_E are the concentrations of D*, DL and E at any given time t.

In order to calculate these concentrations it is necessary to know the specific rotation of each substance. $[\alpha]_{D^*}$ and $[\alpha]$E are already known and $[\alpha]$DL can be obtained from the composition and rotation of the equilibrium mixture of DL and E resulting from complete racemization. From first principles it is apparent that in system (1) the *relative* proportions of D and L at equilibrium are independent of the presence or amount

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[7] Ingold and Wilson, *J. Chem. Soc.*, **93**, 773 (1934); Hsü, Ingold and Wilson, *ibid.*, 1778 (1935); Hsü and Wilson, *ibid.*, 623 (1936).

[8] *Cf.* Bartlett, THIS JOURNAL, **56**, 969 (1934); Watson, Nathan and Laurie, *J. Chem. Phys.*, **3**, 170 (1935); Watson and Yates, *J. Chem. Soc.*, 1208 (1932); Pedersen, *J. Phys. Chem.*, **38**, 619 (1934).

of E or of the mechanism involved. The same mixture of D and L would result if E were negligibly small as in the ordinary partial racemization; therefore it corresponds exactly to the DL of schemes (2) and (3). Making the usual assumption that the rotations are additive in these dilute solutions, and knowing $[\alpha]E$ and the concentrations of E and DL in the equilibrium mixture, $[\alpha]DL$ can be obtained by difference. In the three runs $[\alpha]DL = -67.4, -67.8$ and $-68.5°$, respectively, the individual values being used in each case. For the others the values $[\alpha]E = -56.5°$ and $[\alpha]D^* = -15.8°$ (average) were employed.

The next step toward applying equations (4) and (5) is the calculation of C_{D^*}, C_{DL} and C_E at time t, which will be illustrated for run III. Here $C_{0D^*} = 10.584$ (g. in 100 cc. of solution), t_0 = time when *d*-keto was put into solution, and t was chosen as three hundred and fifty minutes, close to the half time of racemization. From the straight lines plotted for $k_1 + k_2$ of racemization and of enolization (B and A, Fig. 2) were read off the correct values for the rotation ($\alpha D^* + \alpha DL + \alpha E = -10.30°$) and for the concentration of enol ($C_E = 1.903$ g.) at time t. Subtracting C_E from the total concentration 10.584 g. gives equation (6).

$$C_{D^*} + C_{DL} = 8.681 \text{ g.} \qquad (6)$$
$$0.3707\ C_{D^*} + 1.603\ C_{DL} = 7.79° \qquad (7)$$

Subtracting the rotation of 1.903 g. of enol (αE) from $-10.30°$ gives $\alpha D^* + \alpha DL = -7.79°$, which by the use of $[\alpha]D^*$ and $[\alpha]DL$ can be expressed as equation (7). Solving these two equations we now have $C_{0D^*} = 10.584$, $C_{D^*} = 4.972$, $C_{DL} = 3.709$, $C_E = 1.903$, and $t = 350$. Substituting these values in equations (4) and (5) and solving, $k_r = k_{dl} + k_e = 21.6$, $k_{dl} = 14.3$, and $k_e = 7.3(\times 10^{-4})$. The values obtained in the same way for runs I and II are shown in Table I, together with the ratios of k_{dl} to k_e which are close to 2 : 1 and check satisfactorily. From the previous discussion it is evident that k_r is comparable to the rate measured in the ordinary partial racemization; k_{dl} represents the fraction of this racemization (around two-thirds) taking place through the common ion without involving the enol; and k_e the fraction (around one-third) involving actual transformation to the enol.

It seems quite probable that racemization may take place in a similar way in ordinary ketones where no detectable enol ever appears. The fact that only part of the racemization can be ascribed to "enolization" in the usual sense of the word calls into question the validity of the familiar principle that the rate of racemization can be considered as the rate of enolization. The ability of a substance to ionize and the stability of the configuration of the common ion may be the important factors governing its racemization, rather than the actual formation of molecular enol.

The other reaction of ketones commonly regarded as a measure of enolization is halogenation in the α-position to the carbonyl group.[7-9] Recent comparisons have shown that the rate of halogenation and the rate of racemization of optically active ketones are substantially equal both in the presence of acids and of bases,[10] and the suggestion has been made that the halogen actually adds to the intermediate ion, at a rate equivalent to the rate of ionization. Since it now appears that under basic catalysis ionization alone can result in racemization, the rate of halogen absorption may be a measure of racemization (k_r) but not of enolization (k_e) in the sense of actual formation of molecular enol. The more "saturated" character of the intermediate ions or salt-like complexes generally postulated in acid catalysis[7,8,10] would seem to favor a more stable configuration. Rate measurements now being made of the racemization and enolization of the menthyl ester in the presence of acids may serve as a test of this question.

In another respect, however, the present results are difficult to interpret by the ionic theory of prototropic change. On general grounds Ingold and his collaborators[7] have concluded that in basic catalysis the reversible change from anion to enol must be very much faster than that from keto to anion, so that the observed rate of racemization should be substantially equal to the rate of enolization. The same opinion has been expressed by Pedersen[8] from the fact that rapid addition of a hydrochloric acid–bromine water mixture to an alkaline solution of acetoacetic ester indicated complete transformation of the anion to the enol.

In the case at hand, however, the anion apparently reverts to the keto form twice as fast as

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[9] Bartlett and co-workers, THIS JOURNAL, **55**, 4992 (1933); **56**, 967 (1934); **57**, 1596, 2580 (1935); Watson and co-workers, *J. Chem. Soc.*, 217, 220, 890 (1933); 3318 (1931); Watson, *Chem. Rev.*, **7**, 173 (1930), includes a review of the literature.

[10] Bartlett and Stauffer, THIS JOURNAL, **57**, 2580 (1935); Ingold and Wilson, *J. Chem. Soc.*, 773 (1934); Hsü and Wilson, *ibid.*, 623 (1936).

it goes on to the enol. In scheme (1) k_5 is less than $k_3 + k_4$, but the amount of enol at equilibrium is greater than the amount of keto; it follows that $k_1 + k_2$ is greater than k_6, or the *keto form ionizes more rapidly than the enol.* This surprising result may perhaps be explained by the fact that enols of this type probably have a chelated structure, in which the mobility of the hydrogen may be reduced even below that in the ketonic form.

These considerations point to an alternative explanation of the observed difference between the rate of racemization and the rate of enolization of the menthyl ester. We may be dealing with a rapid and highly reversible shift to a small amount of open-chain enol which governs the racemization, followed by a slower accumulation of chelated enol which determines the rate measured by titration. It is hoped that further studies now in progress may aid in answering this and related questions.

Experimental

Acetobenzyl Cyanide, $CH_3COCH(C_6H_5)CN$.—Reagents must be pure and free from water and acids. Ethyl alcohol was dried twice over quicklime. Ethyl acetate was washed and fractionated from phosphorus pentoxide collecting over 0.5° range. Benzyl cyanide was freshly distilled at ordinary pressure and collected over 1.5° range.

Sixty-nine grams (3 moles) of sodium is dissolved in 870 cc. of dry alcohol, and a mixture of 351 g. (3 moles) of benzyl cyanide and 264 g. (3 moles) of ethyl acetate added, the mixture refluxed for an hour and allowed to stand overnight. The solid sodium derivative is quickly dissolved by adding 1.5–2 liters of water at 25°, and cracked ice added to keep the solution ice cold. It is washed with ether and air drawn through the solution under a partial vacuum till free from ether. A cold mixture of 195 cc. of acetic acid and 600 cc. of water is added slowly with shaking and the precipitated acetobenzyl cyanide filtered off and washed. It is purified by dissolving in 800 cc. of hot methyl alcohol, boiling with Norit if necessary, diluting with warm water and cooling; yield 300–310 g. (63–65%) of colorless material m. p. 88.5–89.5°.

Alpha-Phenylacetoacetic Ester, $CH_3COCH(C_6H_5)COOC_2H_5$.—The low yields of the previous methods[4,11] are avoided by hydrolyzing the imido ester in aqueous acid where the insolubility of the product protects it from decomposition.

A solution of 159 g. (1 mole) of acetobenzyl cyanide in 403 cc. of dry alcohol is saturated in the cold with carefully dried hydrogen chloride. After five to eight hours saturation is complete and the flask is allowed to stand overnight at room temperature with occasional shaking for the first hour.

Excess hydrogen chloride is removed by adding boiling chips and evacuating the flask in a water-bath at 40°. Two hundred grams of sodium carbonate is dissolved in 1200 cc. of water and ice added. Into this the reaction mixture is poured with vigorous shaking, the liberated imido ester extracted at once with generous portions of ether, and the ether washed well to remove alcohol.

The imido ester is extracted from the ether and hydrolyzed as follows: 100 g. of 98% C. P. sulfuric acid is poured into 700 cc. of water, and excess ice stirred in. The ether is shaken with cracked ice till cold, and the water separated. About one-half of the ice-cold acid is added, shaken vigorously for exactly fifteen seconds[12] and drawn off at once. The operation is repeated with the remaining acid in two portions. The ether is washed with sodium bicarbonate and dried over sodium sulfate, and yields 20–30 g. of crude α-phenylacetoacetic ester on distillation.

The solution of imido ester sulfate quickly turns cloudy from hydrolysis to the product. This is completed by heating on the steam-bath to 50° for one-half hour, separating the ester and reheating the aqueous layer vigorously for forty-five minutes. Extraction with ether and fractional distillation *in vacuo* yields 103–167 g. (50–81%), b. p. 139–143° (12 mm.).

Menthyl α-Phenylacetoacetate, I.—A mixture of 100 g. of α-phenylacetoacetic ester (freshly distilled) and 94 g. of *l*-menthol (E. K. Co., C. P.) in a 250-cc. modified Claisen flask with a wide side-arm is heated to 150–160° (thermometer in the mixture) for three hours.[4] The excess menthol is removed on the water pump and the menthyl ester distilled on the oil pump between 140–155° (0.5 mm.). From this mixture rich in enol the *d*-keto form is obtained by the asymmetric isomerization which takes place on slow evaporation of a methyl alcohol solution of the oil from an open dish at room temperature, adding alcohol at intervals to maintain a crystalline mush which favors the separation of the less soluble *d*-keto form. After a week or more the accumulated solid is purified by rapid recrystallization five or six times from pure methyl alcohol. The filtrates evaporated slowly in the same way yield a larger crop of pure product, and the process can be continued till most of the material is obtained as the pure *d*-keto form.

Menthyl α-phenylacetoacetate I crystallizes in long colorless prisms melting not quite sharply at 77–78.3° in Pyrex capillary tubes (67–76° in soft glass—Rupe[4] gives 69°). A fresh solution does not absorb bromine and gives no color with ferric chloride, slowly turning deep purple as enolization sets in. It is not completely stable and was always recrystallized shortly before use.

Contrary to Rupe[4] the substance is dextrorotatory in alcohol. Since his alcoholic solution gave an immediate color with ferric chloride it was doubtless partially racemized. This or the use of soft glass melting point tubes may also explain the lower melting point (69°) reported by him. Other constants check satisfactorily.

Anal. Calcd. for $C_{20}H_{28}O_3$: C, 75.9; H, 8.9. Found: C, 76.0, 76.2; H, 8.8, 8.6. Specific rotation in cyclohexane $[\alpha]^{25}{}_D$ $-15.84°$, mutarotating to $[\alpha]^{25}{}_D$ $-59.83°$; $[\alpha]^{25}{}_{5461}$ $-19.0°$; in methyl alcohol $[\alpha]^{25}{}_{5461}$ $+21.9°$.

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(11) Beckh, *Ber.*, **31**, 3160 (1898); Post and Michalek, THIS JOURNAL, **52**, 4359 (1930); Conant and Thompson, *ibid.*, **54**, 4039 (1932); A. F. Thompson, Dissertation, Harvard University, 1932; Bodroux, *Compt. rend.*, **151**, 235 (1910); *Bull. soc. chim.*, [4] **7**, 851 (1910); Walther and Schickler, *J. prakt. Chem.*, [2] **55**, 343 (1897).

(12) Any delay results in hydrolysis of some of the imido ester to the product, which stays in the ether layer.

Per cent. enol at equilibrium: liquid equil. mixt. ord. *t*. 40.0; 5% in methyl alcohol 21.5; 10% in ethyl alcohol 33.3; 10% in benzene 49.2; 10% in cyclohexane 71.0; 4% in petroleum ether 73.8. Effect of concn. on % enol in cyclohexane:

Concn., %	20	10	3.5	1.75	0.87
Enol, %	64.7	71.0	72.8	73.2	73.9

Enolic Form of Menthyl α-Phenylacetoacetate, II.—The pure *d*-keto form racemized quickly at 100° but only slowly at 80°. Since it could not be distilled below 135° by ordinary methods, high vacuum distillation was employed, using a butyl phthalate condensation pump[13] and Hickman high vacuum still (Fisher model) heated by a small metal bath with a tall closed can between dish and flame for even temperature control. In general about 50–60 g. of pure *d*-keto form was catalyzed with a pinch of barium hydroxide and distilled slowly at 85–95°, coming over as a colorless oil with a uniform enol content of 64%. This was redistilled in two portions without catalyst and the first half or two-thirds collected and redistilled in the same way. The temperatures varied from 75–85° (bath temp.) at 2–6 × 10^{-4} mm. pressure. As the fractions became too small they were combined with others of the same grade from additional runs. Four or five fractionations increased the enol content to 92–94%, the highest which could be reached by distillation. Repeated attempts failed to increase this by fractionation under the most favorable conditions; for example, 12 g. containing 93.4% enol was distilled and the first 3.5 g. collected contained 93.8% enol. That this was not the result of ketonization during distillation but shows the presence of a constant boiling mixture of keto and enol was confirmed by distilling 23 g. containing 92% enol and separating it into six fractions which contained, respectively, 93, 90, 94, 93, 89 and 75% of enol. The proportion of enol in the distillate was therefore constant until two-thirds of the material had distilled over, and the effect of ketonization only became apparent in the last two fractions.

This constant boiling mixture contains 93.8% enol as the average of fourteen preparations. It is a colorless viscous oil, hardening to a glass at low temperatures, and is isomeric with the ketonic form.

Anal. Calcd. for $C_{20}H_{28}O_3$: C, 75.9; H, 8.9. Found: C, 75.7; H, 8.8.

Fresh solutions give an immediate deep purple color with ferric chloride and absorb bromine rapidly in the cold. It is quite stable in the absence of catalyst, showing little or no decrease in enol content after two weeks in the refrigerator. A 10% solution in cyclohexane showed a constant rotation $[\alpha]^{25}\text{D}$ −56.9° for an hour but on the addition of a trace of piperidine it mutarotated to the same equilibrium mixture reached by the keto form: from enol $[\alpha]^{25}\text{D}$ −59.2°, −59.5°; 70.9, 70.7% enol; from keto $[\alpha]^{25}\text{D}$ −59.8°; 71.0% enol.

The specific rotation of pure enol was obtained by following the mutarotation in cyclohexane polarimetrically and by titration exactly as described below for the ketonic form. In run I the catalyst was added after the first point (Fig. 3) had been obtained. In run II the catalyst was mixed with the solvent as customary with the keto form and mutarotation had proceeded somewhat before the first reading.

Purification of Materials. Methyl Alcohol.—C. P. absolute acetone-free methanol was distilled three times through an all-glass Pyrex apparatus with a 6-ball Snyder column rejecting about one-third. This was used in the titrations and all apparatus was rinsed with it just before use and dried in a current of air or by evacuation.

Cyclohexane.—E. K. Co. Pract. was treated to remove benzene,[14] washed with potassium hydroxide solution, dried and distilled through the all-glass fractionating apparatus, then a second time over potassium hydroxide and twice alone and obtained constant boiling. In this solvent mutarotation was so slow as to be insignificant compared to the catalytically induced rates.

Piperidine.—The unsaturates present in commercial C. P. piperidine were removed by differential oxidation of nitrosopiperidine[15] and fractionation from potassium hydroxide, yielding material boiling at 105.4–105.7° and stable toward permanganate. The amount used was regulated by adding small drops of a 1:100 solution in cyclohexane.

Rate Measurements.—From 10.0–10.6 g. of freshly recrystallized menthyl ester was weighed into a 100-cc. Pyrex volumetric flask and made up to volume with cyclohexane containing the piperidine catalyst. The solution was quickly transferred to the polarimeter tube (Fig. 1) and reading started, using a Franz Schmidt & Haensch half shade polarimeter read to 0.01° and a G. E. Sodium Lab-Arc. The temperature was held at 25 ± 0.1° by circulating water from the thermostat through the polarimeter tube jacket. The total change of rotation in the 2.340-dm. tube was 10.5° and some 20–30 readings were taken in the range between 7–15 and 50–65% racemization.

The enolization was followed over the same period. At intervals the solution was shaken and 5 cc. removed with a Pyrex pipet, run into 13 cc. of ice-cold methyl alcohol, and titrated with fresh methyl alcoholic bromine of such strength that 10–20 cc. was required. Bromine was absorbed instantly and was added to the first bromine color. The end-point was sharp and persisted for five minutes, and could be restored for an equal time by an additional drop or two of bromine. A correction was applied for the excess of bromine by subtracting the amount needed to bring an equal volume of methyl alcohol to the same color. This corrected volume was run into double the equivalent amount of 0.2 *N* potassium iodide and titrated with standard 0.05 *N* thiosulfate. From seven to nine titrations were made covering the increase from about 3 to 17% of enol.

The equilibrium values for rotation and enol content were obtained by adding more piperidine and allowing the mixture to stand at constant temperature. A series of concordant readings twelve hours apart were accepted as the equilibrium rotation and four of five titrations checking to about 1 part in 100 gave the average per cent. of enol.

Summary

1. Simultaneous measurements have been made of the rate of racemization and of enoli-

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[13] Hickman and Sanford, *Rev. Sci. Instruments*, **1**, 152, Fig. 13 (1930).

[14] Hinrichsen and Kempf, *Ber.*, **45**, 2112 (1912).

[15] Vorländer and Wallis, *Ann.*, **345**, 285 (1906).

zation of menthyl α-phenylacetoacetate.

2. The results show that enolization takes place through some intermediate step. In this step nearly two-thirds of the racemization occurs, only one-third involving actual transformation to the enol.

3. Alternative explanations are offered, one involving loss of configuration in an intermediate anion, the other reversible formation of a small amount of open-chain enol followed by a slower accumulation of chelated enol.

DURHAM, N. H. RECEIVED JULY 7, 1936

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Determination of Activity Coefficients from the Potentials of Concentration Cells with Transference. II. Hydrochloric Acid at 25°

BY THEODORE SHEDLOVSKY AND DUNCAN A. MACINNES

In the first article of this series[1] it was shown that the activity coefficients, f, of chlorides in aqueous solution could be obtained from the potentials, E_t, of galvanic cells of the type

$$\text{Ag; AgCl, MCl } (C_1)\text{: MCl } (C_2)\text{, AgCl; Ag} \qquad \text{(A)}$$

with aid of the relation

$$E_t = \frac{2RT}{F}\int_{C_1}^{C_2} t \, \mathrm{d} \log Cf \qquad (1)$$

in which t is the transference number of the positive ion constituent, M, C is the concentration, and the other terms have their customary significance.[2]

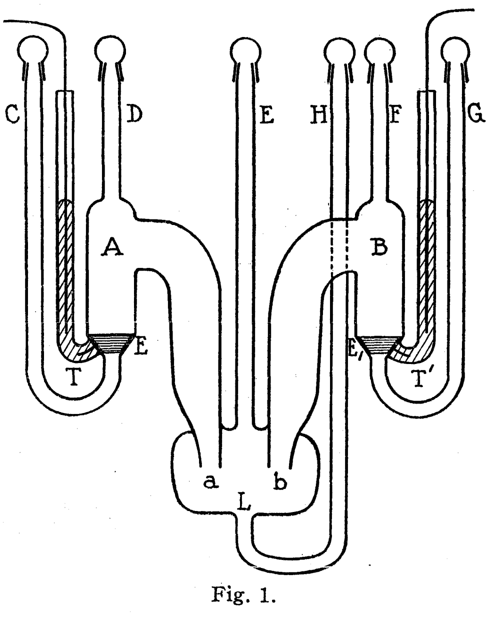

Fig. 1.

However, cells of type A contain a liquid junction and, until the present researches, have not been used to obtain activity coefficients. It was therefore decided to include hydrochloric acid in the series of measurements since the activity coefficients of that substance have been determined, with considerable accuracy, by various workers, using concentration cells without liquid junction of the form

$$\text{Ag; AgCl, HCl } (C_1)\text{; } H_2 \text{ (Pt)} - \text{(Pt) } H_2\text{; HCl } (C_2)\text{, AgCl; Ag} \qquad \text{(B)}$$

Since cells of type B do not involve amalgam electrodes, with their attendant experimental difficulties, this case affords the most favorable comparison of the methods involving cells with and without liquid junction.

This paper will therefore deal with the determination of the potentials of the cell

$$\text{Ag; AgCl, HCl } (C_1)\text{: HCl } (C_2)\text{, AgCl; Ag} \qquad \text{(C)}$$

in which C_2 varied from about 0.003 to 0.08 N, and C_1 was 0.1 N. The results have afforded a test of the Debye-Hückel relations connecting the activity coefficients of aqueous solutions of hydrochloric acid with the concentration.

Apparatus and Experimental Procedure

Although the principle involved is the same as that utilized in the work of Brown and MacInnes[1] decided changes have been made in the apparatus used. The new cell is shown diagrammatically in Fig. 1. Instead of forming the silver–silver chloride electrodes on wire, as in the previous work, hollow truncated cones of platinum foil, indicated at E and E', are used. The outer surfaces of these cones are sealed into the glass, contact being made with the mercury in tubes T and T'. The chief advantage of electrodes of this design is that they are completely protected from mechanical disturbance of their active surfaces. This we have found to be essential if the reproducibility is to reach 0.01 mv. or better. The electrodes are plated with silver and chloridized electrolytically, using the precautions suggested by Brown.[3] It is also found desirable to wash the plated silver with

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(1) Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935).

(2) For a derivation of equation (1) see MacInnes and Brown, *Chem. Rev.*, **18**, 335 (1936).

(3) Brown, THIS JOURNAL, **56**, 646 (1934).

strong ammonia, followed by water, before chloridizing. This assures the removal of the last possible traces of silver cyanide. In filling the cell it is first turned upside down. Solution is run into half-cell A, for instance, through either tube C or D (from a flask of the type shown in Fig. 3 of the article by Brown and MacInnes[1]), and out of the other tube or tube E. Several thorough rinsings are given, after which the half-cell is filled to the point a. The half-cell B is then filled in a similar manner with the second solution. The apparatus is then turned from its inverted to its normal position. A liquid junction is next made at a or b by flowing the heavier of the two solutions through tube H and filling the connecting vessel L. Unless pendent drops are present at a and b air bubbles form that rise through the connecting tubes and mix the solutions. Such pendent drops may be readily formed if necessary by a momentary lifting of an appropriate ground glass cap. The apparatus is next placed in an oil thermostat regulating to ±0.002° and readings of the potential are available as soon as the cell has reached its final temperature. These readings remain constant, within a few microvolts, for many hours. This constancy is due to the fact that the only important source of variation of potential is a change of composition of the solution in immediate contact with the electrodes, such as could be brought about by diffusion or convection. An advantage of this apparatus and procedure over that of Brown and MacInnes is that by avoiding the sliding contact in making the liquid junctions a source of contamination from the grease is avoided.

There is usually a slight difference of potential (of the order of 0.01 mv.) between the electrodes E and E′ which may be corrected for in two ways. In the first place, this potential is measured directly by placing the same chloride solution in both halves of the apparatus. In addition measurements with each pair of solutions are made which are duplicates but with the positions of the solutions reversed. Since the design of the apparatus is symmetrical this is possible. The difference between the potentials of these duplicate determinations should be twice the directly measured difference of potential of the electrodes. This was true within a few microvolts for all the measurements described in this paper.

The potential measurements were made with a calibrated type K potentiometer. The potential standard consisted of five Eppley saturated Weston standard cells kept at 25° in the thermostat. The standard cells were calibrated by the Bureau of Standards.

Results and Discussion

The results of all the measurements are given in columns 1 and 2 of Table I. The solutions of the concentrations given in moles per liter at 25° were prepared by weight from constant boiling acid[4] and their compositions were checked by conductance measurements.[5] As indicated, one of two solutions in the cell was always 0.1 N hydrochloric acid. The water used had a conductance of $2 \pm 1 \times 10^{-7}\ \Omega^{-1}$. Since the greater part of this conductance was due to traces of carbon dioxide the effective conductance of the solvent in the acid solutions was less than this value, and the correction (discussed in the previous paper) for solvent impurities is therefore negligible even at the lowest concentrations.

The method for obtaining the change Δf of the activity coefficient with the concentration from the e. m. f. data, using equation (1), is given in the previous paper.[1] The necessary transference numbers, given in column 3 of the table, are interpolated from the work of Longsworth.[6] The resulting values of $-\Delta \log f$ relative to 0.1 N are given in the fourth column. To obtain activity coefficients f from these data use may be made, as in the earlier paper, of a plot, Fig. 2, of $(\Delta \log f - \alpha \sqrt{C})$ against $(A - \Delta \log f)\sqrt{C}$ in which α is the constant (0.5056 at 25°) of the Debye–Hückel equation

$$-\log f = \alpha \sqrt{C}/(1 + \beta \sqrt{C}) \qquad (2)$$

The constant (A), which is the logarithm of the activity coefficient of the reference 0.1 N hydrochloric acid solution, must be obtained by a short series of approximations in which the value of A chosen finally agrees with the intercept of the plot. The slope of the straight portion of the curve for the lower concentrations yields the constant β of equation (2). The plot yields a value of $A = -0.0973$ from which the activity coefficients f (observed) in column 5 of Table I were obtained from the relation

$$\log f = A - \Delta \log f \qquad (3)$$

The constant β has a value of 1.847, corresponding to a distance of closest approach of 5.62 Å. for the ions. With this value of β equation (2) represents the data up to about 0.04 normal, as is shown in column 6 of the table. Agreement throughout the whole concentration range measured can be obtained, however, with the aid of the Hückel equation

$$-\log f = \alpha \sqrt{C}/(1 + \beta \sqrt{C}) - DC \qquad (4)$$

As is also the case with sodium chloride[1] it is necessary to shift the value of β in order to fit this equation to the results. The computed values of f, using equation (4) and the constants $\beta = 1.527_4$ and $D = 0.105$, are given in the last column of the table. These computed values agree with the "observed" values in column 5 throughout the range of the measurements.

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[4] Foulk and Hollingsworth, THIS JOURNAL, **45**, 1220 (1923).

[5] Shedlovsky, *ibid.*, **54**, 1411 (1932).

[6] Longsworth, *ibid.*, **54**, 2741 (1932).

TABLE I

THE POTENTIALS OF THE CONCENTRATION CELL: Ag: AgCl, HCl (0.1 N): HCl (C_2), AgCl; Ag AT 25°, AND THE COMPUTATION OF THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID

Concn. moles per liter at 25°, C_2	E. m. f., mv.	Trans. no., t_H	Log activity coeff. ratio $-\Delta \log f$	Activity coefficients f, obsd.	f, computed equation (2)	f, computed equation (4)
0.0034468	136.264	0.8234	0.07065	0.9405	0.9402	0.9400
.0052590	118.815	.8239	.06486	.9280	.9283	.9280
.010017	92.529	.8251	.05453	.9062	.9063	.9061
.010029	92.480	.8251	.05450	.9061	.9063	.9060
.019914	64.730	.8266	.04068	.8778	.8777	.8778
.020037	64.464	.8266	.04072	.8778	.8775	.8775
.020132	64.282	.8266	.04051	.8774	.8773	.8773
.040492	36.214	.8286	.02372	.8441	.8430	.8442
.059826	20.600	.8297	.01344	.8244	.8219	.8246
.078076	9.948	.8306	.00630	.8110	.8070	.8113
.1000	0	.8314	0	.7993	.7926	.7993

The most extensive study of cells without liquid junction involving hydrochloric acid has been made by Harned and Ehlers.[7] From their critical summary of their work they have obtained potentials at round molalities from which e. m. f. values of cells of type B may be computed, making allowance for the difference in the concentration scales used in our work and theirs. These results are also plotted in Fig. 2, using the A value given above. It will be seen that there is substantial agreement in the results from the cells with and without liquid junction. Less complete agreement, though probably within the limits of error of the available data, is found with the earlier critical summary of results from cells without liquid junction by Scatchard.[8] Carmody[9] gives his results on cells without liquid junctions only to 0.1 mv. and a plot of his figures indicates errors greater than that amount. However, if allowance is made for this rather large experimental error there is substantial agreement between his results and ours. The deviation produced by an error of 0.1 mv. is shown in the figure.

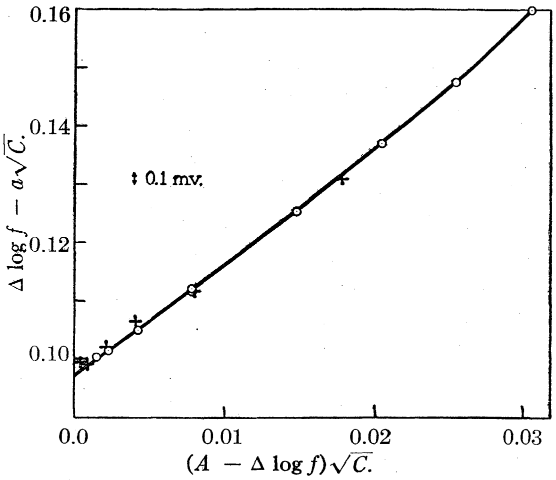

Fig. 2.— O, Shedlovsky and MacInnes; +, Harned and Ehlers.

Summary

Accurate measurements of hydrochloric acid concentration cells, with liquid junction, have been obtained, from which activity coefficients of the ions of the acid have been computed. The results are shown to be in close agreement with those obtained using cells without liquid junctions. The activity coefficients have been found to follow the Debye–Hückel theory with a "distance of closest approach" of 5.62 Å., up to about 0.04 N. Accurate agreement with the Hückel equation is observed throughout the concentration range of 0.003 to 0.1 N.

NEW YORK, N. Y. RECEIVED JULY 10, 1936

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[7] Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932); **55**, 652 (1933); **55**, 2179 (1933).

[8] Scatchard, *ibid.*, **47**, 641 (1925).

[9] Carmody, *ibid.*, **54**, 188 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Partial Vapor Pressures of Aqueous Methylamine Solutions

BY W. A. FELSING AND B. A. PHILLIPS

Object of the Investigation

The purpose of this investigation was the determination of the partial vapor pressures of aqueous solutions of mono-, di- and trimethylamines. This investigation was one of a series[1] dealing with the thermodynamic properties of these amines in relation to their use as refrigerating fluids in the absorption type of refrigerating units. The completeness of the absorption of the gaseous refrigerant by the aqueous absorber can be ascertained from the data of this investigation.

In calculating the free energy decrease attending the reaction Amine (liquid) = Amine (1 *M*), it was found that vapor pressure data for trimethylamine were lacking, except for a few scattered boiling point determinations. Accordingly, the vapor pressures and the densities of liquid trimethylamine were determined.

Incidentally, since no free energy content data for these amines are available in the literature, the data of this investigation yield information leading to a partial determination of such values. A high temperature dissociation investigation, of exploratory nature, has yielded some preliminary data for the calculation at 25° of the free energy content of these gaseous amines; the results of this investigation will be reported in a later paper.

Previous Investigations

No data have been found for the partial vapor pressures of aqueous amine solutions.

Vapor pressure data for monomethylamine have been reported by Felsing and Thomas;[1] for dimethylamine, there are the data of Berthoud;[2] and for trimethylamine, there were found no data.

Density data for liquid trimethylamine also are very meager. Landolt–Börnstein, "Tabellen," list 0.675 g./cc. at $-4°$, Lange[3] gives 0.662 at $-5°$, and Elsey[4] gives a value of 0.702 g./cc. at $-33.5°$.

Methods of the Investigation

(a) The method of determining partial vapor pressures of the aqueous amine solutions was the dynamic or air-saturation method originally developed by Berkeley and Hartley.[5] The method embodied the modifications of Washburn and Heuse[6] and of Bates and Kirschman;[7] additional modifications were made during the investigation, but they were concerned more with minor details of size and design than with departures from the principles of the later modifications listed.

The process consisted of passing, at an optimum rate, an unmeasured volume of dry air through a series of saturators containing pure water and the solutions whose vapor pressures were to be measured. The weights of water vapor carried out by the gas from the pure water saturator, w_1, the weight of the amine absorbed by the acid absorber and the weight of the water carried out from the solutions, w_2, and the barometric pressure, p_B, were the measurements actually made.

A rocking device ensured the continual presentation of a fresh liquid film to the air passing through three sets of saturators in series. The air passed over but not through the liquids. Water vapor was removed by dehydrite-filled absorbers and the amines were absorbed by double, acid-containing absorbers. The rate of air flow varied from 1 to 5 liters per hour for periods of approximately four to five hours, depending upon the particular amine and its concentration. The whole apparatus was immersed in a thermostat maintained at 25 ± 0.05°.

The amine solutions were prepared by dissolving in cold distilled water the gaseous amines generated from C. P. Eastman hydrochlorides by concentrated potassium hydroxide solution. Standard acid and base solutions used in absorption and in titration were prepared from tested C. P. reagents and standardized against each other and against C. P. sodium carbonate. Weight burets were used throughout. The indicator was

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[1] (a) Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929); (b) Felsing and Wohlford, THIS JOURNAL, **54**, 1442 (1932); (c) Felsing and Buckley, *J. Phys. Chem.*, **37**, 779 (1932); (d) Felsing and Jessen, THIS JOURNAL, **55**, 447 (1933); and (e) Felsing and Ashby, *ibid.*, **56**, 2226 (1934).

[2] Berthoud, *J. chim. phys.*, **15**, 3 (1917).

[3] Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1934.

[4] Elsey, THIS JOURNAL, **42**, 2454 (1920).

[5] Berkeley and Hartley, *Proc. Roy. Soc.*, (London), **A177**, 156 (1906).

[6] Washburn and Heuse, THIS JOURNAL, **37**, 309 (1915).

[7] Bates and Kirschman, *ibid.*, **42**, 1992 (1919).

methyl red, as recommended by Treadwell and Hall[8] and by Thompson.[9]

(b) The vapor pressures and the densities of pure liquid trimethylamine were determined by the method of Felsing and Thomas.[1]

The Results Attained

(a) **The partial pressures** of the amines were determined at four concentrations; four to six acceptable determinations were made at each concentration, the mean of which is reported in the table. The partial pressures were calculated by the relation

$$P \text{ (amine from solution)} = \frac{p_w \dfrac{N_2}{N_1}\left[1 - \dfrac{(1 - F)p_w}{p_B - p_w}\right]}{1 + p_w \dfrac{N_2}{N_1}\left[\dfrac{1}{p_B - p_w}\right]}$$

in which F is the ratio p_s/p_w, where p_w is the vapor pressure of pure water at 25° and p_s the partial water vapor pressure of the amine solution and N_2/N_1 is the ratio of the number of moles of amine to water. It was assumed that the vapors of the amines consisted of simple, non-associated molecules and that they obeyed the ideal gas law.

The following table presents the partial vapor pressures of the amines from their solution as calculated by means of the relation above.

Concn. (molar)	p, mm.	p/c, obsd.	"Best" K
	Monomethylamine		
0.250	1.88	7.52	
.525	4.01	7.64	
1.030	8.03	7.79	
2.205	17.08	7.75	7.75
	Dimethylamine		
0.261	2.81	10.76	
.500	5.59	11.18	
.952	10.62	11.15	
2.379	25.58	10.75	11.15
	Trimethylamine		
0.248	16.93	68.26	
.538	38.30	71.18	
1.071	72.67	67.85	
1.961	133.10	67.86	67.87

The value of "best" K was obtained by plotting the data and determining the equation for the "best" straight line that could be drawn through the data; a straight line represents best the data over the range investigated.

(b) **The vapor pressures** of liquid trimethylamine were measured over a temperature range of −20 to +45°. The following equation represents the data obtained, approaching equilibrium at each temperature from above and below: $\log_{10} p(\text{mm.}) = -1410.5/T + 8.57435 - 0.0021158T$. The over-all accuracy of these data is believed to be better than 1 part in 2500. The normal boiling point calculated by this relation is 2.90°.

The densities of liquid trimethylamine were determined over the same temperature range as were the vapor pressures. The relation which reproduced the observed data is density (g./cc.) $= 0.87406 - 4.433 \times 10^{-4}\,T - 1.29236 \times 10^{-6}\,T^2$. This relation presents true values of the density, it is believed, to within 1 part in 5000.

Derived Quantities

(a) **The Free Energy of Solution.**—The partial vapor pressures of the amine solutions at exactly 1 molar were determined, by interpolation, to be 7.60 mm. for the mono-, 11.64 mm. for the di- and 67.64 mm. for the trimethylamine. With the aid of these data, the following free energy values were calculated for the reaction: Amine (760 mm.) = Amine (1 M) + $(-\Delta F)$. The values of $-\Delta F$ were found to be 2727 cal./mole for the mono-, 2502 cal/mole for the di-, and 1434 cal./mole for the trimethylamine.

From the sources cited and from the data of this investigation, the vapor pressures of the three liquid amines at 25° were found to be 2681 mm. for the mono-, 1763 mm. for the di- and 2299 mm. for the trimethylamine. From these values, the free energy decrease attending the change Amine (p, mm.) = Amine (760 mm.) was calculated and then combined with the preceding free energy value to yield the free energy decrease attending the change: Amine (liquid) = Amine (1 M) + $(-\Delta F)$. The results attained for $-\Delta F$ were 3474 cal./mole for the mono-, 2991 cal./mole for the di-, and 2090 cal./mole for the trimethylamine.

(b) **Heat of Vaporization of Trimethylamine.**—

$$\Delta H_v = T(v_2 - v_1)\,\mathrm{d}p/\mathrm{d}T$$

The exact Clapeyron equation was applied at the normal boiling point, 2.90°. The molal volume of the vapor, v_2, was calculated by means of the ideal gas law, since data for another equation of state were lacking, and the molal volume of the liquid, v_1, was calculated from the experimental density relation. The heat of vaporization was thus found to be 95.6 cal./g. or 5706 cal./mole.

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[8] Treadwell and Hall, "Analytical Chemistry," Vol. II, 7th Ed., 1928, p. 470.

[9] R. T. Thompson, *Analyst*, **53**, 315 (1928).

Summary

1. The partial vapor pressures of aqueous solutions of mono-, di- and trimethylamine have been determined over a range of concentration from approximately 0.2 to 2.5 *M*.

2. The vapor pressures and the densities of liquid trimethylamine have been determined over a temperature range from −20 to +45°.

3. Certain free energy values and other derived quantities have been calculated from the data of the investigation.

AUSTIN, TEXAS RECEIVED JULY 31, 1936

[CONTRIBUTION FROM FERTILIZER INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The System Magnesium Sulfate–Urea–Water at 30°

BY COLIN W. WHITTAKER, FRANK O. LUNDSTROM AND JAMES H. SHIMP

Urea and magnesium sulfate are now common constituents of mixed fertilizers. The urea is introduced as a source of nitrogen either in the form of crystal urea or as a solution of urea in ammonia. Magnesium sulfate is an impurity in much of the crude potash imported for fertilizer use and is, therefore, often included in mixtures incidentally. The recent emphasis on the importance of the lesser elements in fertilizer practice has, however, resulted in the occasional use of magnesium intentionally as calcined kieserite or as crude potassium magnesium sulfate or in other forms. Dolomite has been found superior to calcite in some types of mixed fertilizers, and magnesium is now being introduced into mixtures quite extensively in that form. It is possible also for magnesium sulfate to be formed *in situ* by chemical reactions occurring in the mixture. It has recently been found that magnesium phosphate is formed from dolomite under certain conditions[1] and it is not unlikely that this compound would react with the calcium sulfate present in most mixed fertilizers to form magnesium sulfate and one of the calcium phosphates. In view of these considerations, a knowledge of the equilibria in the system magnesium sulfate–urea–water is an aid in understanding the chemistry of mixed fertilizers. The present paper presents data establishing the 30° isotherm in this system.

Experimental

Materials.—Urea was recrystallized from water. In order to avoid any possibility of hydrolysis the temperature of the solution was always kept below 60°. The magnesium sulfate was also recrystallized from water under such conditions that the heptahydrate was obtained. Both compounds were dried *in vacuo* over sulfuric acid, the urea completely and the heptahydrate sufficiently to permit approximation of the amounts taken.

Methods of Analysis.—Urea was determined by the modified urease procedure recently described by Yee and Davis[2] except that 0.025 *N* sodium hydroxide was used to improve the accuracy of titration. Carefully calibrated burets were used. All pipets and other volumetric glassware used bore the official Bureau of Standards stamp. The urease enzyme has been reported to be sensitive to various salts and the effect of added magnesium sulfate was, therefore, determined. It was found, using about 0.15 g. of urease and digesting for twenty-five to thirty minutes, that amounts of magnesium sulfate several times greater than the urea present did not interfere. Tests of the method on the recrystallized urea described gave results ranging from 99.6 to 99.8% urea. These slightly low values are in agreement with those obtained by Yee and Davis and by Dalman,[3] who used the Fox and Geldard[4] modification of the urease procedure. Yee and Davis attribute the slightly low results to impurities in the urea rather than inaccuracy of the method, an opinion in which the writers concur.

Magnesium was weighed as magnesium hydroxyquinolate. If the solution contained urea, the aliquot was evaporated to dryness, the urea destroyed by digestion to dryness with aqua regia and the magnesium sulfate taken up with water. This preliminary destruction of urea was decided upon after experiments had shown that urea interfered slightly when determining high concentrations of magnesium sulfate. All precipitations of magnesium as the quinolate were made in the presence of ammonium acetate by adding sufficient ammonium hydroxide to give a *p*H of at least 9.5 to the solution containing 8-hydroxyquinoline and previously heated to 60–70°. The solution was filtered on a tared fritted glass filter (10G3), the precipitate washed with 1:40 ammonium hydroxide and dried to constant weight at 135°. The procedure was tested by analyzing a pure magnesium sulfate solution by the procedure just described and by evaporating an aliquot to dryness, adding a little sulfuric acid and heating to constant weight at 450°. Satisfactory agreement was obtained.

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(1) W. H. MacIntire and W. M. Shaw, *Ind. Eng. Chem.*, **24**, 1401–1409 (1932).

(2) J. Y. Yee and R. O. E. Davis, *ibid.*, **27**, 259–261 (1935).

(3) L. H. Dalman, THIS JOURNAL, **56**, 549–553 (1934).

(4) E. J. Fox and W. J. Geldard, *Ind. Eng. Chem.*, **15**, 743–745 (1923).

Perhaps the best check on both analytical methods is the good agreement obtained for the solubilities of urea and of magnesium sulfate with those reported in the literature as described below.

Preparation of Equilibrium Solutions.—The systems to be studied were prepared by mixing amounts of the three components sufficient to give convenient quantities of solution and of solid phase after establishing equilibrium conditions. The components were taken in such proportions that the composition of the resulting saturated solutions fell in the desired portion of the curve. Usually each solution was used for determining two to four points on the isotherm, additional magnesium sulfate heptahydrate or urea being added after each determination in order to adjust the composition in the desired direction. It was, of course, necessary to consider the water of crystallization when adding $MgSO_4 \cdot 7H_2O$.

All mixtures were stirred in glass containers in a thermostat, the temperature of which was constant to ±0.01° and was exactly 30°, as closely as it could be read on a Bureau of Standards calibrated thermometer graduated to 0.1°. The stirrers were motor driven and operated through mercury seals to keep out dust and laboratory fumes. In most cases the mixtures were stirred for three to five hours, allowed to stand overnight, stirred another two to three hours and sampled after being allowed to settle. That equilibrium was obtained is indicated by the following. Two solutions analyzed after stirring for three to five hours and standing overnight showed no significant change in composition on an additional three to five hours of stirring and again standing overnight. Some of these solutions were so viscous that settling was extremely slow. Over part of the urea branch of the curve the solid phase floated on top. Suitable precautions were taken to prevent contamination of the liquid samples with the solid phase.

Solubility of Magnesium Sulfate and of Urea

As a check on the entire procedure the solubilities of magnesium sulfate and of urea at 30° were determined. The solubility of magnesium sulfate was found to be 28.42% by weight (average of four determinations). This is higher than the value of 28.05 obtained by interpolation between the values for 29.89 and 34.72° obtained by Ting and McCabe[5] but agrees well with the value of 28.43% (3.30 moles per 1000 g. water) given by the "International Critical Tables."[6]

The solubility of urea at 30° was found to be 57.0% (average of three determinations). The best value to take from the literature is somewhat of a problem. By plotting log N (mole fraction of urea) against $1000/T$, using what Shnidman and Sunier[7] term their best data, the value of 57.08 was obtained. Similar plotting of the data of Dalman[8] gave the value of 57.15%. Pinck and Kelly[9] report a higher value of 57.63%, while graphical interpolation of the data of Speyers[10] and of the "International Critical Tables"[11] yields the lower figure of 56.59%.

These results for magnesium sulfate and urea having indicated that the technique in general was satisfactory, the 30° isotherm of the system was studied. The identification of solid phases was accomplished in the usual way by analysis of the wet solid phase and the use of extrapolated tie lines.

Discussion

The results are shown in Table I and are plotted in Fig. 1. The curve shows three branches, corresponding to the stable solid phases $MgSO_4 \cdot 7H_2O$, $MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$, and $CO(NH_2)_2$.

TABLE I

EQUILIBRIA IN THE SYSTEM MAGNESIUM SULFATE–UREA–WATER AT 30°

Composition of satd. soln.		Composition of wet solid		
$MgSO_4$ Wt., %	$CO(NH_2)_2$ Wt., %	$MgSO_4$ Wt., %	$CO(NH_2)_2$ Wt., %	Stable solid phase
28.42[a]	...	...	...	$MgSO_4 \cdot 7H_2O$
28.16	4.13	42.33	1.41	$MgSO_4 \cdot 7H_2O$
28.00	11.15	41.28	4.56	$MgSO_4 \cdot 7H_2O$
28.17	12.23	39.19	6.20	$MgSO_4 \cdot 7H_2O$
28.08	19.42	39.23	9.74	$MgSO_4 \cdot 7H_2O$
28.44	20.52	38.50	20.00	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O + MgSO_4 \cdot 7H_2O$
28.20	21.18	38.20	18.52	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O + MgSO_4 \cdot 7H_2O$
28.19	22.84	36.92	23.84	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$
25.96	27.36	36.19	26.82	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$
25.39	29.19	34.07	27.59	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$
25.16	32.57	35.57	29.53	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$
23.84	36.66	36.64	30.74	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$
22.71	38.54	30.23	35.10	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$
21.75	43.00	...	...	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$
21.64	43.40	...	...	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$
21.14	46.04	31.96	38.98	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$
20.82	48.88	32.03	40.35	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$
20.81	49.16	30.74	41.82	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$
20.79	50.35	28.97	44.38	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$
21.01	53.02	24.84	56.86	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O + CO(NH_2)_2$
20.91	53.17	16.48	64.48	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O + CO(NH_2)_2$
21.08	53.39	12.83	69.67	$CO(NH_2)_2$
17.63	52.15	11.42	69.02	$CO(NH_2)_2$
14.18	52.93	10.07	65.33	$CO(NH_2)_2$
9.21	54.79	5.86	70.79	$CO(NH_2)_2$
4.47	55.42	2.85	71.37	$CO(NH_2)_2$
...	57.00[b]	...	...	$CO(NH_2)_2$
Most Probable Values at Invariant Points				
28.32	20.80	...	...	$MgSO_4 \cdot 7H_2O + MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$
20.96	53.09	...	...	$MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O + CO(NH_2)_2$

[a] Average of four determinations. [b] Average of three determinations.

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(5) Hsü Huai Ting and Warren L. McCabe, *Ind. Eng. Chem.*, **26**, 1207–1208 (1934).

(6) "International Critical Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, New York, 1928, p. 228.

(7) L. Shnidman and A. A. Sunier, *J. Phys. Chem.*, **36**, 1232 (1932).

(8) L. H. Dalman, THIS JOURNAL, **56**, 549–553 (1934).

(9) L. A. Pinck and M. Kelly, *ibid.*, **47**, 2170 (1925).

(10) C. L. Speyers, *Am. J. Sci.*, IV, **14**, 263–302 (1902).

(11) "International Critical Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, New York, 1928, p. 251.

The tie lines do not all pass exactly through the points corresponding to the composition of the three solid phases mentioned, but it must be considered that the analytical errors become greatly magnified as the tie lines are extended. No evidence of the existence of solid phases other than the three mentioned was obtained. So far as the writers are aware, the compound $MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$ has not been reported previously.

A curious feature of this isotherm is the practically unchanged solubility of magnesium sulfate over a wide range of urea concentration (0–21%). Mixtures of solid urea and $MgSO_4 \cdot 7H_2O$, of such composition that the resulting equilibrium solution falls in the range represented by the middle branch of the isotherm, at first go completely or almost completely into solution, but on continued stirring the reaction

$$MgSO_4 \cdot 7H_2O + CO(NH_2)_2 = MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O + 4H_2O$$

takes place quite rapidly and is probably complete in an hour or so after it starts. The crystals of the complex so obtained are very small. Attempts to prepare large crystals for detailed examination have, so far, been unsuccessful.

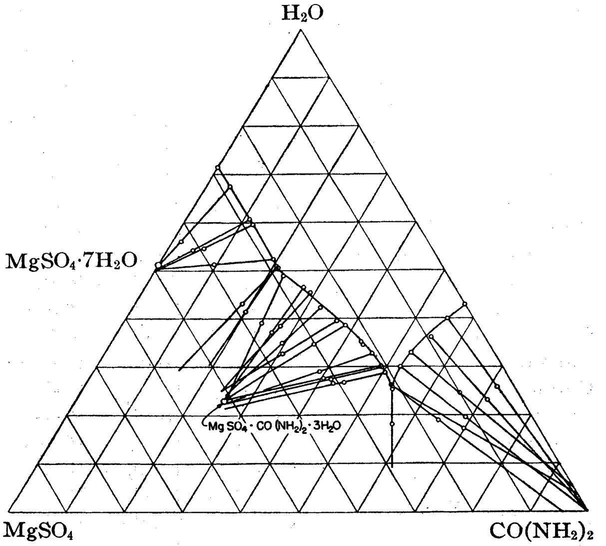

Fig. 1.—The system magnesium sulfate–urea–H_2O at 30°.

Summary

Data were obtained establishing the 30° isotherm of the system magnesium sulfate–urea–water. It was found to consist of three branches corresponding to the solid phases $MgSO_4 \cdot 7H_2O$, $MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$ and $CO(NH_2)_2$.

WASHINGTON, D. C.

RECEIVED JULY 7, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE COLLEGE]

Optical Crystallographic Data for Some Salts of the Cinchona Alkaloids

BY MARY LOUISE SHANER AND M. L. WILLARD

Introduction

Very few data on the optical properties of the salts of quinine, quinidine, cinchonidine and cinchonine can be found in the literature. Groth,[1] Poe and Swisher,[2] Wright,[3] and Wherry and Yanovsky[4] have listed some optical properties of these four alkaloids. However, the information is very scant.

Many salts of quinine were available, while just a few of quinidine, cinchonidine and cinchonine could be obtained. All salts were of commercial origin.

Optical Crystallographic Data

The optical properties, given in the table, were determined by methods given by Chamot and Mason.[5] Refractive indices were determined by the Becke line method. In several cases it was impossible to determine the indices because the crystals dissolved in the immersion oils. The quartz wedge and selenite plate were used in various determinations.

The fluorescence of the salt and its aqueous solution were determined by means of an ultraviolet lamp.

All crystals were found to be biaxial and to give parallel extinction, except in the case of quinine bihydrochloride carbamate and quinine tetrasulfate where oblique extinction was obtained. The sign of elongation was positive in all cases except quinine nitrate and picrate.

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(1) Groth, "Chemische Krystallographie," 1908–1919.

(2) Poe and Swisher, THIS JOURNAL, **57**, 748 (1935).

(3) Wright, *ibid.*, **38**, 1647 (1916).

(4) Wherry and Yanovsky, *ibid.*, **40**, 1063 (1918).

(5) Chamot and Mason, "Handbook of Chemical Microscopy," Vol. I, John Wiley and Sons, Inc., New York, New York, 1930.

TABLE I

Salt	Color	Soly. in water	Habit	Refractive indices Alpha	Beta	Gamma	Bire-fringence	Fluorescence Salt	Soln.
QUININE									
Acetate	Colorless	Soluble	Needles	..	1.62	1.68	Weak	Neg.	Blue
Anisate	Yellow	Insol.	Diamond	1.58	1.62	..	Moderate	Faint	Faint
Arsenate	Pink	Insol.	Rods	1.61	1.62	1.69	Strong	Neg.	Blue
Benzoate	Colorless	Insol.	Rods	1.60	1.66	1.69	Strong	Neg.	Blue
Bihydrobromide	Yellow	Slight	Rods	1.58	1.61	1.69	Strong	Yellow	Blue
Bihydrochloride carbamate	Colorless	Slight	Rods	1.58	1.64	1.72	Strong	Faint	Blue
Bisulfate	Colorless	Soluble	Rods	1.58	..	1.67	Strong	Blue	Intense blue
Borate	Yellow	Insol.	Plates	..	..	..	.....	Yellow	Green
Camphorate	Yellow	Insol.	Rods	1.58	1.61	1.62	Moderate	Neg.	Intense blue
Chlorate	Colorless	Soluble	Rods	1.62	1.64	1.69	Moderate	Neg.	Intense blue
Chromate	Yellow	Insol.	Rods	..	1.65	1.69	Moderate	Neg.	Neg.
Citrate	Colorless	Insol.	Rods	1.58	1.65	..	Strong	Faint	Intense blue
Ferrocitrate	Yellow	Insol.	Plates	..	..	..	.....	Neg.	Green
Formate	Colorless	Insol.	Rods	..	1.62	1.69	Strong	Neg.	Intense blue
Hydrobromide	Colorless	Insol.	Rods	1.61	1.63	1.68	Strong	Neg.	Intense blue
Hydrochloride	Colorless	Soluble	Rods	1.59	1.61	1.67	Strong	Neg.	Intense blue
Hydroferrocyanide	Green	Insol.	Amorph.	..	..	..	.....	Neg.	Faint
Hydrofluosilicate	Colorless	Insol.	Rods	1.56	1.58	1.62	Strong	Neg.	Intense blue
Hypophosphite	Colorless	Slight	Rods	1.69	1.62	1.65	Moderate	Faint	Intense blue
Hyposulfite	Colorless	Pptd.	Rods	..	1.64	1.70	Strong	Neg.	Neg.
Lactate	Brown	Insol.	Amorph.	..	..	..	.....	Neg.	Green
Nitrate	Orange	Insol.	Rods	1.56	1.61	1.64	Strong	Neg.	Intense blue
Oxalate	Colorless	Insol.	Rods	1.60	1.61	1.69	Strong	Neg.	Intense blue
Phosphate	Colorless	Insol.	Rods	1.58	..	1.64	Moderate	Neg.	Faint
Phthalate	Colorless	Soluble	Rods	1.61	1.62	1.69	Moderate	Neg.	Intense blue
Picrate	Yellow	Insol.	Rods	1.61	1.64	1.72	Strong	Neg.	Green
Quinolate	Colorless	Insol.	Amorph.	..	..	..	.....	Neg.	Faint
Salicylate	Colorless	Insol.	Rods	1.62	1.63	1.67	Strong	Faint	Intense blue
Succinate	Colorless	Insol.	Rods	..	1.59	1.68	Strong	Neg.	Intense blue
Sulfate	Colorless	Insol.	Rods	1.62	1.63	1.67	Moderate	Neg.	Intense blue
Sulfoiodide	Gray	Insol.	Plates	..	..	..	.....	Neg.	Intense blue
Tannate	Yellow	Insol.	Amorph.	..	..	..	.....	Neg.	Intense blue
Thiocyanate	Colorless	Slight	Rods	..	1.61	1.69	Moderate	Neg.	Intense blue
Valerate	Brown	Insol.	Plates	..	..	..	.....	Faint	Intense blue
QUINIDINE									
Hydrobromide	Colorless	Soluble	Rods	1.58	1.60	1.68	Strong	Faint	Intense blue
Sulfate	Colorless	Soluble	Rods	1.59	1.61	1.65	Moderate	Neg.	Intense blue
CINCHONIDINE									
Free base	Colorless	Insol.	Rods	1.61	1.62	1.68	Moderate	Neg.	Neg.
Acetate	Colorless	Slight	Rods	1.59	1.61	1.64	Moderate	Neg.	Faint
Bihydrochloride	Colorless	Slight	Rods	1.59	..	1.70	Strong	Slight	Faint
Hydrobromide	Colorless	Insol.	Rods	..	1.66	1.72	Strong	Neg.	Neg.
Hydrochloride	Colorless	Insol.	Fragments	..	..	..	.....	Neg.	Neg.
Tetrasulfate	Colorless	Slight	Rods	1.55	1.56	1.65	Strong	Bright	Intense blue
CINCHONINE									
Free base	Colorless	Insol.	Rods	1.58	1.62	1.69	Strong	Neg.	Neg.
Bisulfate	Colorless	Insol.	Rods	1.56	..	1.62	Moderate	Blue	Blue
Hydrobromide	Colorless	Insol.	Rods	1.61	..	1.69	Moderate	Neg.	Neg.
Hydrochloride	Colorless	Soluble	Rods	1.55	1.62	1.67	Strong	Neg.	Faint
Sulfate	Colorless	Insol.	Rods	1.59	1.64	1.66	Moderate	Neg.	Faint

Summary

The crystallographic data for four cinchona alkaloids—quinine, quinidine, cinchonine and cinchonidine—have been worked out. The fluorescent properties in ultraviolet light also have been determined.

STATE COLLEGE, PENNA.

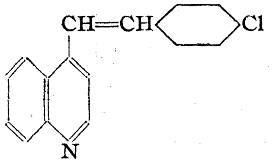
RECEIVED JUNE 9, 1936

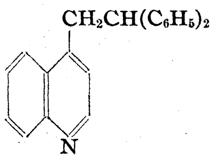
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Addition of Benzene to Benzalquinaldines and Benzallepidines

BY REYNOLD C. FUSON, L. L. ALEXANDER, ELLSWORTH ELLINGBOE AND ARNOLD HOFFMAN

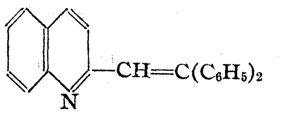
The conversion of benzalquinaldines[1] and similarly constituted compounds[2] into the corresponding α-benzohydryl derivatives appears to involve a reversible 1,4-addition of aromatic compounds to conjugated systems. The principle of vinylogy[3] suggests that a similar result might be obtained with benzallepidines in which the reaction would depend on a reversible 1,6-addition. To test this, benzallepidine and *p*-chlorobenzallepidine (I) were prepared and subjected to the treatment with benzene in the presence of aluminum chloride and hydrogen chloride. A compound corresponding to the expected α-benzohydryllepidine (II) was produced. The action of phenylmagnesium bromide likewise converted benzallepidine into a compound with the same composition as II. The two products proved, however, to be isomeric rather than identical.

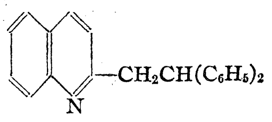

I


II

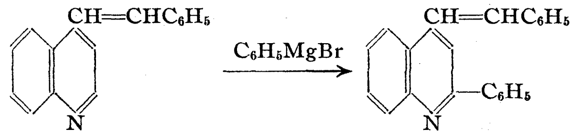
In view of this result, it became necessary to determine the structures of these isomers as well as that of α-benzohydrylquinaldine whose structure had been assigned upon the results of these two types of addition reactions which have now been called in question.

The structure of α-benzohydrylquinaldine (IV) was established by synthesis. β-Phenylbenzalquinaldine (III) was made from benzophenone and lithiumquinaldine according to the method of Ziegler and Zeiser[4] and reduced catalytically. The hydrogenation was also effected by the use of benzene, aluminum chloride and hydrogen chloride. Efforts to synthesize the corresponding chloro compound from 1-*p*-chlorophenyl-1-phenyl-2-(2-quinolyl)-ethanol were unsuccessful.


III


IV

The product obtained by the action of phenylmagnesium bromide on benzallepidine was shown to be 2-phenyl-4-styrylquinoline (VI). This compound was prepared by condensing α-phenyllepidine with benzaldehyde according to the method of John and Fischel.[5] From this result it became evident that the addition of phenylmagnesium bromide involved the 1,2- rather than the 1,6-positions


V VI

The isomer produced by the addition of benzene to benzallepidine is evidently α-benzohydryllepidine (II). This is indicated by the close analogy with α-benzohydrylquinaldine, the structure of which is now certain. The synthesis from the *p*-chlorobenzallepidine by the action of benzene, aluminum chloride and hydrogen chloride shows that the phenyl group takes the position adjacent to the *p*-chlorophenyl radical rather than that adjacent to the quinoline ring. Otherwise, the quinolyl rather than the *p*-chlorophenyl radical would have been replaced.

Experimental

***p*-Chlorobenzallepidine.**—Equivalent amounts of lepidine and *p*-chlorobenzaldehyde were heated for six hours at 125° in the presence of a small amount of anhydrous zinc chloride. The product was triturated with ammonium hydroxide, removed by filtration and washed with cold alcohol. It crystallized from alcohol in yellow fibrous needles melting at 127–128°; yield 70%. The benzal compound decolorized a solution of bromine in carbon tetrachloride and discharged the color of permanganate solutions in acetone.

Anal. Calcd. for $C_{17}H_{12}NCl$: C, 76.83; H, 4.56; Cl, 13.4. Found: C, 76.95; H, 4.61; Cl, 13.2.

α-Benzohydryllepidine

A. From Benzallepidine.—Following the general procedure of Fuson, Farlow and Hoffman,[1a] dry hydrogen chloride was passed into a mixture of 2 g. of benzallepidine, 4 g. of anhydrous aluminum chloride and 40 cc. of

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[1] (a) Hoffman, Farlow and Fuson, THIS JOURNAL, **55**, 2000 (1933); (b) Fuson, Kozacik and Eaton, *ibid.*, **55**, 3799 (1933).

[2] For other references, see Woodward, Borcherdt and Fuson, *ibid.*, **56**, 2103 (1934).

[3] Fuson, *Chem. Rev.*, **16**, 1 (1935).

[4] Ziegler and Zeiser, *Ann.*, **485**, 174 (1931).

[5] John and Fischel, *Ber.*, **59**, 722 (1926).

dry benzene until the gas was no longer absorbed. The mixture was stirred for three hours and then poured into an ice–hydrochloric acid mixture. The semi-solid product was heated with ammonium hydroxide for a short time, cooled and extracted with ether. The crystalline product remaining after the evaporation of the ether was recrystallized from alcohol; m. p. 130–131°.

Anal. Calcd. for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.18; H, 6.21; N, 4.60.

B. From *p*-Chlorobenzallepidine.—α-Benzohydryllepidine was obtained from *p*-chlorobenzallepidine by a procedure similar to the preceding one.

β-Phenylbenzalquinaldine (III).—This compound was prepared by the method of Ziegler and Zeiser.[4] Its structure was confirmed by oxidation. With chromic acid it gave benzophenone.

α-Benzohydrylquinaldine (IV).—This compound was prepared by the reduction of β-phenylbenzalquinaldine. The reduction was carried out in two ways.

(a) By the Friedel–Crafts Method.—A mixture of 5.5 g. of β-phenylbenzalquinaldine, 50 cc. of dry benzene and 15 g. of anhydrous aluminum chloride was saturated at room temperature with dry hydrogen chloride gas. The mixture was shaken in a closed container for twenty hours. The color changed from bright red to brown. The reaction mixture was decomposed in an ice–hydrochloric acid mixture. The semi-solid hydrochloride was separated on a filter, washed with benzene and with water and finally heated with ammonium hydroxide for one hour to regenerate the free amine. The solid was recrystallized from alcohol; m. p. 119–121°. The yield was 92%. A mixed melting point determination with α-benzohydrylquinaldine showed no depression.

(b) By Catalytic Reduction.—Hydrogenation in the presence of a platinum–platinum oxide catalyst converted the β-phenylbenzalquinaldine into α-benzohydrylquinaldine. The samples prepared by methods (a) and (b) and that of Hoffman, Fuson and Farlow proved to be identical.

1-*p*-Chlorophenyl-1-phenyl-2-(2-quinolyl)-ethanol.—The method of Ziegler and Zeiser for the halogen-free carbinol was used. From 30 g. of *p*-chlorobenzophenone was obtained 43 g. of carbinol melting at 127–130°. The pure compound (from alcohol) melted at 140.5–141°.

Anal. Calcd. for $C_{23}H_{18}ONCl$: C, 76.75; H, 5.02. Found: C, 76.60; H, 5.18.

Attempts to dehydrate this carbinol by treatment with sulfuric acid, iodine, potassium bisulfate or acetic anhydride were unsuccessful. The only solid product which was isolated was *p*-chlorobenzophenone.

2-Phenyl-4-styrylquinoline (VI).—To an ether solution of benzallepidine an excess of phenylmagnesium bromide was added. The mixture was heated, with stirring, for five hours. Decomposition with ice and hydrochloric acid gave a gummy mass which, when treated with ammonium hydroxide, gave the free base. The pure compound (from alcohol) melted at 102.5–103.5°.

Anal. Calcd. for $C_{23}H_{17}N_3$: N, 4.56. Found: N, 4.74.

A mixture of this compound with a specimen of 2-phenyl-4-styrylquinoline, prepared by the method of John and Fischel,[5] melted at 102–103°.

Summary

1. Benzallepidine and *p*-chlorobenzallepidine react with benzene in the presence of aluminum chloride and hydrogen chloride to give α-benzohydryllepidine.
2. Benzallepidine reacts with phenylmagnesium bromide to give 2-phenyl-4-styrylquinoline.
3. The structure of α-benzohydrylquinaldine has been confirmed by synthesis.

URBANA, ILLINOIS RECEIVED JULY 20, 1936

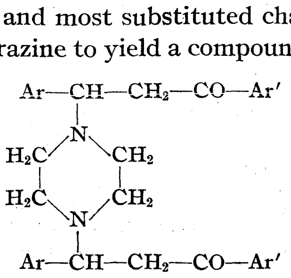
[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

Derivatives of Piperazine. IX. Addition to Conjugate Systems. I

BY VINCENT E. STEWART AND C. B. POLLARD

Additive compounds of benzalacetophenone (chalcone) with ammonia and primary aromatic amines were prepared by Tambor and Wildi.[1] The reaction goes readily in the cold, generally with or without alkali. They were not successful in adding secondary aromatic or mixed secondary bases. An addition compound of benzalacetophenone with piperidine was prepared by Georgi and Schwyzer;[2] upon heating with water it splits into the original substances. Bain[3] reported that he obtained an addition compound of benzalacetophenone with piperazine. We have verified his results, and have endeavored to determine the generality of this addition.

Chalcone and most substituted chalcones readily add piperazine to yield a compound of the type



The addition is effected readily by refluxing the

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[1] Tambor and Wildi, *Ber.*, **31**, 349 (1898).

[2] Georgi and Schwyzer, *J. prakt. Chem.*, **86**, 273–276 (1912).

[3] Bain, unpublished work, University of Florida.

TABLE I

	Piperazine	M. p. (corr.), °C.	Formula	Analyses, % N Found	Calcd.
1	1,4-Bis-chalcone	128.0–128.3	$C_{34}H_{34}O_2N_2$	5.58	5.57
2	1,4-Bis-(3-nitrochalcone)	143.0–144.0	$C_{34}H_{32}O_6N_4$	9.45	9.46
3	1,4-Bis-(2-chlorochalcone)	110.9–111.3	$C_{34}H_{32}O_2N_2Cl_2$	4.85	4.91
4	1,4-Bis-(4′-chlorochalcone)	117.7–118.1	$C_{34}H_{32}O_2N_2Cl_2$	4.88	4.91
5	1,4-Bis-(4-chlorochalcone)	146.8–147.0	$C_{34}H_{32}O_2N_2Cl_2$	5.03	4.91
6	1,4-Bis-(4,4′-dichlorochalcone)	148.4–158.7	$C_{34}H_{30}O_2N_2Cl_4$	4.42	4.38
7	1,4-Bis-(4′-bromochalcone)	116.3–117.3	$C_{34}H_{32}O_2N_2Br_2$	4.24	4.24
8	1,4-Bis-(4-methylchalcone)	145.5–146.0	$C_{36}H_{38}O_2N_2$	5.22	5.28
9	1,4-Bis-(4′-methylchalcone)	132.0–132.5	$C_{36}H_{38}O_2N_2$	5.38	5.28
10	1,4-Bis-(4-methoxychalcone)	109.5–110.1	$C_{36}H_{38}O_4N_2$	5.16	4.98
11	1,4-Bis-(4,4′-dimethylchalcone)	175.4–175.8	$C_{38}H_{42}O_2N_2$	4.96	5.02
12	1,4-Bis-(4-methoxy-4′-methylchalcone)	149.8–150.2	$C_{38}H_{42}O_4N_2$	4.74	4.75

chalcone with anhydrous piperazine in toluene solution for a few hours; alkali does not facilitate the reaction. The addition compounds separate in minute crystals upon cooling. They can be recrystallized readily from toluene, and in most cases are pure white. The compounds are insoluble in water, alcohol and ether, moderately soluble in hot benzene and toluene and readily soluble in chloroform and other halogenated solvents. In most cases the yield of crude product is almost the theoretical; however, subsequent recrystallizations increase the melting point markedly although a substantial loss of product is incurred.

The compounds are all stable under ordinary conditions, and are not decomposed by heating with water as is the case with the piperidine additive compound. Treatment of 1,4-bischalcone piperazine with dilute hydrochloric acid, or passing dry hydrogen chloride into a chloroform or hot toluene solution of the compound, induces complete decomposition into piperazine dihydrochloride and chalcone. Similarly, refluxing the toluene solution of the compound with ethyl iodide results in complete decomposition into chalcone and a substance identical with the product obtained by refluxing piperazine with ethyl iodide. These decompositions are noteworthy, since the unsaturated ketone results; however, this is entirely analogous to the usual degradation of amines whereby the alkyl group is split off as an unsaturated hydrocarbon.

Certain α,β-unsaturated ketones, including some chalcones, apparently do not yield addition compounds with piperazine. These are being investigated further, and a classification of these compounds will form the basis of a forthcoming publication.

Experimental

Preparation of Chalcones.—These were prepared readily by the Claisen reaction. The theoretical quantities of the corresponding aldehyde and the ketone were dissolved in a suitable quantity of alcohol, and 100 g. of 10% aqueous sodium hydroxide was added per mole of reactant. Separation of the chalcone generally occurred immediately. Alcohol or commercial heptane is most suitable as a solvent for recrystallization.

Preparation of Addition Compounds.—Anhydrous piperazine (0.05 mole) was dissolved in a minimum amount of toluene under reflux, and a toluene solution of the chalcone (0.1 mole) was added. The solution was refluxed for about ten hours and then allowed to stand in the icebox for several hours. The addition compound separated upon cooling. It was filtered, washed with alcohol and water to remove unreacted piperazine, air-dried and recrystallized from toluene three times before being subjected to analysis.

Summary

1. Addition compounds of piperazine with conjugate systems have been studied. One mole of piperazine and two moles of a chalcone are involved in the addition.

2. Some α,β-unsaturated ketones apparently do not yield addition compounds with piperazine. These are being investigated further.

GAINESVILLE, FLA. RECEIVED AUGUST 1, 1936

[CONTRIBUTION FROM DIVISION OF INSECTICIDE INVESTIGATIONS, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, UNITED STATES DEPARTMENT OF AGRICULTURE]

Helenalin. I. Helenalin, the Bitter Sternutative Substance Occurring in *Helenium Autumnale*

BY E. P. CLARK

From the plant *Helenium autumnale* Reeb[1] obtained a crystalline compound which he designated as "helenic acid (d'acide helenique)." He assigned the formula $C_8H_{10}O_2$ to the material, but the combustion data presented indicate that his results were miscalculated. In reality his figures are in good agreement with the formula $C_{15}H_{18}O_4$, which will be shown in the experimental part to be the correct composition of the substance.

Later Lamson,[2] working with some of Reeb's preparations, studied their physiological action and made some chemical observations. He designated the material "helenin," and on the basis of one combustion analysis arrived at the molecular formula $C_{20}H_{25}O_5$, a formula which inspection shows to be impossible. His analytical figures are in moderate agreement with Reeb's results, but they constitute insufficient evidence upon which to base a correct formula.

Since Reeb states that the crystalline material is a vermifuge and our experiments indicate that it is a fairly effective fish poison, its possibilities as an insecticide are being investigated. In the course of this work a method of preparing the material in a pure condition has been elaborated, and sufficient chemical data have been obtained to indicate that the compound has the molecular formula $C_{15}H_{18}O_4$, as suggested by Reeb's analysis.

The compound is a colorless, crystalline, optically active material, which melts at 167°. It has a bitter taste, and its dust causes violent sneezing. A 1–5000 aqueous solution kills *ca.* 3 g. goldfish in three hours.

From a chemical standpoint the compound is highly unsaturated. In the presence of catalysts it absorbs 4 atoms of hydrogen per molecule, indicating that it has two double bonds. It adds bromine to give a dibromide, and it forms monoacyl derivatives, indicating the presence of one hydroxyl group. The acetyl compound was prepared with ease, but as acetyl determinations on this preparation were not entirely satisfactory, a methoxyacetyl derivative was prepared, and the methoxyl value was taken as an indication of the number of acyl groups present. In this way it was proved definitely that only a monoacyl derivative was formed. The compound has no methoxyl groups and is neutral.

Tests for other functional groups have not yet been successful, but further work is in progress.

It is proposed to designate the compound "helenalin," a euphonious combination of syllables of the generic and specific names of the plant. This nomenclature is adopted because Reeb's name, "helenic acid," does not apply inasmuch as the material is not an acid, and Lamson's name, "helenin," has been applied for a long time to alantolactone.[3]

Experimental

Preparation and Properties of Helenalin.—Twenty-five hundred grams of the ground whole plant of *Helenium autumnale*[4] was moistened with 2 liters of chloroform and allowed to stand in a tight container overnight. The drug was then packed in a percolator and extracted with 10 liters of chloroform. The percolate was concentrated under reduced pressure to a thick sirup and then dissolved in 1.5 liters of hot ethanol. The alcoholic liquid was diluted with 6 liters of boiling water and acidified (litmus) with acetic acid, and a solution of 20 g. of normal lead acetate was added. After standing overnight the solution cleared and was filtered through a folded filter paper. The filtrate was evaporated under reduced pressure to 1 liter and then extracted with chloroform.

The chloroform extract was dried with sodium sulfate and evaporated *in vacuo* to a thick sirup, which was then dissolved in 50 cc. of hot benzene. The solution was allowed to crystallize at low temperature, after which the crystals were separated from the mother liquor by filtration and washed with cold benzene. The crude material melted at 167°. The yield varied considerably with different lots, but from 27.5 kg. 97.7 g. of helenalin, or a yield of 0.36%, was obtained.

The material was recrystallized from boiling benzene. Thus obtained it consisted of colorless rods and irregular fragments which melted at 167°. In parallel polarized light (crossed nicols) the extinction was straight and the elongation was positive. The refractive indices as determined by the immersion method were η_α, 1.550 (crosswise

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[1] E. Reeb, *J. Pharm. Elsass Lothringen*, **37**, 149 (1910).

[2] P. D. Lamson, *J. Pharmacol.*, **4**, 471 (1913).

[3] L. Gerhardt, *Ann.*, **34**, 192 (1840); J. Kallen, *Ber.*, **6**, 1506 (1873); **9**, 154 (1876).

[4] This material was obtained through the coöperation of H. R. Reed, Bureau of Animal Industry, U. S. Department of Agriculture, McNeill, Miss.

on rods); η_β, 1.568 (common, crosswise on rods), η_γ, 1.603 (lengthwise).[5]

Helenalin is optically active; 0.5017 g. dissolved in 10 cc. of 95% alcohol at 20° rotated the plane of polarized light in a 1-dm. tube 5.11° to the left; therefore $[\alpha]^{20}_D$ is $-101.9°$.

When 6.46 mg. of helenalin was dissolved in 49.26 mg. of camphor, the melting point of the latter was depressed 17.5°. This corresponds to a molecular weight of 300.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92; mol. wt., 262. Found: C, 68.60; H, 6.91; mol. wt., 300.

Acetylhelenalin.—A mixture of 1 g. of helenalin, 0.25 g. of dry sodium acetate and 4 cc. of acetic anhydride was boiled for ten minutes. Approximately one-half the acetic anhydride was then removed by distillation, and the residue was treated with 5 cc. of methanol. After the reaction had subsided, water was added to the solution, and the acetyl compound was allowed to crystallize. The yield was 1 g. It was recrystallized from its solution in methanol by adding an equal volume of water. Thus obtained, it consisted of colorless crystals which melted at 184°.

Anal. Calcd. for monoacetate $C_{17}H_{20}O_5$: C, 67.09; H, 6.63; mol. wt., 304. Found: C, 67.15; H, 6.67; mol. wt. (Rast), 333.

Methoxyacetylhelenalin.—A solution of 0.5 g. of helenalin in 2 cc. of pyridine was treated with 1 cc. of methoxyacetic anhydride. The liquid was heated to its boiling point and then allowed to cool and stand for two hours. Water was then added, and the oil which separated crystallized at once. The yield of the crude product was 0.55 g., and its melting point was 131–132°. It was recrystallized by adding 5 volumes of water to its methanolic solution, which had been filtered through norit. The purified product consisted of colorless six-sided rods that melted at 135°. In parallel polarized light (crossed nicols) its extinction is straight and its elongation is positive. In convergent polarized light (crossed nicols) fragments showing sections perpendicular to the acute bisectrix are common. The optic sign is negative and the axial angle (2E) is small. The refractive indices determined by the immersion method are: η_α, 1.525 (usually shown crosswise); η_β, 1.580; η_γ, 1.590 (usually shown lengthwise), all ±0.003.

Anal. Calcd. for $C_{18}H_{22}O_6$: C, 64.66; H, 6.44; OCH_3 (1), 9.28. Found: C, 64.27; H, 6.80; OCH_3, 9.39.

Tetrahydrohelenalin.—Five grams of helenalin dissolved in 150 cc. of ethyl acetate was reduced at atmospheric pressure with hydrogen and the platinum catalyst of Voorhees and Adams.[6] Two mols of hydrogen was absorbed. After the catalyst had been removed, 50 cc. of *n*-butyl ether was added to the solution, and the ethyl acetate was removed by distillation. Practically a quantitative yield of tetrahydro compound was obtained. It melted at 174–175°, and in a high vacuum it could be sublimed or distilled.

Recrystallized from boiling *n*-butyl ether, it consisted of long, colorless needles which melted at 176°. In parallel polarized light (crossed nicols) the extinction is straight and the elongation is negative. Many of the fragments do not extinguish sharply. In convergent polarized light (crossed nicols) many fragments show sections perpendicular to the acute bisectrix and extinguish in a hazy, indefinite manner. The optic sign is positive and the axial angle (2E) is small. Its refractive indices as determined by the immersion method are η_α, 1.545 (lengthwise on rods); η_β, 1.550; η_γ 1.570 (crosswise on rods) all ±0.003.

Anal. Calcd. for $C_{15}H_{22}O_4$: C, 67.65; H, 8.33. Found: C, 67.78; H, 8.40.

Acetyltetrahydrohelenalin.—This compound was made and purified in the same manner as acetylhelenalin. Its melting point was 145°.

Anal. Calcd. for $C_{17}H_{24}O_5$: C, 66.22; H, 7.85; mol. wt., 308. Found: C, 66.39; H, 8.0; mol. wt., 321.

Dibromohelenalin.—A solution of 1 g. of helenalin in 10 cc. of chloroform was treated with a chloroform solution of 0.63 g. of bromine. The liquid was soon decolorized without the evolution of hydrobromic acid. The solvent was removed in a current of air, and the residue dissolved in hot ethanol. Two volumes of hot water were then added to the alcoholic liquid, and the dibromide was allowed to crystallize. It was recrystallized to a constant melting point of 161° from 50% acetic acid.

Anal. Calcd. for $C_{15}H_{18}O_4Br_2$: Br, 37.88. Found: Br, 37.87 and 37.97.

Summary

A method for the preparation of the physiologically active material that occurs in *Helenium autumnale* has been developed. The name "helenalin" has been proposed for this compound. It has been shown by analysis of the material itself, as well as of several of its derivatives, that it has the formula $C_{15}H_{18}O_4$ and that the molecule contains a hydroxyl group and two double bonds.

WASHINGTON, D. C. RECEIVED AUGUST 1, 1936

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[5] The optical crystallographic data were determined by George L. Keenan, of the Food and Drug Administration, U. S. Department of Agriculture.

[6] V. Voorhees, and R. Adams, THIS JOURNAL, **44**, 1397 (1922).

[CONTRIBUTION NO. 162 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

Monosodium Urea and its Reactions

BY RALPH A. JACOBSON

The preparation of monopotassium urea and dipotassium urea by the reaction of potassium amide on urea in liquid ammonia solution has been described by Franklin and Stafford,[1] and more recently by Blair.[2] The corresponding sodium derivatives have been prepared by the action of sodium hydride on urea,[3] but the properties of the sodium compounds apparently have not been investigated. The present paper is concerned with the formation and properties of monosodium urea and its use for the synthesis of ureides.

Monosodium urea is obtained readily by the action of metallic sodium on urea in liquid ammonia solution, using ordinary laboratory equipment. The most convenient procedure consists in slowly adding the theoretical amount of sodium to a well-agitated solution of urea in ammonia. Evolution of hydrogen and precipitation of monosodium urea begin almost immediately and the blue color disappears as the sodium is utilized. The product is obtained either by evaporation of the liquid ammonia or by filtration of the ammonia suspension.

The monosodium urea obtained in this manner is a dusty white powder. It has no definite melting point but begins to decompose in a capillary tube at about 150–160°. It is insoluble in aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, ethers and other inert solvents. It dissolves with reaction in water, alcohols and in other compounds containing an hydroxyl group. It is rather hygroscopic but can be handled in the dry condition and can be retained indefinitely in a closed container.

Attempts to prepare disodium urea were only partly successful. While one equivalent weight of sodium reacted readily with urea in boiling liquid ammonia, sodium in excess of this amount reacted only very slowly. Presumably, the insolubility in ammonia of the monosodium derivative initially formed was an important inhibiting factor. By employing very dilute solutions of urea in liquid ammonia and permitting the reaction to continue for several days, considerably more than one equivalent weight of sodium was finally introduced. The product was an exceedingly hygroscopic white powder which formed a dibenzoyl derivative upon reaction with benzoyl chloride. The analytical data, however, indicated that the product was not pure disodium urea but a mixture of the mono- and the disodium derivatives.

Reaction of Monosodium Urea with Halogen Compounds.—Benzoyl chloride, oleyl chloride and stearyl chloride reacted with sodium urea to yield the corresponding acyl derivatives. Benzyl chloride also reacted with monosodium urea to give benzyl urea. On the other hand, several unsuccessful attempts were made to prepare alkyl ureas by the reaction of monosodium urea with alkyl halides, *e. g.*, butyl iodide, butyl chloride and dodecyl bromide. These results indicate that a fairly active halogen is required for reaction.

Reaction of Monosodium Urea with Esters.—Esters reacted at room temperature with monosodium urea to yield acyl derivatives. It was usually necessary to add acetone or some other ketone (or an alcohol) to the mixture in order to obtain reaction. In a few instances condensation was effected in the absence of acetone by treating a solution of the ester and urea in liquid ammonia with sodium, thereby forming the monosodium urea *in situ*.

The reaction has been applied to simple esters such as ethyl acetate, ethyl benzoate and ethyl oleate for the preparation of the corresponding acyl derivatives. It has also been applied to dibasic esters such as malonic ester, ethylmalonic ester, isopropylmalonic ester, butylmalonic ester and to such higher esters as ethyl glutarate and ethyl pimelate. The malonic ester derivatives yielded the corresponding cyclic barbituric acids, whereas the higher esters appeared to yield straight chain diureides, *e. g.*, glutaryl diureide.

Another interesting application of the sodium urea-ester reaction is its use for the preparation of mixed long-chain acyl ureas by the reaction of monosodium urea with vegetable oils, *i. e.*, esters of glycerol. Such naturally-occurring ester de-

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[1] Franklin and Stafford, *Am. Chem. J.*, **28**, 98 (1902).

[2] Blair, THIS JOURNAL, **48**, 96 (1926).

[3] Pfleger and Scheller, U. S. Patent 1,816,911.

rivatives as coconut oil, Chinawood oil and linseed oil react with monosodium urea in the presence of acetone to yield the corresponding mixed acyl ureas. The latter are white, crystalline, rather high-melting compounds of limited solubility in most organic solvents though crystallizable from hot acetic acid or dioxane. The acyl ureas from linseed and Chinawood oils retain the unsaturation of the oil acids and are characterized by rather high iodine numbers (around 130).

During this study the monosodium derivatives of a number of other amides and amines also were prepared, some of which have already been described by Franklin,[1,4] Titherley[5] and others.[2,6] In general, the condensation of these with esters followed the expected course, and furnished a convenient method for preparing certain acyl derivatives not readily obtained by other methods.

Experimental Part

Monosodium Urea.—Two-mole lots of monosodium urea were prepared by slowly adding 46 g. of sodium to 120 g. of urea dissolved in 1.5 liters of liquid ammonia contained in a 3-necked 2-liter flask provided with a mercury-sealed stirrer. The product was obtained as a white powder upon evaporation of the ammonia; yield 160 g.

Anal. Calcd. for CH_3ON_2Na: Na, 28.05. Found: Na, 27.85 (as sodium sulfate), 28.40 (by titration with acid).

Attempted Preparation of Disodium Urea.—Sodium in excess of one atom reacted slowly and incompletely with a very dilute solution of urea in liquid ammonia. Apparently the product was a mixture of monosodium urea and disodium urea. *Anal.* Calcd. for $CH_2ON_2Na_2$: Na, 44.23. Found: Na, 34.72. Upon treatment of the product with benzoyl chloride, dibenzoyl urea (m. p. 204–205° from benzene) was obtained. *Anal.* Calcd. for $C_{15}H_{12}O_3N_2$: N, 10.44. Found: N, 10.70.

Oleyl Urea.—To 13.5 g. of monosodium urea was added, slowly during gentle warming, 50 g. of oleyl chloride. Boiling isobutanol was added to the mixture and then sufficient water to dissolve the sodium chloride formed in the reaction. The isobutanol layer deposited crystals of oleyl urea upon cooling; m. p. 155–160° (literature 161°).[7]

Anal. Calcd. for $C_{19}H_{36}O_2N_2$: C, 70.37; H, 11.11; N, 8.64. Found: C, 69.77; H, 10.65; N, 8.24.

Stearyl urea (m. p. 175°) and benzoyl urea (m. p. 212°) were similarly prepared but satisfactory results were not obtained with some of the lower aliphatic acid chlorides.

Benzyl urea, m. p. 147–148°, was obtained from benzyl chloride and monosodium urea in liquid ammonia (literature m. p. 147°). *Anal.* Calcd. for $C_8H_{10}ON_2$: N, 18.66. Found: N, 18.24.

Reaction of Monosodium Urea and Simple Esters

Benzoyl Urea.—To 30 cc. of methyl benzoate was added 10 g. of powdered sodium urea and 15 cc. of acetone. Considerable heat was evolved and the mixture became pasty. The mixture was allowed to stand overnight, diluted with water, and acidified with hydrochloric acid. The benzoyl urea thus obtained was filtered, washed in a beaker with boiling alcohol and dried. The product melted at 213–214° (literature 215°); yield 12 g. (60%).

Acetyl urea (m. p. 213°) and oleyl urea (m. p. 160°) were similarly prepared from ethyl acetate and methyl oleate, respectively.

Reaction of Monosodium Urea and Esters of Dibasic Acids.—Monosodium urea reacted with substituted malonic esters in the presence of acetone to yield substituted barbituric acid derivatives. Thus, butylbarbituric acid (m. p. 208° from alcohol)[8] was obtained in 79% yield from butylmalonic ester.

Anal. Calcd. for $C_8H_{12}O_3N_2$: C, 52.17; H, 6.52; N, 15.21. Found: C, 52.46; H, 6.23; N, 14.79.

Ethylbarbituric acid (m. p. 185–186°, yield 79%), isopropylbarbituric acid (m. p. 212°) (*Anal.* Calcd. for $C_7H_{10}O_3N_2$: C, 49.41; H, 5.88. Found: C, 49.62; H, 5.94), and barbituric acid (m. p. 192°) were prepared from the corresponding malonic esters. The unsubstituted barbituric acid was obtained as the dihydrate.

Anal. Calcd. for $C_4H_4O_3N_2\cdot 2H_2O$: N, 17.07. Found: N, 17.48.

The melting points given in the literature are: ethylbarbituric acid, m. p. 193–194° corr.; isopropylbarbituric acid 214–214.5°.[8]

The reaction of monosodium urea with esters of dibasic acids higher in the series than malonic yielded high melting insoluble products which appeared to be diureides. From ethyl glutarate a white compound melting at 247–248° was obtained. (*Anal.* Calcd. for $C_7H_{12}O_4N_4$: C, 38.88; H, 5.55; N, 25.92. Found: C, 38.75; H, 5.81; N, 24.62.)

A product of similar properties (m. p. 240–245°) was obtained from ethyl pimelate. A small amount of a compound melting at 205–206° (crystallized from acetic acid) was also obtained. This appeared to be the monoureide of pimelic acid ($NH_2CONHCO(CH_2)_5COOH$).

Anal. Calcd. for $C_8H_{14}O_4N_2$: N, 13.86. Found: N, 13.48.

Reaction of Monosodium Urea with Natural Oils.—The mixed acyl ureas from coconut oil were prepared from 300 g. of coconut oil, 200 cc. of acetone and 100 g. of sodium urea. The white solid after an alcohol wash melted at 165–170°. Upon crystallization from acetic acid or dioxane, it melted at 172°; yield 150 g. The product contained 9.95% nitrogen.

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[4] Franklin, THIS JOURNAL, **27**, 820 (1905); **37**, 2279 (1915); **44**, 490 (1922); **46**, 2143 (1924); **46**, 2148 (1924); *Am. Chem. J.*, **47**, 304 (1912); "The Nitrogen System of Compounds," Reinhold Publishing Corporation, New York, 1934.

[5] Titherley, *J. Chem. Soc.*, **71**, 460 (1897); **79**, 391 (1901); **81**, 1520 (1902); **85**, 1673 (1904); Titherley and Hicks, *ibid.*, **87**, 1216 (1905); **89**, 708 (1906).

[6] Blacher, *Ber.*, **28**, 432 (1895); Chablay, *Compt. rend.*, **154**, 364 (1912); Freer and Sherman, *Am. Chem. J.*, **18**, 580 (1896); Parts, *Ber.*, **60**, 2520 (1927); Priestley, *J. Chem. Soc.*, **95**, 454 (1909); Rakshit, *ibid.*, **103**, 1557 (1913); Werner, *ibid.*, **109**, 1126 (1916).

[7] Stendal, *Compt. rend.*, **196**, 1810 (1933). Oleyl urea (m. p. 161°) and stearyl urea (m. p. 176–178°) were obtained by heating urea with the corresponding esters in the presence of sodium ethylate and pyridine.

[8] Volwiler, THIS JOURNAL, **47**, 2239 (1925), reported 208–209°.

The mixed acyl ureas from linseed oil and from Chinawood oil were obtained in low yield. The former melted at 154–158° (from alcohol) and the latter at 155–162° (from alcohol). The iodine numbers were, respectively, 128 and 108.8, and the nitrogen contents 7.71 and 8.13%.

Summary

1. Monosodium urea has been prepared by the reaction of urea in liquid ammonia with one equivalent of sodium. It is a white powder insoluble in inert solvents. A mixture of disodium urea and monosodium urea was obtained from urea and two equivalents of sodium.

2. Several acyl ureas including stearyl, oleyl and benzoyl have been prepared by the reaction of monosodium urea with acid chlorides. Alkyl halides such as butyl iodide and dodecyl bromide did not react with monosodium urea.

3. Simple esters such as ethyl acetate and methyl benzoate reacted with monosodium urea in the presence of acetone to yield acyl ureas. Natural oils such as coconut, linseed and Chinawood also reacted to yield high-melting mixed acyl ureas.

4. Malonic ester and its substituted derivatives reacted with monosodium urea to give barbituric acid derivatives. Barbituric acid, ethylbarbituric acid, isopropylbarbituric acid and butylbarbituric acid have been prepared in this manner.

5. Esters of higher dibasic acids, such as ethyl glutarate and ethyl pimelate, apparently yielded diureides.

WILMINGTON, DELAWARE RECEIVED JULY 9, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Interconversion of Mixed Benzoins

BY H. H. WEINSTOCK, JR., AND REYNOLD C. FUSON

The reduction of 2,4,6-trimethylbenzoin (II) and 2′,4′,6′-trimethylbenzoin (III) to the same desoxybenzoin, phenyl 2,4,6-trimethylbenzyl ketone,[1] can be explained on the basis of an initial transformation of one of the benzoins into its isomer. If this explanation is correct, the benzoins should be interconvertible under mild conditions. This has proved to be the case, for when either 2,4,6- or 2′,4′,6′-trimethylbenzoin was warmed in alcoholic sodium acetate solution, the corresponding isomer was formed. Isolation of starting material in each case indicated the existence of an equilibrium.

Because of this ease of interconversion, an investigation was made of the reaction of the two benzoins toward reagents commonly employed in testing for the hydroxyl group. The benzoins, when treated with benzoyl chloride, yielded a single benzoate instead of the expected isomeric benzoates. Presumably in one case benzoylation had been preceded by conversion of the benzoin into its isomer.

Such a conversion suggests the intermediate formation of the ene-diol. Longer treatment was, accordingly, attempted in the hope of obtaining the dibenzoate of the ene-diol. The monobenzoate was, however, the only product which could be isolated. The dibenzoate was made for reference by the action of benzoyl chloride on the sodium derivative of the diketone (I). Two forms (VI and VII) of the dibenzoate were isolated. The lower-melting form (139°) was converted into its isomer (170°) by heating above the melting point.

It was found possible, however, to obtain the diacetate of the ene-diol (V) by a method similar to that which was unsuccessful in the case of the corresponding dibenzoate. Subjection of either of the isomeric benzoins to the action of acetic anhydride resulted in the formation of the diacetate. This structure was proved by preparing the compound by the action of acetyl chloride on the disodium salt of mesityl phenyl diketone (I). Compound III formed the diacetate more readily than did its isomer (II); when II was treated with acetic anhydride for five hours a monoacetate was formed while, under the same conditions, III formed the diacetate.

This implies that in the benzoylation III rather than II isomerizes. It is for this reason that the monobenzoate (IV), the structure of which is conjectural, is represented as a derivative of II rather than of III.

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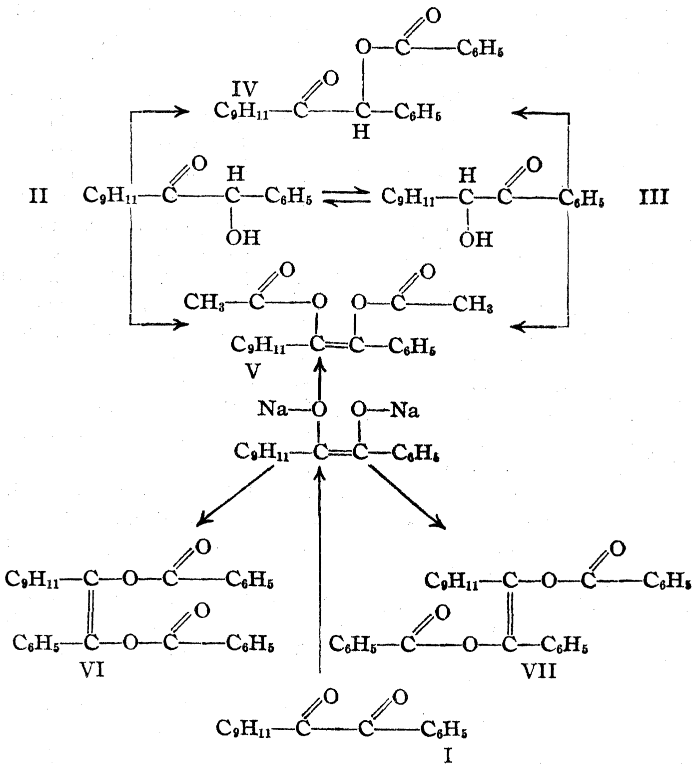
[1] Weinstock and Fuson, THIS JOURNAL, **58**, 1233 (1936).



That both II and III readily rearrange to the ene-diol form was confirmed by treatment of the two benzoins with methylmagnesium iodide, according to the method of Kohler, Stone and Fuson.[2] Considerably more than one mole of gas was formed by each of the isomers and, as would be expected, II, which contains the sterically hindered carbonyl group, and thus would have a longer period of time to enolize before addition took place, gives the greater amount of methane.

The action of iodine upon the isomeric benzoins produced an unexpected result In the presence of small amounts of iodine, both II and III were found to undergo disproportionation to yield mesityl phenyl diketone (I), and phenyl 2,4,6-trimethylbenzyl ketone.[3]

The reaction took place in hot, glacial acetic acid or at high temperatures in the absence of solvent. Disproportionation could not be made to take place in the absence of a trace of iodine. One explanation would be that the iodine oxidized one molecule of the benzoin to I with the formation of hydrogen iodide, which then reduced another molecule of the benzoin to phenyl 2,4,6-trimethylbenzyl ketone, regenerating the iodine.

Experimental

Because of the ease of oxidation of 2,4,6- and 2′,4′,6′-trimethylbenzoin in solution, all reactions were carried out in an atmosphere of nitrogen.

Interconversion of the Benzoins.—Two grams of 2,4,6-trimethylbenzoin (II),[4] 0.75 g. of sodium acetate, 30 cc. of ethyl alcohol and 1 cc. of water were heated under reflux for twenty hours. The solution was diluted with water and cooled. From 1.2 g. of colorless material which separated, there was obtained on fractional crystallization, 0.1 g. of substance which melted at 93–94°. A mixed melting point with a known sample of 2′,4′,6′-trimethylbenzoin (III) showed no depression.

From 1 g. of III[5] 0.1 g. of II was obtained by the same method. In both cases the equilibrium mixture was difficult to separate, and the yield of converted isomer was probably higher than given above.

A simple *monobenzoate* (IV) was obtained from both II and III by the following procedure. One gram of the benzoin was added to 1 cc. of benzoyl chloride in 5 cc. of pyridine. The reaction was maintained at a temperature of 80° for thirty minutes, and poured into 10 cc. of sodium carbonate solution. The emulsion was extracted with ether, the ether layer dried over calcium chloride, and the ether removed by evaporation. The residual oil was taken up in alcohol. When allowed to stand, the solution deposited a colorless, granular substance, melting at 127–127.5°, which was only slightly soluble in alcohol. The benzoates obtained from II and III were shown to be identical by the method of mixed melting points.

Anal. Calcd. for $C_{24}H_{22}O_3$: C, 80.44; H, 6.14. Found: C, 80.55; H, 6.29.

Allowing the reaction to proceed for a longer period of time did not yield the dibenzoate. Two grams of II, 15 cc. of pyridine and 2.5 cc. of benzoyl chloride were boiled under reflux for ten hours. There was obtained 1.5 g. of substance, melting at 115°, which, on purification, proved to be the monobenzoate. Hydrolysis of the monobenzoate with alcoholic potassium hydroxide solution gave I, m. p. 134–135°. A mixed melting point with mesityl phenyl diketone showed no depression. It seems probable that the monobenzoate has the structure represented by formula IV.

The isomeric dibenzoates of 2,4,6-trimethyl-α,α′-stilbenediol (VI and VII) were prepared by the action of benzoyl chloride on the disodium derivative of mesityl phenyl diketone. In a typical experiment, 3.5 g. of one dibenzoate was obtained from 8 g. of I. No method was evolved by which one could predict the isomer which would be

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(2) Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927).

(3) Matsumura [*ibid.*, **57**, 955 (1935)] by treating β-*p*-dimethylaminobenzoin with alcoholic hydrochloric acid, obtained *p*-dimethylaminobenzil, and α-*p*-dimethylaminodesoxybenzoin. Compound II would not undergo disproportionation under the same conditions. It is interesting to note that the desoxybenzoin formed by disproportionation of both benzoins is the same one which is formed exclusively in the reduction of I, II and III.[1]

(4) Fuson, Weinstock and Ullyot, *ibid.*, **57**, 1803 (1935).

(5) Arnold and Fuson, *ibid.*, **58**, 1295 (1936).

formed. The isomers were both colorless compounds and melted at 138.5–139° and 169.5–170°. They were recrystallized from ethyl alcohol, in which they were difficultly soluble.

Anal. Calcd. for $C_{31}H_{26}O_4$: C, 80.52; H, 5.63. Found: (139°) C, 80.58; H, 5.79; (170°) C, 80.35; H, 5.68.

The substance melting at 139° was quantitatively converted into its isomer by heating above the melting point for five minutes. The high-melting isomer was hydrolyzed with alcoholic potassium hydroxide to give a mixture from which I (m. p. 133–135°) and II (m. p. 100–101°) were isolated. These substances were identified by mixed melting point determinations. The spatial configuration of the dibenzoates was not determined.

The monoacetate of 2,4,6-trimethylbenzoin was obtained by heating a solution of 2 g. of II and 1 g. of sodium acetate in 20 cc. of acetic anhydride under reflux for five hours. The solution was cautiously treated with water and extracted with ether. The ether layer was dried over calcium chloride, and the ether removed by evaporation. The residual yellow oil was taken up in alcohol and allowed to stand at room temperature; 1.5 g. of a colorless, granular substance separated. On recrystallization from dilute ethyl alcohol, the compound melted at 73–73.5°.

Anal. Calcd. for $C_{19}H_{20}O_3$: C, 77.03; H, 6.76. Found: C, 77.10; H, 6.75.

Diacetate of 2,4,6-Trimethyl-α,α′-stilbenediol (V).—A. Treatment of II by the above procedure, except that heating was carried out for twenty-four hours, gave 0.8 g. of a colorless product; m. p. 92–98°. The pure compound melted (from alcohol) at 104–104.5°.

Anal. Calcd. for $C_{21}H_{22}O_4$: C, 74.56; H, 6.51. Found: C, 74.61; H, 6.49.

B. Treatment of III by the same procedure, except that the reaction mixture was heated for five hours, resulted in the formation of the diacetate; m. p. 104–104.5°. A mixed melting point with the product prepared from II showed no depression.

C. The diacetate was prepared by the action of acetyl chloride on the sodium derivative of mesityl phenyl diketone, according to the usual procedure. From 2 g. of I, 0.4 g. of sodium and 6 cc. of acetyl chloride was obtained 0.6 g. of product, m. p. 95–100°. The melting point was 103–104° after recrystallization. A mixed melting point with the diacetate prepared from II and III showed no depression.

Reaction with the Grignard Reagent.[6]—The benzoins (II and III) were treated with methylmagnesium iodide, in an apparatus of the type described by Kohler and Richtmyer.[7] Approximately 0.0005 mole of substance was used in each run. The solution of the benzoin in the excess Grignard reagent was held at a temperature of 90° for thirty minutes before decomposition to allow the reaction to go to completion. The results showed that II gave 1.78 moles of gas, and 0.29 mole of the reagent was added. Compound III likewise used two moles of reagent, but in this case 1.30 moles of gas was evolved and 0.75 mole of reagent was added.

Reaction with Iodine.—A. A solution of 1 g. of II and 0.1 g. of iodine in 50 cc. of glacial acetic acid was heated under reflux for three hours. The solution was poured, while hot, into 25 cc. of 2% sodium bisulfite solution. The hot solution was filtered and allowed to cool. A solid formed which, by a process of slow crystallization and decantation from alcohol, was separated into two sets of crystals: (a) 0.40 g. of large, yellow needles which melted at 135–136°—a mixed melting point with mesityl phenyl diketone showed no depression; (b) 0.37 g. of colorless fibrous clusters; m. p. 161–162°. After recrystallization from alcohol, the crystals melted at 164–165°. This substance was shown to be identical with phenyl 2,4,6-trimethylbenzyl ketone by means of a mixed melting point determination.

In another experiment, 2 g. of II and a small crystal of iodine were placed in a small Pyrex flask and held at a temperature of 200° for five minutes. The water which was formed in the reaction collected as a vapor on the upper surface of the flask. The product was taken up in alcohol after cooling. There was obtained 0.60 g. of mesityl phenyl diketone (m. p. 135.5–136.5°) and 0.55 g. of phenyl 2,4,6-trimethylbenzyl ketone (m. p. 162–163°).

Only starting material was recovered when II was heated to 220° or boiled under reflux in glacial acetic acid for three hours, no iodine being used in either case. Treatment of II with alcoholic hydrochloric acid and copper sulfate caused no disproportionation.

B. One and four-tenths grams of III was heated at 220° in the presence of a crystal of iodine. There was obtained 0.60 g. of phenyl 2,4,6-trimethylbenzyl ketone (m. p. 158–161°) and 0.55 g. of mesityl phenyl diketone (m. p. 133.5–135°). Mixed melting points of the purified substances with authentic samples showed no depression.

Summary

2,4,6-Trimethylbenzoin (II) and its isomer, 2′,4′,6′-trimethylbenzoin (III), underwent interconversion when heated in the presence of sodium acetate. It is postulated that the ene-diol is an intermediate in these transformations. Evidence in support of this is that with benzoyl chloride the two benzoins yield the same monobenzoate, and with acetic anhydride they give the same diacetate.

With methylmagnesium bromide, II and III react in the ene-diol form to the extent of 78 and 30%, respectively.

When heated in the presence of a crystal of iodine, II and III underwent disproportionation to the diketone and phenyl 2,4,6-trimethylbenzyl ketone.

URBANA, ILLINOIS RECEIVED JULY 27, 1936

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[6] The Grignard analyses were made by Mr. J. W. Robinson, Jr.

[7] Kohler and Richtmyer, THIS JOURNAL, **52**, 3736 (1930).

[Contribution from Mellon Institute of Industrial Research, and E. R. Squibb and Sons]

Local Anesthetics Containing the *ac*-Tetrahydro-beta-naphthylamine Pressor Group[1]

By Harold W. Coles[2] and William A. Lott[3]

Attempts are being made continually to prepare local anesthetics with vasoconstricting properties in order to eliminate the use of pressor drugs (usually epinephrin) to localize and synergize the local anesthetic action.[4] Until recently,[5] however, the compounds synthesized to this end have shown little or no pressor action on pharmacological assay.

Although the powerful pressor activity of *ac*-tetrahydro-β-naphthylamine is well known,[6] no attempt has been made previously to employ this amine as the nitrogen-containing portion of a local anesthetic molecule. It is known[7] that the introduction of an acid group, such as the acetyl or formyl, on the nitrogen atom, completely reverses the vasoconstricting and pyretic properties of *ac*-tetrahydro-β-naphthylamine, whereas the replacement of a hydrogen atom by an alkyl group changes them only in degree. There is a double action if an acid and alkyl group are both introduced. However, it was believed possible that the reversal effect of the acyl groups might not take place if the acyl groups were separated from the pressor amine portion by means of an alkylene group. As shown later, this hope was not realized in the large number of local anesthetics prepared.

Experimental Part

The *ac*-tetrahydro-β-naphthylamine was prepared according to the directions given in "Organic Syntheses."[8]

Preparation of the (*ac*-Tetrahydro-β-naphthylamino)-alkanol Hydrochlorides.—The general literature methods were changed in some respects. Two molecular equivalents of freshly distilled *ac*-tetrahydro-β-naphthylamine, one molecular equivalent of ethylene chlorohydrin (or trimethylene chlorohydrin) and some xylene (as diluent) were placed in a round-bottomed 3-necked flask equipped with a thermometer, reflux condenser and glass tubing reaching to the bottom of the flask through which a steady stream of dry nitrogen was passed during the entire reaction. The nitrogen prevents almost completely the formation of the usual red color. The flask and contents were immersed in an oil-bath, the temperature of the flask contents was raised to 110° and the reaction was allowed to continue for three hours at a temperature of 110–115°. The mixture was cooled, a large excess of ether added and the precipitated *ac*-tetrahydro-β-naphthylamine hydrochloride was filtered off and washed repeatedly with ether.

The ether–xylene filtrate was chilled, and both nitrogen and dry hydrogen chloride were passed slowly through the solution, until precipitation of the amino alcohol hydrochloride was complete. The precipitate was filtered off and washed well with ether, then recrystallized from isopropyl alcohol to a constant melting point with a yield of 80–85%. The compounds are white crystalline solids, soluble in water, acetone and the different alcohols, but insoluble in ether and benzene.

Beta-(*ac*-tetrahydro-β-naphthylamino)-ethanol Hydrochloride (m. p. 183.8–184.8°).[9]—*Anal.* (Volhard). Calcd. for $C_{12}H_{18}NOCl$: Cl, 15.58. Found: Cl, 15.59, 15.64.[10]

Gamma-(*ac*-tetrahydro-β-naphthylamino)-propanol Hydrochloride (m. p. 161°).—*Anal.* Calcd. for $C_{13}H_{20}NOCl$: Cl, 14.67. Found: Cl, 14.75, 14.89.

Preparation of the Esters.—These were prepared essentially by general methods reported in the literature[11] in which one molecular equivalent of the (*ac*-tetrahydro-β-naphthylamino)-alkanol hydrochloride was allowed to react with 1.5 molecular equivalents of the acyl chloride until no further hydrogen chloride was evolved. No attempt was made to work out the conditions for optimum yields, but these were satisfactory in most cases. The reaction product was washed repeatedly with ether to remove the excess acid chloride, and was then recrystallized from mixtures of methyl and isopropyl alcohols.

In most cases, little trouble was experienced in securing nicely crystalline hydrochlorides. Certain aliphatic derivatives, however, as the caproyl, propionyl and furylacryloyl, produced gums and were not secured in pure form. The *p*-toluene sulfonyl chloride seemed to react normally[12] with formation of a compound containing chlorine but the halogen was not precipitated by silver nitrate in nitric acid solution. The compound produced appreciable anesthesia when applied to the tongue, but it has not yet been separated completely from about 25% of inert material.

The nitro esters were reduced with iron and hydrochloric acid.[13] The aminobenzoates were isolated and tested as

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[1] Presented before the Division of Medicinal Chemistry at the Pittsburgh Meeting of the American Chemical Society, September 7–11, 1936.

[2] Industrial Fellow, E. R. Squibb and Sons Industrial Fellowship, Mellon Institute.

[3] E. R. Squibb and Sons, Brooklyn, N. Y.

[4] Hartung, Munch and Kester, This Journal, **54**, 1526 (1932), for literature references.

[5] Alles and Knoefel, *J. Pharmacol.*, **48**, 268 (1933); *Arch. intern. pharmacodynamie*, **47**, 96 (1934).

[6] Fränkel, "Die Arzneimittel-Synthese," 6th Edition, Verlag Julius Springer, Berlin, 1927.

[7] Cloetta and Waser, *Arch. exptl. Path. Pharmakol.*, **73**, 398 (1913).

[8] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 486.

[9] All melting points recorded in this paper are U. S. P., corrected.

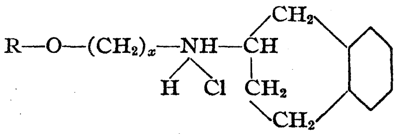
[10] The authors are indebted to Dr. W. W. Mills and Miss Elinor Sackter of the Mellon Institute analytical department for many of the assays.

[11] McElvain, This Journal, **48**, 2240 (1926); Thayer and McElvain, *ibid.*, **50**, 3351 (1928).

[12] Compare Gilman and Pickens, *ibid.*, **47**, 245 (1925).

[13] Cope and McElvain, *ibid.*, **53**, 1591 (1931).

the dihydrochlorides. The compounds have the general formula



where R represents an aliphatic or aromatic group, and x is 2 or 3. All of the compounds are white, crystalline solids of limited solubility in water which, in some cases, did not permit of pharmacologic testing. A table of the chlorine (Parr bomb method) assays with melting points is given.

TABLE I

PHYSICAL CONSTANTS OF THE HYDROCHLORIDES

R	x	M. p., °C.	Chlorine, % Calcd.	Chlorine, % Found (av.)
p-Nitrobenzoyl	3	228–229	9.07	8.96
m-Nitrobenzoyl	3	173.4–177.4	9.07	9.00
Benzoyl[a]	2	214.9	10.69	10.65
Benzoyl[b]	3	195.6	10.25	10.02
m-Aminobenzoyl	2	205–206	18.51	18.20
m-Nitrobenzoyl	2	216–217	9.41	9.59
Cinnamoyl	2	194–195.8	9.91	9.77
Cinnamoyl	3	204.8–206.8 (dec.)	9.54	9.43
p-Chlorobenzoyl	2	219–220	19.37	19.15
p-Chlorobenzoyl	3	188.8–189.8	18.65	18.51
p-Nitrobenzoyl	2	236.2	9.40	9.25
p-Aminobenzoyl	2	223.3	18.51	18.31
β-Phenylpropionyl	3	95.0 (indef.)	9.48	9.80
o-Nitrobenzoyl	2	232–233	9.41	9.33
o-Aminobenzoyl	2	150	18.51	18.20
p-Iodobenzoyl	2	232	...	...[c]
Phthaloyl	2	185–186	12.11	12.33

[a] Sulfate (m. p. 216–218°). Calcd. for $C_{38}H_{44}N_2O_8S$: S (Parr bomb), 4.65. Found: S, 4.70. [b] Picrate (m. p. 83.86°). Calcd. for $C_{20}H_{23}NO_2\cdot HOC_6H_2(NO_2)_3$: N, 10.40. Found: N, 10.02. [c] Calcd.: I, 27.74. Found: I, 27.58.

Pharmacologically,[14] the compounds showed no mydriatic action on the rabbit's cornea, and produced no blanching of tissues when injected intradermally or subcutaneously in guinea pigs. The onset of anesthesia was usually delayed, although the duration and depth of anesthesia was satisfactory in most cases. However, the steep slope of the dose-effect curves and the marked difference between the duration of anesthesia following endermic and subcutaneous injections of the same concentration in the guinea pig were undesirable characteristics. The compounds were not irritating. Kymograph tracings of their action on the blood pressure of the rabbit revealed a sudden drop in the pressure, with considerable disturbance of the rhythm as the blood pressure rose gradually again to normal.

It should be recorded, too, that *ac*-tetrahydro-β-naphthylamine hydrochloride, in practical concentrations (up to 1%), does not exhibit sufficient peripheral vasoconstriction to synergize or localize the effect of a local anesthetic such as procaine (up to 2%). Injections were made subcutaneously in guinea pigs. These results are similar to those obtained with ephedrine.[15]

The authors wish to record their appreciation of the helpful advice of Dr. George D. Beal, Assistant Director of Mellon Institute.

Summary

Two new alkanol derivatives of *ac*-tetrahydro-β-naphthylamine have been prepared and described.

From these two derivatives, a series of seventeen new local anesthetics has been prepared. Although possessing, in most cases, satisfactory local anesthetic properties, they lack vasopressor characteristics.

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BROOKLYN, N. Y.
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[14] The authors are grateful to Mr. H. A. Holaday and associates of the E. R. Squibb and Sons Biological Laboratories, New Brunswick, N. J., for these assays.

[15] Meeker, *J. Lab. Clin. Med.*, **17**, 773 (1932).

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Hydrogen Bond Formation between Hydroxyl Groups and Nitrogen Atoms in Some Organic Compounds

BY S. B. HENDRICKS, O. R. WULF, G. E. HILBERT AND U. LIDDEL

Many molecules containing hydrogen bonds between oxygen atoms have no measurable absorption in the infra-red region where characteristic OH absorption occurs in other hydroxylic compounds.[1] Such absence of absorption was used as an analytical method in our previous work. In extending that study, the question naturally arises as to what groups can take part in the formation of hydrogen bonds. The following work deals with some molecules in which a hydrogen bond if formed would be between an hydroxylic oxygen and a nitrogen atom of the type =N—.

Moore and Winmill's[2] explanation of the difference in the basicity of the tertiary and quaternary ammonium bases was that a hydrogen bond could be formed between oxygen and nitrogen atoms in the former case but not in the latter. Hydrogen bond formation was also suggested by Latimer and Rodebush[3] as an explanation for the weak basicity of ammonium hydroxide. Sidgwick[4] has reviewed this evidence and further has pointed out that nitrogen can act as a "donor," that is, form coördination compounds with appropriate groups or elements including OH. Pfeiffer and his co-workers[5] postulated hydrogen bond (partial valence) formation to explain the unusual properties of the phenylazo-1-naphthol-2.

The experimental technique and the spectroscopic procedure was the same as that described in previous work from this Laboratory.[6] However, some comment should again be made about the region 7100–7400 cm.$^{-1}$. Atmospheric water absorption lies here and makes observation difficult, so that weak absorption could be missed. The curves of Fig. 2 have been brought down to the axis of abscissa, but since the accuracy attained permits a considerable variation from zero they *must not be construed as indicating no absorption in this region* (7100–7400 cm.$^{-1}$). Very weak absorption due to presence of CH is known to lie here and there have been frequent indications of its presence in variations that were too small, at the concentrations used in this work, to be established definitely.

Compounds used were either prepared by known methods with analysis as a criterion of purity or were purified commercial products. We are indebted to Dr. T. W. J. Taylor, of Oxford University, for generous samples of 1-benzoylnaphthol-2-hydrazone and 1-benzoylnaphthol-2-acetonylhydrazone and to Dr. A. H. Blatt, of Howard University, for 2-hydroxy-5-methylbenzophenoneoxime acetate, 2-hydroxyacetophenoneoximeacetate, *cis*- and *trans*-2-hydroxybenzophenoneoximeacetates and 2,2′-dihydroxybenzophenoneoximeacetate. Drs. H. L. Haller and D. L. Vivian of the Bureau of Entomology kindly supplied us with samples of α-(β-naphthol)-2,5-dichloroazobenzene, 2,5-dichloro-2′-hydroxy-4′-methyl-5′-chloroazobenzene and 4-hydroxyazobenzene.

Results and Discussion

Absorption in the region 6200–7500 cm.$^{-1}$ characteristic of the presence of OH groups was found to be absent for a number of compounds having configurations that would favor formation of a hydrogen bond between hydroxyl oxygen and a nitrogen atom. It was found to be present in related compounds the configurations of which excluded possible formation of such bonds. Absence of a measurable amount of such absorption thus can probably be used as a positive analytical device in detecting the presence of a hydrogen bond in this type of molecule.

Factors similar to those previously discussed as possibly affecting hydrogen bond formation between oxygen atoms are also to be considered here. One of the important requirements is that the nitrogen and oxygen atoms sharing the hydrogen bond be correctly placed, the interatomic distance, N to O, being about 2.6 Å. The ring formed should contain a minimum number of single bonds about which there could be free

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[1] Hilbert, Wulf, Hendricks and Liddel, THIS JOURNAL, **58**, 548 (1936); *Nature*, **135**, 147 (1935); Errera and Mollet, *Compt. rend.*, **200**, 814 (1935); *J. phys. radium*, **6**, 281 (1935).

[2] Moore and Winmill, *J. Chem. Soc.*, **101**, 1635 (1912).

[3] Latimer and Rodebush, THIS JOURNAL, **42**, 1419 (1920).

[4] Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933, p. 164.

[5] Pfeiffer, Angern, Wang, Seydel and Quehl, *J. prakt. Chem.*, **126**, 97 (1930).

[6] Wulf and Liddel, THIS JOURNAL, **57**, 1464 (1935).

rotation and the entire system should be one relatively free of strain produced by deformation of valence angles. These conditions were best met in the case of oxygen compounds by formation of six-membered rings including hydrogen, there being possibly a single example of a seven-membered ring but none of five. Other important factors are electron affinities of groups sharing hydrogen bonds and resonance phenomena, particularly those associated with a conjugate system of double bonds. Absence of discussion of resonance phenomena arises from the authors' lack of familiarity with the subject.

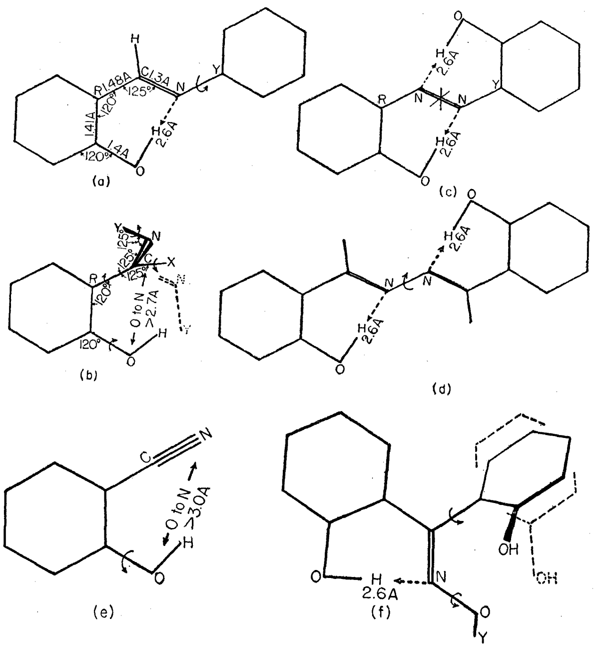

Fig. 1.—Structural formulas showing probable interatomic distances. A converging line indicates that the line departs from the plane of the figure.

Nitrogen compounds are of particular interest in that additional steric factors, arising from three rather than two directed valences, are introduced. Thus compounds R—CX=N—Y where R is unsymmetrical, can theoretically exist in two isomeric forms. Difficulty of determining their configurations by chemical methods is well recognized. The nitrogen atom of the —CX=N—Y group would be expected to have an additional coördination valence, associated with its single pair of non-binding electrons,[7] and hydrogen bond formation under otherwise favorable conditions would be possible for one isomer but not for the other. A method is thus available for absolute assignment of configuration.

The influence of the various factors mentioned above can be best studied on the ortho substituted phenols and a number of these having —CX=N—Y substituents were examined, X and Y being varied widely. Among these was salicylaldehydeanil ($2\text{-HOC}_6\text{H}_4\text{CH}{=}\text{NC}_6\text{H}_5$), which did not give characteristic OH absorption. The probable geometrical configuration of this compound, which serves to illustrate the type, is shown as (a) in Fig. 1, the rotation of the second benzene ring (Y) about the NY bond being unknown. Formation of a hydrogen bond between the oxygen and nitrogen atoms restricts the rotation about the bond RC, the only single bond involved, and requires RCNO to be approximately coplanar with the neighboring benzene ring. Moreover the bond NY is required to have a *trans* (*anti*) configuration with respect to RC.

Presence or absence of hydroxyl absorption is used below as a criterion for determining the structures of some oximes. The methods that have been used in the past usually involved chemical transformations and thus alteration of the molecule investigated. Prominent among these are the Beckmann rearrangement and condensations presumably involving adjacent groups, such as that leading to formation of isoxazole rings, both of which are open to criticism.[8]

Absorption characteristic of the presence of OH was not observed for 2-hydroxy-5-methylbenzophenoneoxime acetate ($2\text{-HO-5-CH}_3\text{C}_6\text{H}_3\text{C}({=}\text{NO-COCH}_3)\text{C}_6\text{H}_5$, m. p. 114°) which thus must contain a hydrogen bond and have an *anti* configuration of the (—OCOCH_3) group with respect to the C—ROH group. Acetyl groups were introduced into this compound and most of those discussed below in order to prevent confusion arising from absorption due to the NOH group.

Since the energy of binding enhances the stability of the isomeric form having a hydrogen bond, it is not surprising to find that most such compounds have been obtained in only one form. However, Kohler and Bruce have prepared geometrical isomers of 2-hydroxybenzophenoneoxime and have shown that no evidence independent of the Beckmann rearrangement, with its corollary assumption of a *trans* shift, exists as to their

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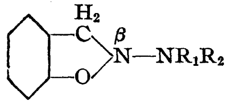
(7) N. V. Sidgwick, "The Electronic Theory of Valence," Oxford University Press, Oxford, 1929, p. 72; W. D. Kumler, This Journal, **57**, 600 (1935).

(8) A. H. Blatt, *Chem. Rev.*, **12**, 215 (1933). This review particularly clarified the subject for us and we are indebted to Dr. Blatt for further discussion and for placing his wide experience in the field at our disposal.

configurations.[9] Their "n" form of the oxime (m. p. 141–142°) was considered to have a *syn* configuration with respect to the RC bond (Fig. 1a) and was less stable thermally with respect to the isomeric "h" or *anti* oxime[7] (m. p. 142–143°). Acetates of these two compounds, namely, the *syn* acetate (m. p. 156°) and the *anti* acetate (m. p. 95°) ($2\text{-}HOC_6H_4C({=}NOCOCH_3)C_6H_5$), were placed at our disposal by Dr. Blatt. The former compound gave the absorption shown in Fig. 2[10] while no measurable value was obtained for the latter. Thus a hydrogen bond is present in the *anti* acetate and this is in agreement with the configuration assigned on the basis of Meisenheimer's interpretation of the Beckmann rearrangement. A probable geometrical configuration for the *syn* acetate, which does not contain a hydrogen bond and is thus the unstable form, is shown in Fig. 1b. Spatial proximity of H and Y as in the dotted position would necessitate rotation of the CNY group about the RC bond.

Considerably less is known about the structures of the aldoximes than of the ketoximes. As might be expected the common forms, and thus probably the stable forms, that we have studied, all contain hydrogen bonds. Thus neither salicylaldoxime acetate ($2\text{-}HOC_6H_4CH({=}NOCOCH_3)$) nor the 2-hydroxy-5-methylbenzophenoneoxime acetate ($5\text{-}CH_3\text{-}2\text{-}HOC_6H_3C({=}NOCOCH_3)C_6H_7$) gave measurable OH absorption. Both of these compounds therefore have configurations similar to that of salicylaldehydeanil, that is, NY of $R{-}\overset{H}{C}{=}N{-}Y$ *anti* with respect to R—C. Salicylaldoxime ($2HOC_6H_4CH{=}NOH$) (absorption measured at 0.00333 and 0.0100 molal) was also examined and found to have the absorption shown in Fig. 2.[11] Similarity of this absorption to that of other oximes indicates that it is entirely to be accounted for by the presence of oxime OH. Chemical methods applied to studying the configuration of the aldoximes have been handicapped by lack of evidence as to whether the Beckmann rearrangement involved a *syn* or an *anti* shift, the former being assumed in the older literature. The results given above for the aldoximes, however, support the chemical findings of Brady and Bishop[12] in favor of the *anti* shift in the Beckmann rearrangement.

Salicylaldehyde α-methyl-α-phenylhydrazone ($2\text{-}HOC_6H_4CH{=}NN(CH_3)C_6H_5$) and salicylaldehydedimethylhydrazone ($2\text{-}HOC_6H_4CH{=}NN(CH_3)_2$) failed to give characteristic OH absorption. Hydrogen bond formation in these compounds probably takes place between the OH group and the β nitrogen atom, the NR_2 group being a variant of Y as defined above. Where the hydrogen bond is present the Y substituent must necessarily be *trans* with respect to the aromatic grouping. It is possible, however, that these results, namely, absence of measurable OH absorption in the region studied could be explained by the presence of five membered rings such as



The ordinary hydroxylic reactions of these compounds is strong evidence against this explanation.

In order further to vary the basicity of the Y group several hydrazones were studied in which NH groups were present. Salicylaldehydehydrazone ($2\text{-}HOC_6H_4CH{=}NNH_2$) and salicylaldehydephenylhydrazone ($2\text{-}HOC_6H_4CH{=}NNHC_6H_5$) gave the absorptions shown in Fig. 2. Comparisons of these absorptions with those of analogous compounds that do not contain hydroxy groups shows that the absorptions are entirely to be accounted for by the presence of NH_2 or NH groups. Both compounds are thus thought to contain hydrogen bonds. In varying the substituent Y group of the hydrazone from $—N(CH_3)C_6H_5$ to NH_2 the limits of basicity were approximately encompassed and thus shown not to be determinative at least in this series of compounds for hydrogen bond formation.

Two substituted naphthols, 1-benzoylnaphthol-2-hydrazone ($2\text{-}HOC_{10}H_6\text{-}1\text{-}CH({=}NNH_2)C_6H_5$) and 1-benzoylnaphthol-2-acetonylhydrazone ($2\text{-}HOC_{10}H_6\text{-}1\text{-}C({=}NN{=}C(CH_3)_2)C_6H_5$) were examined. The former of these compounds[13] gave the absorption shown in Fig. 2, which should be compared with that of salicylaldehydehydrazone, the complexity of which is to be accounted for by

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[9] Kohler and Bruce, THIS JOURNAL, **53**, 1569 (1931).

[10] This absorption showed a change with temperature (60 to 20°) which is indicative of association as might be expected for this compound. Decomposition, which was not tested for, could give rise to a similar effect.

[11] The absorption of this compound showed a slight change with concentration. This is indicative of association which is well known for oximes (N. V. Sidgwick, *Ann. Reports Chem. Soc.*, **31**, 41 (1934)).

[12] Brady and Bishop, *J. Chem. Soc.*, **127**, 1357 (1925).

[13] Neither of these compounds is described in the literature. The first as supplied to us by Dr. Taylor, was recrystallized from benzene and found to have the following constants: m. p. 157°. *Anal.* (M. S. Sherman) C, 78.44; H, 5.65; N, 10.51. Calcd. C, 77.84; H, 5.39; N, 10.68.

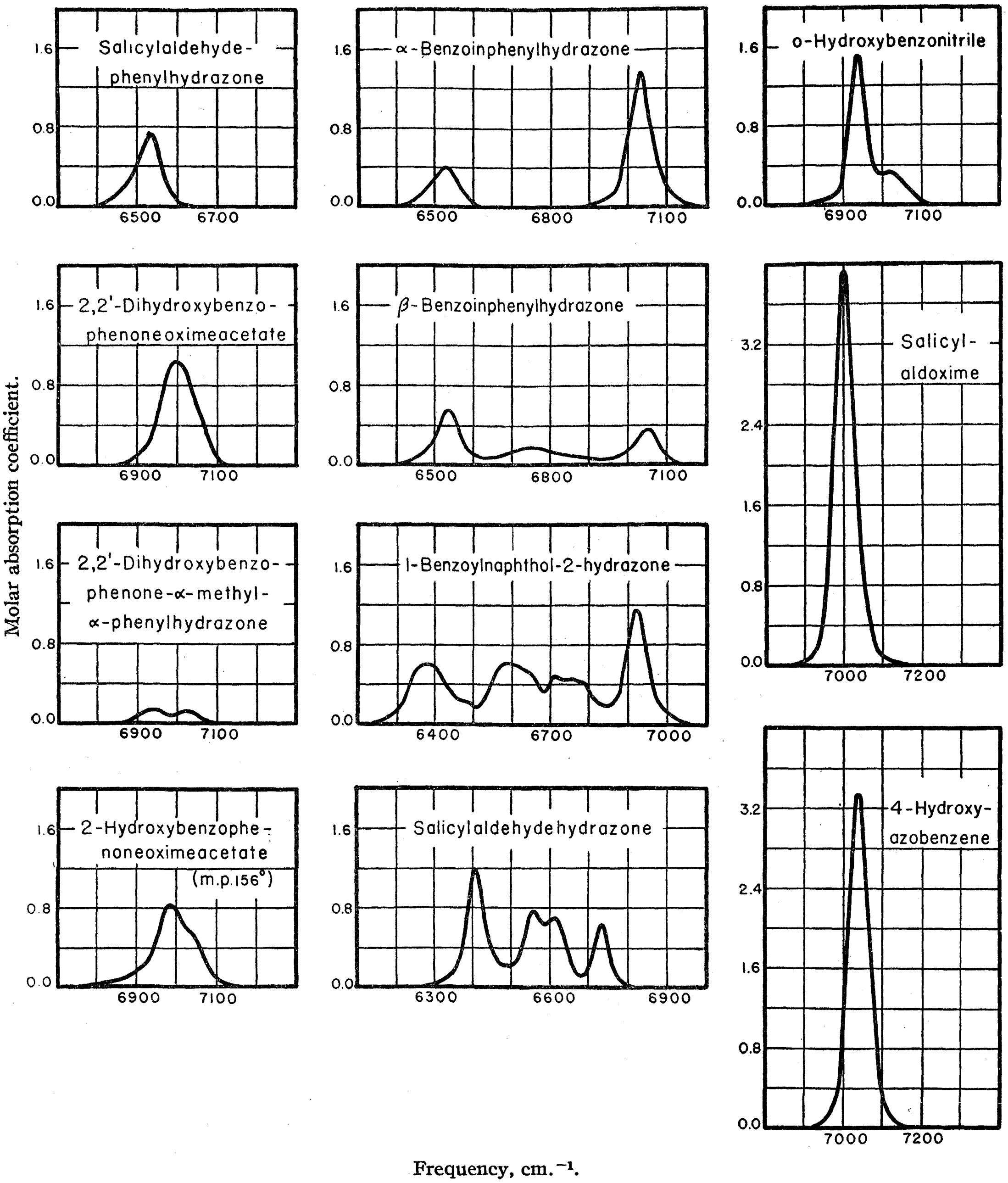
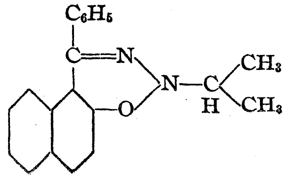
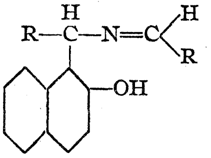


Fig. 2.—Molar absorption coefficients for some compounds of interest in the question of hydrogen-bond formation.

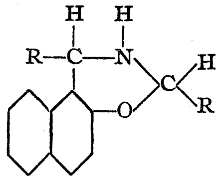
the presence of the hydrazine —NH_2 group. However, the absorption in the region of 7000 cm.$^{-1}$ is similar in shape and area to that found in many other phenolic compounds. It thus would seem that this substance does not contain a hydrogen bond and the possibility of ring formation through nitrogen is also eliminated. The latter compound on the other hand gave no absorption in the region studied which is of particular interest since it is derived from the hydrazone. Several explanations can be suggested for this behavior, one of which is that a six-membered ring through nitrogen



is present in the acetonyl derivative which, of course, is impossible in the case of the hydrazone. This situation is analogous to that existing in Schiff bases of the type



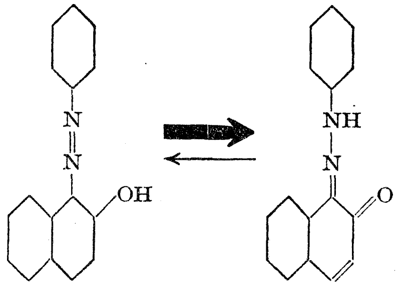
that in certain cases[14] are considered to be cyclicized as



Another possibility is that a hydrogen bond really is present in the one compound but not in the other. If this is the case it might arise from a combination of steric factors associated with an added *ortho* substituent, namely, the eight position of the naphthalene ring. Such a substituent is effective in preventing hydrogen bond formation in 2,5-dihydroxy-3,6-dibromodiethylterephthalate[1] but does not prevent it in 1-acetylnaphthol-2, a result in accord with the greater size of the bromine atom. If this explanation is correct the difference in behavior of the two naphthol derivatives probably arises from alteration of the electron affinity of the β-nitrogen atom, induced by variation of the Y group.

Characteristic OH absorption was absent for several *ortho* hydroxyazo compounds which are of the general type $R_1—N=N—R_2$. Among these were 2,5-dichlorobenzeneazo-1-naphthol-2 ($2,5\text{-}Cl_2C_6H_3N=N\text{-}1\text{-}C_{10}H_6OH\text{-}2$), 2,5-dichloro-2′-hydroxy-4-methyl-5′-chloroazobenzene ($2,5\text{-}Cl_2C_6H_3N=NC_6H_2OH(2)CH_3(4)Cl(5)$) and phenylazo-1-naphthol-2 ($1\text{-}C_{10}H_6OH(2)N=NC_6H_5$). In these compounds formation of five- or six-membered rings through nitrogen would require the presence of NH absorption which was not observed. Absorption due to the presence of OH in 4-hydroxyazobenzene is shown in Fig. 2 for comparison in order further to emphasize the striking departure of the hydrogen bonded compounds from normal behavior. The geometrical configurations of these compounds are probably similar to that of salicylaldehyde anil (Fig. 1) with hydrogen bonds between the hydroxylic oxygen and the β-nitrogen atom leading to six-membered rings including hydrogen. It also follows that the R_2 group is *trans* with respect to R_1 which is of particular value since chemical evidence on this point is lacking.

Presence of hydrogen bonds in the above azo compounds is further of interest in that the question of their configuration has been the subject of much discussion in the recent literature. The argument has chiefly centered upon phenylazo-1-naphthol-2 about which three discordant points of view have been held. Chemical evidence led Pfeiffer and his co-workers[5] to suggest that a hydrogen bond (partial valence) is present. Kuhn,[15] however, challenged this interpretation and suggested rather that the compound exists as a "Zwitter ion." The character of the ultraviolet absorption spectrum, however, later led Kuhn and Bär[16] to retract the earlier speculations and to interpret their results on the basis of an equilibrium between a quinoid and azo form of the molecule



the equilibrium being predominantly on the quinoid side. Burawoy,[17] who had earlier suggested, with Markowitsch,[18] a quinoid formula challenged the evidence indicative of such an equilibrium. Absence of absorption in the region studied characteristic of the presence of OH or NH definitely eliminates this third possibility. Since resonance is probably an important factor in the formation of hydrogen bonds in compounds of this type, both of the above forms possibly contribute to the stable state of the molecule.

Presence of two hydrogen bonds between oxygen and nitrogen atoms within a single molecule is indicated by the absence of OH absorption in 2,2′-dihydroxyazobenzene ($2\text{-}HOC_6H_4N=N\text{-}C_6H_4OH\text{-}2$) and salicylaldehydeazine ($2\text{-}HOC_6H_4\text{-}$

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[14] Betti, *Gazz. chim. ital.*, **31**, II, 176 (1901); **33**, II, 28 (1903); Almed, Hemphill and Ray, THIS JOURNAL, **56**, 2403 (1934).

[15] Kuhn, *Naturwissenschaften*, **20**, 622 (1932).

[16] Kuhn and Bär, *Ann.*, **516**, 143 (1935).

[17] Burawoy, *ibid.*, **521**, 298 (1936).

[18] Burawoy and Markowitsch, *ibid.*, **503**, 180; 197 (1933); **504**, 71 (1933); **509**, 60 (1934).

CH=NN=CHC$_6$H$_4$OH-2). The geometrical requirements are interesting in both these cases but particularly so in the former which probably has the configuration shown in Fig. 1c, the atoms of the entire molecule being co-planar with a center of symmetry (x). In both compounds the R groups of R—X=N—R must have a *trans* configuration which gives a *trans trans* arrangement for salicylaldehydeazine as shown in Fig. 1d.

Factors limiting the number of hydrogen bonds to a particular atom are obscured by our general lack of understanding of the entire phenomenon. Experimental work, however, showed that at least two such bonds could form to oxygen;[1] either within a single molecule, 2,2′-dihydroxybenzophenone, or by association of two molecules, salicylic acid (2-HOC$_6$H$_4$COOH)$_2$. The steric factors introduced by the three directed valences of nitrogen unfortunately make it difficult to devise a suitable molecule for testing possible formation of two hydrogen bonds to a single nitrogen atom within a molecule. Examination of 2,2′-dihydroxybenzophenoneoxime acetate (2-HOC$_6$H$_4$C(=NOCOCH$_3$)C$_6$H$_4$OH-2) and 2,2′-dihydroxybenzophenone - α - methyl - α - phenylhydrazone (2-HOC$_6$H$_4$C(=NNCH(C$_6$H$_5$))C$_6$H$_4$-OH-2) showed that both compounds gave absorptions that probably are to be associated with the presence of OH groups (Fig. 2). For neither substance, however, does the molal absorption exceed that given by normal phenolic compounds containing single OH groups and that of the latter compound is extremely low. If a hydrogen bond is formed in 2,2′-dihydroxybenzophenoneoxime acetate, then the geometry of the molecule is probably that shown in Fig. 1f, the ring R$_2$ being forced out of the plane of the figure by the proximity of the —OCOCH$_3$ group. Thus the molecule has a configuration similar to both the *syn* and *anti* forms of 2-hydroxybenzophenoneoxime acetate and would be expected to give an absorption similar to that of the non-hydrogen bonded form of this latter substance as was observed. The absorption of the α-methyl-α-phenylhydrazone derivative on the other hand is much less than that of the oxime acetate. This is possibly to be associated with the fact that while one of the —C$_6$H$_3$OH(R) groups must be *syn* with respect to the R$_2$(—NCH$_3$C$_6$H$_5$) substituent of R$_1$—C=N—R$_2$ the other can tend to form a hydrogen bond with the α nitrogen atom. The weak absorption naturally brings up the question of the limit dividing hydrogen bonded from non-hydrogen bonded compounds or possible gradations from one extreme to the other. The body of experimental evidence is not yet sufficient to permit of reasonable discussion of this point.

Measurements were made on a number of compounds in which hydrogen bond formation was not particularly expected. Among these was 2-hydroxybenzonitrile (2-HOC$_6$H$_4$CN) and this gave OH absorption as shown in Fig. 2. In this compound the nitrogen atom of the —C≡N group, note Fig. 1e, is so far from the OH group as to make impossible hydrogen bond formation within the molecule. Absorptions given by α- (m. p. 155°) and β- (m. p. 106°) benzoinphenylhydrazones are shown in Fig. 2. These compounds give absorptions near 6600 cm.$^{-1}$ which is to be expected from the presence of NH groups. However, additional absorption between 6600 and 7100 cm.$^{-1}$ is probably due to the presence of OH groups. Results obtained from α- and β-benzoinoxime acetates[1] and from 8-hydroxyquinoline[6] have been published previously. While all these compounds show complex absorption which is worthy of further analysis, it is sufficient for the present purpose to point out that they give considerable absorption in the OH region. A hydrogen bond to a nitrogen atom forming a five-membered ring including hydrogen is possible for all these compounds but apparently is not present in any of them.

Summary

Presence of hydrogen bonds in a number of *ortho* hydroxy aromatic compounds of the general type 2-HOC$_6$H$_4$X=NY, where X is nitrogen or carbon, and Y is carbon, nitrogen or oxygen was indicated by absence of infrared absorption associated with presence of hydroxyl groups. Formation of hydrogen bonds requires the HOC$_6$H$_4$ group to have a *trans* configuration with respect to Y and this is true for the oximes, hydrazones, substituted imides and azo compounds that were studied.

WASHINGTON, D. C. RECEIVED JULY 20, 1936

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

Concerning "β"-2,3,4,6-Tetraacetyl-*d*-glucose

BY S. B. HENDRICKS, O. R. WULF AND U. LIDDEL

During a general study of the absorption of organic compounds in the infra-red region of the spectrum in progress in this Laboratory, an attempt was made to obtain information about the structures of the sugar hydrazones and oximes. In the course of this work, which now does not hold much of promise, various acetylated hexoses and pentoses were prepared. Results of some observations, that started in a rather accidental manner, on β-2,3,4,6-tetraacetyl-*d*-glucose are described below.

Two different 2,3,4,6-tetraacetyl-*d*-glucoses are described in the literature and, in harmony with sugar nomenclature, are designated as α and β. The β-form, as prepared by Fischer and Delbrück,[1] melted at 117°, but later investigators, particularly Georg[2,3] using Fischer and Delbrück's method of preparation, obtained materials melting near 135° with somewhat more negative optical activities. Georg[2] concerned himself about these differences, accounting for the depressed melting points by presence of alkaline impurities from the melting point tubes. Actually more abstruse factors are present and further study shows that the differences in properties of the various preparations arise from admixture of two different molecular forms to which peculiar interest attaches because of the nature of their mutarotations.

Samples of "β"-2,3,4,6-tetraacetyl-*d*-glucose prepared after the method of Fischer and Delbrück gave, when crude, melting points between 118 and 128° and specific optical activities from +28 to +7° in ethyl alcohol. Melting points and optical activities were brought into agreement with the values found by Georg, m. p. 138°, $[\alpha]^{25}_{\mathrm{D}}$ −3.0°, by recrystallization from ether. Several samples of this recrystallized material (later referred to as Ia) after standing for two years had melting points near 120° and positive optical rotations. Recrystallization of the altered materials from ether changed them back into Ia. Change of Ia to this second form (later referred to as Ib) could also be effected by several days' heating in carbon tetrachloride or benzene solutions.

That the explanation for these observations is not simply the presence of impurities is best shown by the absorptions of the various materials in the infra-red region, 6000–7500 cm.$^{-1}$. Absorption due to the presence of OH groups is found near 7000 cm.$^{-1}$ [4] and since tetraacetylglucose contains only one OH group measurements in this region are particularly valuable for characterizing its possible molecular forms. According to the present technique measurements are made on carbon tetrachloride solutions, preferably about 0.02 molal, since it is undesirable to have RH groupings present in the solvent. Samples of the two forms of "β"-2,3,4,6-tetraacetyl-*d*-glucose gave the molal absorptions shown in Fig. 1, Ia showing two maxima and Ib a single maximum. Absorption curves for α-2,3,4-triacetyl-*d*-xylose and β-2,3,4,6-tetraacetyl-*d*-galactose are also shown in Fig. 1 in order that one unfamiliar with this type of measurement might have a more general basis for evaluating the work.

The specific optical activity of Ib in ethyl alcohol indicates that it might be a compound[5] containing three parts of Ia and one part of α-2,3,4,6-tetraacetyl-*d*-glucose. This possibility is not supported by the optical activity in chloroform and is definitely eliminated by the absorption data. It would not be possible to derive the absorption curve for Ib from any mixture, xIa + yI (hypothetical), with $x = y$ since then I (hypothetical) would have negative absorption values.

That Ia and Ib are strictly isomorphous is shown by the microscopic examination, the identity of their x-ray powder diffraction patterns, and by the fact that the transition in the solid state takes place without destruction of single crystals. This isomorphism suggests that the geometrical shapes of Ia and Ib are similar.

Thirteen or more reasonable forms can be suggested for the configurations of Ia and Ib; α and β on the 1 carbon atom, ortho acetate formation between the OH in the 1-position and the 2- or 3-acetyl group either of which might exist in *d*

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[1] Fischer and Delbrück, *Ber.*, **42**, 2779 (1909).

[2] Georg, *Helv. Chim. Acta*, **15**, 924 (1932).

[3] Note also Haworth, Hirst and Teece, *J. Chem. Soc.*, 1405 (1930).

[4] Wulf and Liddel, THIS JOURNAL, **57**, 1464 (1935).

[5] R. C. Hockett and C. S. Hudson, *ibid.*, **53**, 4454, 4455 (1931).

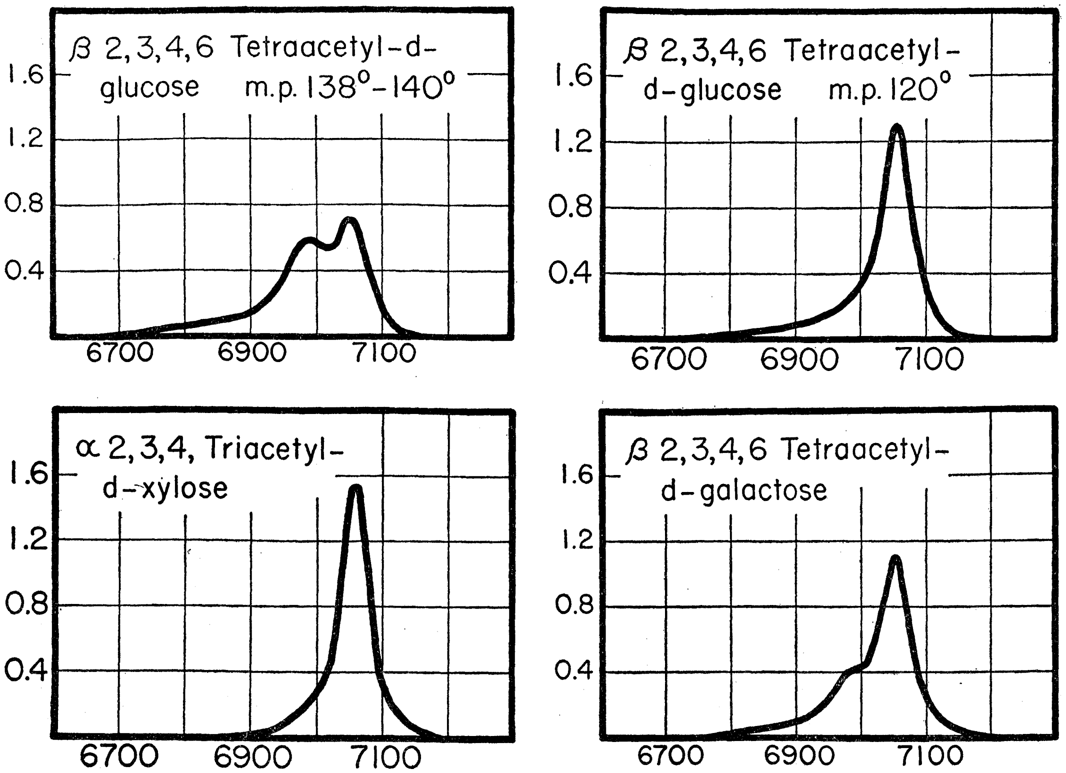

Fig. 1.—Molar absorption coefficients (ordinates) of some acetylated sugar derivatives in dilute carbon tetrachloride solution against frequency in wave numbers (abscissa).

or *l* forms, aldehydo and *cis* and *trans* isomers. Neither Ia nor Ib is probably the *α* form since it would have a considerably more positive optical activity.[6] Neither form gave the usual aldehyde tests nor did they react with diazomethane which was tried at the suggestion of Dr. G. E. Hilbert of this Laboratory. It was thought that an ortho acetate would be a sufficiently strong acid to be methylated by diazomethane. The presumptive conclusion then is that the materials are *cis* and *trans* ring isomers, the danger being that the chemical tests are not trustworthy.

"*β*"-2,3,4,6-Tetraacetyl-*d*-glucose as prepared after the method of Weizmann and Haskelberg[7] showed a rather peculiar behavior. The crude material was similar in optical activity and melting point to that prepared according to the method of Fischer and Delbrück but many recrystallizations from ether did not change it into Ia. Large crystals with intermediate melting points (125–131°) could be grown from ether solutions and various fractions from these solutions had the same characteristics. It would seem either that some minor impurity difficult to separate is present or that an obscure catalyst is needed.

Experimental

"*β*"-2,3,4,6-Tetraacetyl-*d*-glucose was prepared from acetobromoglucose and moist silver carbonate after the method of Fischer and Delbrück save that the acetone was evaporated after reaction for a few minutes at 0°. The crude residue was immediately washed with ether and recrystallized from dry ether; yield 40–60%. Crude crystalline materials (m. p.'s 105–120°) upon standing gave odors of acetic acid and could not then be recrystallized from ether.

A number of methods of purification were tried and some of these are indicated schematically below, starting materials, solvent, number of recrystallizations, and final melting points, optical activities, etc., being given: (a) crude, twice ethyl acetate, m. p. 122–125°, $[\alpha]^{20}_D$ +15° (1.3% in C_2H_5OH) calcd. for $C_{14}H_{20}O_{10}$: C, 48.25; H, 5.79. Found: C, 48.33; H, 5.94. (b) crude, twice amyl acetate, m. p. 125–128°, twice dry ether, m. p. 136–138°, $[\alpha]^{20}_D$ −3° (1.0% in C_2H_5OH); (c) crude, four times from dry ether, m. p. 136–138°, twice benzene, m. p. 138–140°, $[\alpha]^{20}_D$ $-4.2 \longrightarrow +75°$ after ten days (1.9% in C_2H_5OH) $+18.8° \longrightarrow +78°$ after ten days (1.7% in $CHCl_3$). Five grams of (c) was dissolved in 10 cc. of freshly distilled nitromethane and set aside in the ice box.

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(6) Schlubach and Wolf, *Ber.*, **62**, 1507 (1929), have prepared a form of 2,3,4,6-tetraacetyl-*d*-glucose having $[\alpha]_D$ +139.4° (in ethyl alcohol) and have designated it as *α*.

(7) Weizmann and Haskelberg, *J. Chem. Soc.*, 1023 (1935).

A single crystal weighing *ca.* 3 mg. separated during two days, m. p. 138°, the mother liquor was concentrated and the material was thrown out with ether. The final fraction had a melting point of 138°. Acetylation of (b) yielded pentaacetyl-*d*-glucose melting at 130°, unchanged upon mixing with an authentic sample.

Transformation of Material Melting at 138 to 120° Form.—Four separate samples of (b) above were set aside for two years at the end of which time they had the following melting points: (d) 114–118°, (e) 119–120°, (f) 118–124°, (f′) strong odor of acetic acid, material quite spongy. Sample (d) was recrystallized twice from ether and gave (g) with a melting point of 136–139°. Five grams of (d) kept at 60° in carbon tetrachloride solution for two days gave 1.0 g. of material melting at 120–120.5°, $[\alpha]^{20}_D$ +30° + ⟶ (1% in C_2H_5OH). Five grams of (c) heated, near the boiling point, for three days with 800 cc. of carbon tetrachloride upon concentration to 200 cc. gave 1.5 g. of crystals, m. p. 120–122° (h) $[\alpha]^{20}_D$ +32.6 ⟶ +79° after ten days (1.9% in C_2H_5OH) +40° ⟶ (1.6% in $CHCl_3$). Five grams of (c) refluxed with 50 cc. of benzene gave (j) about 1.0 g. of crystals, m. p. 114–117° $[\alpha]^{20}_D$ +36° (1.6% in C_2H_5OH) +46° (1.4% in $CHCl_3$). Sirups from (h) and (j) were not brought to crystallization upon long standing and repeated addition of (c) in 0.5-g. amounts.

Microscopic and X-Ray Examination.—Samples (b) and (c) gave well-formed crystals about 2.0 × 0.5 × 0.5 mm. from ether, with parallel extinction; α_D = 1.483, γ_D = 1.495, biaxial positive with large optic axial angle. Crystals from (g) and (h) had the same constants but differed in habit. Samples (d), (e) and (f) contained only crystals similar to (b) and (c) and showed uniform extinction. X-ray powder diffraction patterns of (j) and (c) were identical in all details (Cu K radiation).

Attempted Methylation of 138 and 120° Materials.—One gram ($^{1}/_{340}$ mole) of (c) was treated in 75 cc. of ether solution with $^{1}/_{25}$ mole of fresh diazomethane. No reaction was apparent and the yellow color remained after five days of standing. The ether was removed and after recrystallization 0.7 g. of material melting at 133–136° was obtained. One-half gram of (h) ($^{1}/_{680}$ mole) was treated in a similar manner in carbon tetrachloride solution without evident evolution of nitrogen. After five days the solution was evaporated but the residues could not be brought to crystallize.

"β"-2,3,4,6-Tetraacetylglucose after Weizmann and Haskelberg.[7]—Acetobromoglucose (115 g.) was treated as directed with sodium nitrite solution. After five days the acetone-rich phase was evaporated and a sirup was obtained which did not crystallize overnight but from which 10 g. of a material melting between 118–123° separated after two days' standing with ether. During a month in the presence of ether and ligroin 15 g. more of this material was obtained. These combined samples designated as (m) had $[\alpha]^{20}_D$ +14° (1.6% in C_2H_5OH) and +27° (2.4% in $CHCl_3$). The following results were obtained when purification was attempted, the number of crystallizations and melting points being indicated: one carbon tetrachloride (121–124°), two ether (125–128°), two hours of boiling ether (125–128°), residues from mother liquors (125–128°), twenty-four hours of boiling in absolute ether (fraction 1 (125–128°) fraction 2 (125–128°)), three hours of boiling in absolute ether with 0.1% acetic acid (125–128°), four hours of boiling with charcoal in ether (125–131°), absolute ether (128–131°). The final material was divided into two parts one of which was refluxed for two hours in ether solution with the silver carbonate–silver bromide residues from preparation (c) (124–131°) and the other was recrystallized from the mother liquors of (c) which contained about 10% as much of Ia (133–137°).

Infra-red Absorption.—Molal absorptions were measured for carbon tetrachloride solutions, usually about 0.018 molal, that were maintained near 60°. Preparation (c) gave the results shown in Fig. 1, the absorption being measured about one and one-half hours after preparation of the solution, and this slowly changed (at 60°) over a three-day period to that having a single maximum. Qualitative absorption data obtained from various samples are described below. Crude materials from the preparation after the method of Weizmann and Haskelberg gave absorptions corresponding to about equimolal mixtures of Ia and Ib, after many recrystallizations from ether the results were nearer those obtained for Ia but still indicated the presence of Ib. Samples prepared after the method of Fischer and Delbrück were examined after a single recrystallization from ether and were found to be quite pure Ia. A sample of Ia after standing for two years gave the absorption of Ib and after recrystallization from ether that of Ia.

We are indebted to Dr. R. T. Milner and Mrs. M. S. Sherman for the various microanalyses.

Summary

"β"-2,3,4,6-Tetraacetyl-*d*-glucose can be separated into two different molecular forms having different optical activities, spectral absorptions and melting points. The form having the higher melting point usually can be obtained by recrystallization from ether. Upon standing for a long time in the solid state it changes to the second form through a complete series of solid solutions.

WASHINGTON, D. C. RECEIVED AUGUST 13, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Single Bond Energies. IV. The Vapor Pressure of Hexaphenylethane

BY G. R. CUTHBERTSON AND H. E. BENT

The first three papers of this series[1] present data on the heat of oxidation and hydrogenation of certain organic free radicals. From these data conclusions are drawn regarding the strength of the C–C bond in the substituted ethane which gives rise to a free radical on dissociating.[2] If one makes certain assumptions regarding the strength of single bonds, one can calculate the effect of steric hindrance in the substituted ethane, which shows up as an increased heat of oxidation or hydrogenation. Without making any assumptions regarding the absolute values for single bond energies, one can compare various substituted ethanes and determine the relative significance of steric hindrance in passing from one to another. Finally one can estimate the significance of resonance energy in each case in promoting dissociation.

The above study led to the conclusion that both steric hindrance and resonance are very important factors in describing the behavior of free radicals. Furthermore these two factors may vary in passing from one free radical to another in such a way as largely to cancel each other and therefore give no evidence of their importance in a determination of the degree of dissociation alone.

The results heretofore reported have been obtained by a study of reactions involving solutions only. In order to draw conclusions free from uncertainty introduced by the presence of solvent, we determined to carry out experiments which would enable us to calculate the heat of oxidation and hydrogenation in the vapor state. Presumably these experiments would also give an answer to the time-honored question of the importance of the solvent in the whole phenomenon of the existence of free radicals. The experiments of Ziegler and Ewald[3] make it seem very probable that the solvent is not of prime importance since the free energy and the heat of dissociation are not greatly affected by a change in solvent. Nevertheless, a direct determination of the importance of the solvent is greatly to be desired.

The problem of determining the vapor pressure of a free radical is not easy. The instability of the compound precludes the possibility of working at elevated temperatures and the extremely low vapor pressure of even the simplest free radical at ordinary temperatures eliminates most methods of study. We have chosen a quartz fiber gage. Coolidge has greatly improved the design of this gage and has suggested its use in such problems as the one in hand.[4] From the vapor pressure curve can be calculated the heat of sublimation of hexaphenylethane. Similar measurements on triphenylmethane and on the peroxide formed in the oxidation of hexaphenylethane then give data which can be combined with the values obtained for the heat of hydrogenation and oxidation of hexaphenylethane in solution. We have already reported data on the heats of solution and therefore have a method for calculating the heat of hydrogenation and of oxidation in the vapor phase. From these data we may discover the effect of the solvent on the heat of the reaction and can estimate the effect on the free energy of dissociation.

As Coolidge has pointed out, it is not possible to determine with the quartz fiber gage the molecular weight of a vapor, some independent means of measuring the pressure being necessary for this purpose. It seemed barely possible, however, that a temperature and concentration might be available at which dissociation of the ethane was incomplete and the temperature dependence of the pressure would then give the second desired relation necessary for a determination of the molecular weight. This did not prove to be the case and we were therefore forced to devise additional experiments in order to solve this part of the problem. The most convenient determination seemed to be that of the vapor density. Unfortunately this part of the work is incomplete at the present time. Since the work has been temporarily interrupted it seems best to report progress to date.

Materials

The hexaphenylethane was part of the material used in the work reported in the first two papers of this series. The determination of the purity of the material by means

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[1] Bent, *et al.*, THIS JOURNAL, **58**, 165, 170, 1624 (1936).

[2] See also, *ibid.*, **57**, 1245 (1935); Pauling and Wheland *J. Chem. Phys.*, **1**, 362 (1933).

[3] Ziegler and Ewald, *Ann.*, **473**, 163 (1929).

[4] Coolidge, THIS JOURNAL, **45**, 1637 (1923).

of oxygen absorption indicated that any impurity was probably not more than 1%. The sample of triphenylmethyl peroxide was also prepared in connection with the oxidation of hexaphenylethane and was purified by recrystallization. The sample of triphenylmethane, after crystallization, melted at 92.1 ± 0.1°.

Experimental Procedure

The quartz fiber gage is of the type described and developed by Coolidge.[4] In order to simplify the calculations the fibers were made rather long (about 15 cm.) and small in diameter. The loss of energy in the fiber thus becomes so small as to be entirely negligible. When the gage is highly evacuated, many hours are required for the amplitude to die down to one-half while in the course of ordinary measurements the time required is from twenty to one hundred seconds. This justifies the neglect of the energy dissipated in the fiber.

The gage was calibrated by measuring the pressure of nitrogen with the quartz fiber gage and a McLeod gage. As a second method it was calibrated by measuring the pressure of mercury at various temperatures. The latter method agrees quite well with the former and has been used to calculate the constant "b" in the equation

$$\log p = \log \ln A_1/A_2 - \log b + {}^1/_2 \log T - {}^1/_2 \log M - \log t$$

in which p is the pressure expressed in millimeters of mercury, A_1 and A_2 are the amplitudes of the fiber, usually being about 10 and 5 mm., respectively. b is a constant characteristic of the fiber, M is the molecular weight, T is the absolute temperature and t is the time required for the fiber to die down from A_1 to A_2. The following table will indicate the reliability of the gage, the value of log b being 0.665. The values for the vapor pressure of mercury are calculated by the formula[5]

$$\log p = 8.99393 - 3250/T - 0.30 \log T - 0.00018\,T$$

in which p is expressed in millimeters.

TABLE I

THE VAPOR PRESSURE OF MERCURY

Temp., °C.	Pressure, mm.	
	Found	Calcd.
16.8	0.00097	0.00099
29.8	.00291	.00294
40.8	.00781	.00789
49.0	.0127	.0124
52.2	.0158	.0156
52.4	.0160	.0158

At the beginning of a run the gage and tube in which the sample is to be placed are baked at 400° for several hours while evacuating the apparatus to a pressure of 10^{-5} mm. The apparatus is then allowed to cool and the capsule containing the triphenylmethane broken and allowed to drop down into the apparatus. The tube containing the capsule and magnetic hammer is sealed off and the triphenylmethane twice sublimed to different parts of the tube with intermittent pumping to remove gases which might be liberated. In making a measurement the system is pumped, using a liquid air trap, to remove any foreign gas and then the system shut off from the pump and trap by means of a magnetically controlled ground-glass stopper. The fiber is set oscillating by means of a slight impulse given to the furnace in time with the natural frequency of the fiber. A micrometer eyepiece on a telescope serves to give any convenient change in amplitude, the time required for this change being noted with a stop watch. After taking a reading the system is again pumped at the same temperature and the pressure again determined.

The thermostat is an electrically heated air-bath with windows of thin mica and a blower within the thermostat to circulate the air. The reasons for choosing an air thermostat (which of course cannot be regulated easily with high precision) are to allow high temperatures for baking the apparatus, to avoid parallax in reading the gage, and to be able to change the temperature rapidly in the case of hexaphenylethane in order to avoid decomposition as much as possible.

In the case of hexaphenylethane and the peroxide it was not possible to sublime the material without undue decomposition. Probably some of the earlier determinations are in error on account of foreign gas. However, the final runs which are here reported indicate that the method of pumping just before each determination gave reproducible results which could be repeated with either a rising or falling temperature.

As was to be expected, decomposition took place with both the ethane and the peroxide. We therefore made careful measurements of the pressure over a period of time sufficiently long to enable us to extrapolate back to zero time for the true pressure. Fortunately the rate of decomposition is less than the rate of evaporation or this procedure would not have been possible. The pressure turns out to vary nearly as a linear function of the time so that it is possible to take the time required for the fiber to decrease in amplitude by a given amount as an accurate measure of the pressure at the mid-point of this time interval. This may readily be justified as follows. If we assume that the pressure is a linear function of the time and is represented by the expression

$$p = \alpha + \beta t$$

we can substitute this in the expression given for the gage[4] to give

$$\mathrm{d}A/A\mathrm{d}t = a + b\sqrt{M}\,(\alpha + \beta t)$$

Neglecting the constant "a" which we have shown to be justified for this gage we have on integration

$$1/t \ln A/A_0 = b\sqrt{M}\,(\alpha + \beta t/2)$$

which enables one to solve for the quantity in parentheses, namely, the pressure at a time half-way between the initial and the final time for the gage reading. These values for the pressure, when plotted against the total time, since the apparatus was closed from the pump, give a smooth curve which can be extrapolated back to zero time to give the pressure which would be obtained if no decomposition had taken place. The error introduced by this extrapolation is probably of the order of 10% in the pressure.

Discussion of Experimental Results

The experimental values for the pressure are given with the values calculated from the following equations. For triphenylmethane the pres-

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(5) *C. A.*, **28**, 4935 (1934).

sures can be expressed by the equation $\log p = -5260/T + 12.72$, which gives a value for ΔH of 24.1 ± 1.0 kcal. For hexaphenylethane the equation is $\log p = -5987/T + 12.85$, giving a value for ΔH of sublimation of 27.4 ± 1.5 kcal. For triphenylmethyl peroxide the equation is $\log p = -8259/T + 16.98$ and the value for ΔH is 37.8 ± 1.5 kcal.

Table II

Vapor Pressure of Triphenylmethane, Hexaphenyl ethane and Triphenylmethyl Peroxide

Temp., °C.	Pressure, mm.	
	Found	Calcd. by eq.
	Triphenylmethane	
26.5	0.000026[a]	0.0000148
46.0	.000181	.000174
46.5	.000199	.000186
46.6	.000201	.000188
59.35	.000773	.000796
60.8	.000980	.000937
75.2	.00444	.000420
75.6	.00459	.00436
87.6	.0123	.0139
90.5	.0146	.0181
	Hexaphenylethane, Run 1	
75.4	0.0000541	0.0000479
76.5	.0000633	.0000537
90.6	.000253	.000246
106.0	.001053	.001150
106.2	.001038	.001180
120.8	.00419	.00447
	Run 2	
92.7	.000283	.000309
93.6	.000306	.000339
105.8	.000997	.00112
106.0	.000935	.00115
76.8	.0000464	.0000550
121.8	.00512	.00490
	Triphenylmethyl peroxide	
119.8	0.000125	0.000091
129.3	.00038	.00029
129.8	.00029	.00031
140.3	.00122	.00102
140.4	.00077	.00102
151.4	.0044	.0034
161.0	.0089	.0091

[a] The experimental values at low pressures may be brought into agreement with those calculated from the equation by assuming the presence of foreign gas to the extent of about 10^{-5} mm.

We may now combine these values with those previously reported for the heat of oxidation and hydrogenation of solid hexaphenylethane to give solid product. We thus obtain a value for the heat of hydrogenation of gaseous hexaphenylethane of −19.7 kcal. and of oxidation of gaseous hexaphenylethane of −35.1 kcal. We may compare these values with the values to be predicted from single bond energies and thermal data of −8 and −4 kcal. The fact that the energy change for the reaction in the gaseous phase is so much more negative than that predicted, we take to be an indication of the steric hindrance in the molecule. The weakening of the C–C bond is therefore inferred to be equivalent to 12 kcal. if we consider the reaction of hydrogenation and 31 kcal. if we consider the oxidation. The agreement between these two figures is not satisfactory but at present we have no explanation.

The measurements on the rate of decomposition shed some light on the nature of this reaction. The reaction appears to be a unimolecular reaction with zero heat of activation, one of the products of the reaction being triphenylmethane. The rate of decomposition, as measured by the increase in pressure while the gage was open to the sample but closed from the pump, varied from $1\text{–}5 \times 10^{-3}$. However, as the concentration was varied by a factor of 200 and the temperature by 45° the variation in rate probably is not significant. Furthermore, the variation in rate was little more than the variation obtained in successive runs at a given temperature and when plotted gave no indication of a variation dependent upon the temperature. The product of the reaction was identified by a mixed melting point as triphenylmethane. Other products are also formed of high molecular weight and having a yellow color.

The rate of decomposition of the peroxide appeared to be much more reproducible and in fact a plot of the log of the rate constants against the reciprocal of the absolute temperature permits one to draw a smooth curve through the points. However, the curve has a maximum at about 140° and therefore we attach little significance to these data. The activation energy for the decomposition as determined from the lower part of the curve is roughly 30 kcal.

The data on the heat of vaporization of triphenylmethane and hexaphenylethane give a pretty conclusive answer to the question of dissociation in the vapor phase. The value for triphenylmethane is 24.1 and for hexaphenylethane is 27.4. We would expect the latter compound to have a greater heat of vaporization on account of its greater molecular weight. The most probable explanation of these figures is that hexaphenylethane is not dissociated in the vapor state and that the value 27.4 represents the true heat of vaporization of hexaphenylethane. The possibility of dissociation being negligible at the lower temperatures but becoming important at higher temperatures is ruled out on account of the straight line obtained by plotting log p against $1/T$. Dissociation would increase the pressure, the partial pressure of the undissociated material being that given by the sublimation pressure of the ethane at that temperature. Hence the curve would be convex toward the temperature axis. Almost complete dissociation of the ethane at all temperatures reported in this work would give a straight line plot but seems very improbable for two reasons. In the first place the total pressure would have to be the sublimation pressure of the ethane plus the pressure of the free radical. If the ethane were practically completely dissociated, this would lead to a total pressure of perhaps 100–1000 times that of the ethane, since the solid ethane would have to be in equilibrium with its vapor. This is not compatible with the observed pressure which is only 1/100 of that of triphenylmethane at about 90°. Furthermore, the slope of the curve would give in this case half the heat of dissociation plus half the heat of sublimation of the ethane. If we were to assume 10 kcal. for dissociation, this would lead to 50 kcal. for sublimation, which seems unreasonably large when compared with the value of 24.1 for triphenylmethane. The fact that hexaphenylethane has twice the molecular weight of triphenylmethane would not lead to doubling the heat of sublimation, as an increase of only 50% is observed in going from triphenylmethane to the peroxide.

If we assume that the dissociation is less than 10% at the lowest temperature, we can calculate that ΔF must be at least + 15 kcal., expressing concentrations in atmospheres. If there is an increase in entropy on dissociation, as seems very probable, the value for ΔH of dissociation in the vapor state may be considerably more than 15 kcal.

Summary

1. The vapor pressures of triphenylmethane, hexaphenylethane and triphenylmethyl peroxide have been measured by means of a quartz fiber gage.

2. The values calculated for the heat of vaporization of these compounds indicate that the C–C bond in hexaphenylethane in the vapor state is weaker than a normal C–C bond. The heat of dissociation, however, is probably greater than that found for hexaphenylethane in solution.

CAMBRIDGE, MASSACHUSETTS RECEIVED JULY 22, 1936

[CONTRIBUTION FROM THE CHEMICAL AND OCEANOGRAPHIC LABORATORIES OF THE UNIVERSITY OF WASHINGTON]

Equilibria in the Saturated Solutions of Salts Occurring in Sea Water. II. The Quaternary System $MgCl_2$–$CaCl_2$–KCl–H_2O at 0°

BY IVER IGELSRUD WITH THOMAS G. THOMPSON

No data on the quaternary system $MgCl_2$–$CaCl_2$–KCl–H_2O occur in the literature. This system is of importance in the study and utilization of the secondary salts in natural deposits originating from sea water. Data at lower temperatures are important to an adequate understanding of the geological processes to which the natural salts and their solutions are subject during cold winter periods.

A survey of the literature on the bounding ternary systems, together with data for their 0° isotherms, has been given in a previous paper.[1] The experimental procedure, the methods of purification of the salts, and the methods of chemical analysis used in the study of the quaternary isotherm were the same as for the ternary systems. Samples of the saturated solutions and solid phases in equilibrium were taken for chemical analysis as described. The time found sufficient for the attainment of equilibrium in the quaternary system was from twelve to fifteen hours as compared with eight to ten hours for the ternary solutions.

The results of the chemical analyses for solutions and residues are given in Table I. The data for the saturated solutions are depicted graphically in Figs. 1, 2 and 3. Figures 4 and 5 illustrate the methods used for the identification of the solid phases.

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[1] Iver Igelsrud and T. G. Thompson, THIS JOURNAL, **58**, 318 (1936).

TABLE I

THE QUATERNARY SYSTEM $MgCl_2$–$CaCl_2$–KCl–H_2O AT 0°

Point or line	Solution weight, %			Residue weight, %			Solution mol., %			Solid phases
	$MgCl_2$	$CaCl_2$	KCl	$MgCl_2$	$CaCl_2$	KCl	$MgCl_2$	$CaCl_2$	K_2Cl_2	
E	...	37.27	1.96	...	...	...	...	9.02	0.35	$CaCl_2 \cdot 6H_2O$ + KCl
EI	1.33	35.53	1.93	...	...	...	0.37	8.55	.35	$CaCl_2 \cdot 6H_2O$ + KCl
	1.64	35.10	1.91	1.57	36.56	5.73	0.46	8.43	.34	$CaCl_2 \cdot 6H_2O$ + KCl
	2.53	34.62	1.88	...	...	...	.71	8.35	.34	$CaCl_2 \cdot 6H_2O$ + KCl
	2.62	34.21	1.86	...	...	...	.73	8.22	.33	$CaCl_2 \cdot 6H_2O$ + KCl
	2.68	34.70	1.86	...	...	...	.76	8.39	.34	$CaCl_2 \cdot 6H_2O$ + KCl
	2.98	33.84	1.82	...	...	...	.83	8.12	.33	$CaCl_2 \cdot 6H_2O$ + KCl
I	3.27	33.52	1.85	...	...	...	.92	8.04	.33	$CaCl_2 \cdot 6H_2O$ + KCl + carnallite
	3.34	33.26	1.85	...	...	...	.93	7.96	.33	$CaCl_2 \cdot 6H_2O$ + KCl + carnallite
	3.30	33.40	1.92	8.96	25.55	16.15	.92	8.01	.34	$CaCl_2 \cdot 6H_2O$ + KCl + carnallite
Mean	(3.30	33.39	1.87)				(.92	8.01	.33)	
IF	6.55	27.66	2.02	12.20	18.43	18.66	1.78	6.44	.35	KCl + carnallite
	10.37	21.13	2.10	14.56	12.89	21.91	2.72	4.76	.35	KCl + carnallite
	14.19	16.05	2.13	16.24	10.33	22.30	3.67	3.56	.35	KCl + carnallite
	15.32	14.55	2.15	...	...	...	3.94	3.21	.35	KCl + carnallite
	19.17	9.33	2.15	...	...	...	4.85	2.03	.35	KCl + carnallite
	20.54	7.65	2.15	21.36	4.74	19.85	5.18	1.65	.35	KCl + carnallite
F	26.78	...	2.13	...	...	...	6.63	..	.34	KCl + carnallite
IH	3.68	32.99	1.88	5.18	32.25	10.49	1.03	7.91	.34	$CaCl_2 \cdot 6H_2O$ + carnallite
	8.13	28.75	0.59	...	...	...	2.24	6.78	.105	$CaCl_2 \cdot 6H_2O$ + carnallite
	11.77	25.33	.32	...	...	...	3.23	5.96	.055	$CaCl_2 \cdot 6H_2O$ + carnallite
	23.77	13.99	.031	20.14	20.18	5.27	6.52	3.29	.0055	$CaCl_2 \cdot 6H_2O$ + carnallite
H	23.95	14.08	.032	23.21	17.46	4.50	6.59	3.32	.0055	$CaCl_2 \cdot 6H_2O$ + carnallite + $MgCl_2 \cdot 6H_2O$
	23.91	13.99	.027	21.78	19.24	3.30	6.57	3.30	.0047	$CaCl_2 \cdot 6H_2O$ + carnallite + $MgCl_2 \cdot 6H_2O$
	24.05	14.05	.050	...	...	...	6.62	3.32	.0089	$CaCl_2 \cdot 6H_2O$ + carnallite + $MgCl_2 \cdot 6H_2O$
Mean	(23.97	14.04	.036)				(6.59	3.31	.0064)	
HG	29.30	6.96	.021	...	...	...	7.88	1.61	.0036	$MgCl_2 \cdot 6H_2O$ + carnallite
	29.29	6.79	.036	...	...	...	7.86	1.56	.0061	$MgCl_2 \cdot 6H_2O$ + carnallite
G	34.68	...	.024	...	...	...	9.13	..	.0040	$MgCl_2 \cdot 6H_2O$ + carnallite
HD	23.88	14.01	.019	21.21	20.45	0.001	6.56	3.30	.0034	$MgCl_2 \cdot 6H_2O$ + $CaCl_2.6H_2O$
D	23.94	14.00	...	...	...	...	6.58	3.30	....	$MgCl_2 \cdot 6H_2O$ + $CaCl_2.6H_2O$

The Quaternary Isotherm.—The quaternary isotherm requires a three-dimensional coördinate system for a complete representation of the compositions of the saturated solutions. It is schematically so represented in the conventional regular tetrahedron in Fig. 1. The usefulness of this figure is impaired because it is impossible to represent a three-dimensional figure on a flat sheet of paper in a manner so that quantitative measurements may be made upon it. It is necessary, therefore, to resort to projections. The most simple method of projection of the tetrahedral figure is that suggested by Schreinemakers.[2] One of the vertices, the H_2O vertex, is made the origin of a coördinate system. The three edges radiating from this vertex and making angles of 60° with one another, are the magnesium, calcium and potassium chloride axes. The three planes determined by the three pairs of axes are the coördinate planes of the system. In the coördinate planes are represented the ternary equilibria in the usual manner. Projections of the quaternary equilibria upon the coördinate planes are made parallel to the axes. For example, a quaternary point representing 30% $MgCl_2$, 15% $CaCl_2$, 2% KCl, and (100 − 30 − 15 − 2)% H_2O projected parallel to the $CaCl_2$-axis appears on the $MgCl_2$–H_2O–KCl plane at 30% $MgCl_2$ and 2% KCl; projected parallel to the $MgCl_2$-axis, it appears on the $CaCl_2$–H_2O–KCl plane at 15% $CaCl_2$ and 2% KCl. Two of the three possible projections are sufficient to determine the point completely.

Figures 2 and 3 present, in this way, the complete data for the saturated solutions of the quaternary isotherm. The space figure has been projected upon the two planes $MgCl_2$–H_2O–KCl and $CaCl_2$–H_2O–KCl. Because some of the saturation surfaces, notably that of $MgCl_2 \cdot 6H_2O$, are small it was necessary for the sake of clearness to make the scale on the KCl-axis three times as great as on the other two axes.

The most striking feature of this system is the smallness of the area representing solutions satu-

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(2) F. A. H. Schreinemakers, *Z. physik. Chem.*, **59**, 641 (1907).

rated for $MgCl_2 \cdot 6H_2O$. The same characteristic of magnesium chloride solutions is noted in the quaternary system that was found in the ternary system, namely, that carnallite is almost wholly insoluble in solutions saturated for $MgCl_2 \cdot 6H_2O$. Calcium chloride solutions dissolve, relatively, more carnallite.

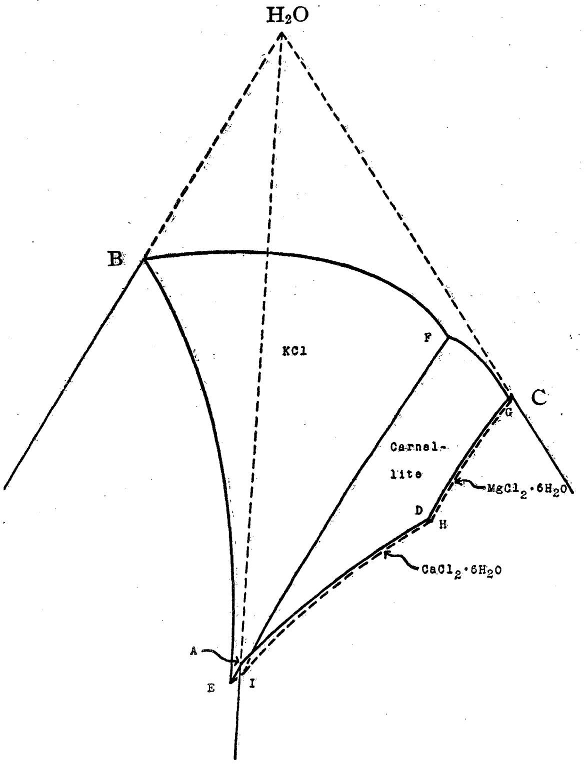

Fig. 1.—The system $MgCl_2$–$CaCl_2$–KCl–H_2O at 0°. Only the upper portion of the tetrahedron is shown.

The saturation surface for $CaCl_2 \cdot 6H_2O$ is also small but not so small as that for $MgCl_2 \cdot 6H_2O$. The chief reason for the larger area is undoubtedly the fact that calcium and potassium chlorides, at this temperature, form no hydrated double salt similar to carnallite. Menge,[3] working with the fused salts, obtained an anhydrous calcium carnallite, $CaCl_2$–KCl, which melted at 754° and formed eutectics at 641 and 597°.

The solubility of potassium chloride in solutions saturated for $CaCl_2 \cdot 6H_2O$ is but slightly less than in solutions saturated for carnallite. In going from F to I along the KCl–carnallite curve, the solubility drops only about 0.3%. The effect of the addition of calcium chloride to carnallite solutions on this curve is, however, quite marked. In proceeding along FI the magnesium chloride in solution is exchanged for calcium chloride and precipitates as carnallite. As shown by the data in Table I, the magnesium chloride content is decreased from 26.7% at F to 3.3% at I by successive additions of calcium chloride. When the magnesium chloride content of the solution falls below 3.3% or the calcium chloride content rises above 33.4%, carnallite cannot exist as a solid phase and KCl and $CaCl_2 \cdot 6H_2O$ become the only two possible solid phases.

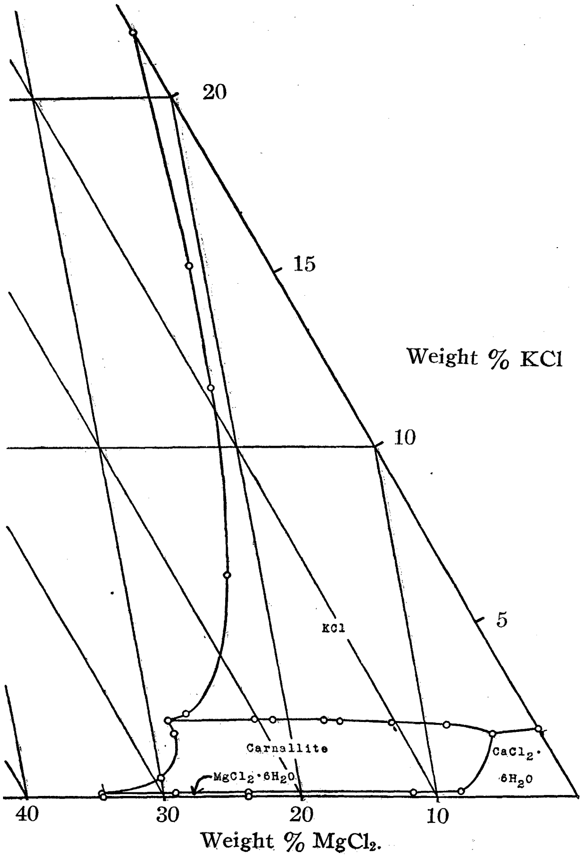

Fig. 2.—The quaternary isotherm projected upon the plane $MgCl_2$–H_2O–KCl.

In discussing the system $MgCl_2$–KCl–H_2O,[1] it was remarked that all solutions saturated for carnallite were incongruently saturated. The same may be said of all saturated carnallite solutions in the quaternary system. The ratio of potassium chloride to magnesium chloride, by weight, in carnallite is the ratio of their molecular weights, 74.56/95.23 = 0.783. All points on the curve FI which borders on the carnallite saturation surface, have lower ratios than this. The point I thus represents an incongruently saturated solution in equilibrium, in the presence of an ex-

(3) O. Menge, *Z. anorg. Chem.*, **72**, 162 (1911).

cess of solid potassium chloride, with the three solid phases $CaCl_2 \cdot 6H_2O$, KCl and carnallite. The point H, on the other hand, represents a congruently saturated solution in equilibrium with $CaCl_2 \cdot 6H_2O$, carnallite and $MgCl_2 \cdot 6H_2O$. The composition of the solution at I is 3.30% $MgCl_2$, 33.39% $CaCl_2$ and 1.87% KCl; the composition of that at H is 23.97% $MgCl_2$, 14.04% $CaCl_2$ and 0.035% KCl.

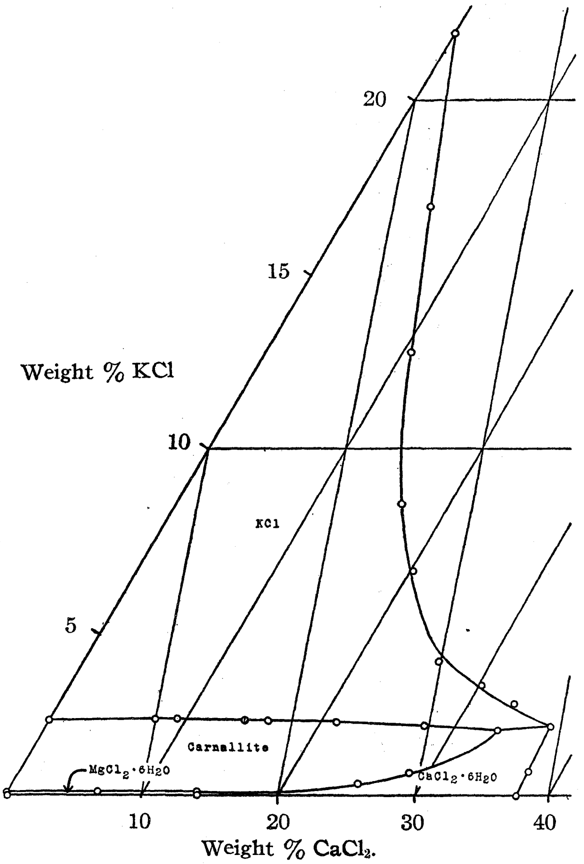

Fig. 3.—The quaternary isotherm projected upon the plane $CaCl_2$–H_2O–KCl.

A point of interest in connection with this isotherm is the water content of some of the solutions. At the monovariant point of the 0° isotherm of the system $CaCl_2$–KCl–H_2O, the percentage of water was 60.77.[1] At I, it is 61.44 and at H, 61.95. From the motion observed along the curves, on successive additions of the fourth component, during the experimental work, the point H appeared to be the isothermal drying-up point of the solutions. This anomaly disappears when the percentages are computed on a molecular basis. The molecular percentages of water are 90.63, 90.74 and 90.09, respectively. The difference between the values for the first two points, 0.11%, is of no significance since it lies within the experimental error of the analytical determinations.

The Quaternary Solid Phases.—The Schreinemakers residue method, since originally published in 1893, has been widely used for the identification of unknown phases in ternary systems. This method was later extended by the discoverer[2] to quaternary systems, but this extension has received no notice in the more common treatises on phase rule methods. It was used in the present investigation and, since it is a valuable tool, its application is described somewhat in detail.

In applying it to a quaternary system, it need only be remembered that where the single solid phase occurs along a saturation curve in the ternary system, it occurs on a saturation surface in the quaternary system. If the compositions of two or more saturated solutions of this surface and the compositions of the corresponding residue samples are determined, conjugation lines are obtained which intersect at the point representing the composition of the unknown phase. The method may be used also to show the simultaneous presence of two or more solid phases in contact with a saturated solution. This is of great convenience in experimental work because it furnishes an absolute check on the phases present and eliminates much uncertainty when working with complicated systems.

In the three component system $CaCl_2$–KCl–H_2O, Fig. 4, for example, a series of conjugation lines, EE′, EE″ and EE‴, determined by the residue method, radiate from the point E which represents saturation for the two salts $CaCl_2 \cdot 6H_2O$ and KCl. The points on any one of these lines represent mixtures of the saturated solution with various amounts of the two coexisting solid phases. Each of these lines, since it lies in the same plane, intersects the line joining the points corresponding to the compositions of the two salts $CaCl_2 \cdot 6H_2O$ and KCl and thus shows the presence of both of these solid phases. Now consider this system and its relation to the four-component system. If a small amount of magnesium chloride be added to the solution, the resultant solution has a composition represented by a point on the quaternary line EI. But the solid phases are still KCl and $CaCl_2 \cdot 6H_2O$. If the composition of the residue sample is represented by the point a′, the conjugation line aa′ must intersect the line KCl–$CaCl_2 \cdot 6H_2O$ in the point a″.

If enough magnesium chloride is added so that the composition of the solution becomes that at the point I, a third solid phase, carnallite, separates. Because carnallite contains magnesium chloride, the composition of the mixture of solid phases can now no longer have a value lying on the line KCl–$CaCl_2·6H_2O$. While the composition of a mixture of three substances cannot be represented on a straight line, it can be represented in a triangle each of whose vertices corresponds to 100% of one of the substances. In the present case, the triangle KCl–carnallite–$CaCl_2·6H_2O$ is the one required. The appearance of carnallite shifts the foot of the conjugation line to I′′ for a residue sample whose composition corresponds to I′ and to K′ for one whose composition corresponds to K.

In order to show the simultaneous presence of two or more solid phases in a four-component system, it is thus only necessary to find the point of intersection of a given conjugate line with the plane determined by the three phases concerned. If the intersection falls in the interior of the triangle determined by the three solid phases, it shows that all three are present; if it falls on the edge of the triangle, that is, on a line joining the points representing the compositions of two solid phases, it shows that the two phases determining this line are present and that the third phase is absent.

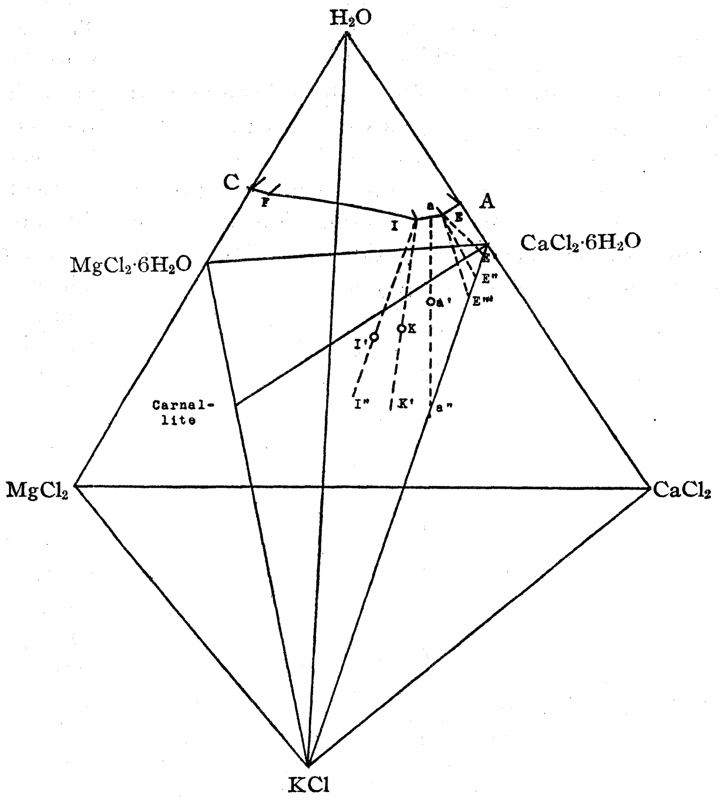

Fig. 4.—Diagram illustrating the method for determining the simultaneous presence of two and of three solid phases.

The intersection of a conjugation line with a plane may be found either analytically or graphically. The analytical problem is equivalent to finding the point of intersection of three planes, two of which pass through the conjugation line. This is done by solving the equations of the three planes simultaneously for the coördinates, or percentages of the three salts, at the point of intersection. The analytical method has, as far as is known to the authors, never been described in the chemical literature.

The analytical process will be illustrated by finding the point of intersection of the plane KCl–carnallite–$CaCl_2·6H_2O$ with the conjugation line from the point I in Fig. 4. The necessary data are taken from Table I. The saturated solution contains 1.92% KCl, 33.40% $CaCl_2$ and 3.30% $MgCl_2$ and the residue sample 16.15% KCl, 25.55% $CaCl_2$ and 8.96% $MgCl_2$. These values furnish two points. Since three points determine a plane, two more are needed, one for each of the two planes through the conjugation line. The points representing pure KCl and pure $CaCl_2·6H_2O$ are convenient. The amounts of the three salts in KCl are 100% KCl, 0% $CaCl_2$ and 0% $MgCl_2$ and in $CaCl_2·6H_2O$ are 0% KCl, 50.64% $CaCl_2$ and 0% $MgCl_2$. The equation of the plane through the conjugation line and the KCl corner of the tetrahedron, in determinant form, is then

$$\begin{vmatrix} x & y & z & 1 \\ 100 & 0 & 0 & 1 \\ 1.92 & 33.40 & 3.30 & 1 \\ 16.15 & 25.55 & 8.96 & 1 \end{vmatrix} = 0$$

where x = % KCl, y = % $CaCl_2$ and z = % $MgCl_2$. Upon expanding this determinant, there is obtained the equivalent equation

$$x + 2.801y + 1.371z - 100 = 0.$$

The equation of the plane through the conjugation line and the point representing $CaCl_2·6H_2O$, obtained in a similar manner, is

$$x - 0.5036y - 3.213z + 25.50 = 0.$$

That through the points representing all three solid phases is

$$x + 1.975y + 2.135z - 100 = 0.$$

Solving the three equations simultaneously there are obtained as the coördinates of the point of intersection, I″

$$x = 35.0\%\ \text{KCl}$$
$$y = 15.2\%\ \text{CaCl}_2$$
$$z = 16.4\%\ \text{MgCl}_2$$

The projections of the point I″ have been plotted in Fig. 5 as e and e′. It lies well within the triangle determined by the three solid phases.

The points of intersection, with their proper planes, of the remaining conjugation lines, for which analytical values are given in Table I, were obtained by similar procedures.

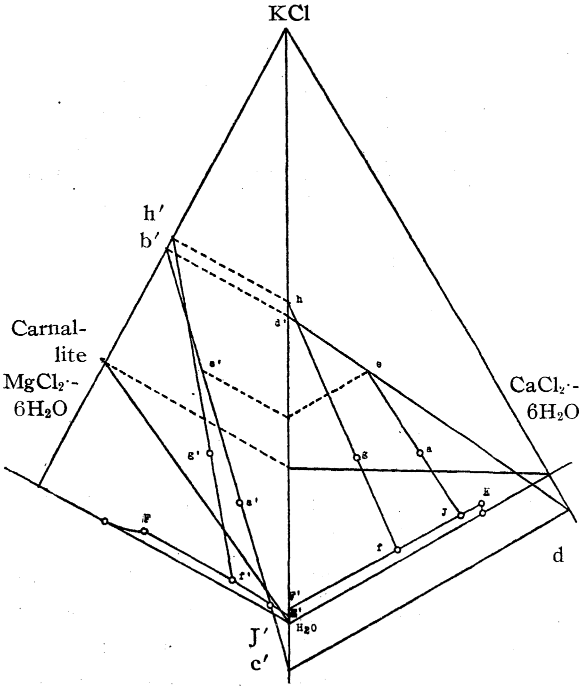

Fig. 5.—Method for determining the solid phases by projection of the conjugation lines upon the sides of the tetrahedron.

It usually involves less labor to obtain the points of intersection graphically as done by Schreinemakers. The points determined by chemical analysis are projected upon two sides of the tetrahedron taken as coördinate planes. The projections of the conjugation line for each solution and residue are drawn through the proper points and intersection with the plane determined by the three solid phases found by the methods of ordinary descriptive geometry.

The graphical method is illustrated to scale in Fig. 5 for the point I and for the line FI of Fig. 4. At I the solid phases are supposed to be KCl, carnallite and $CaCl_2 \cdot 6H_2O$ and on FI, carnallite and KCl. If the data used in illustrating the analytical method are plotted, the two projections of the point I are J and J′ and of the point corresponding to the composition of the residue, a and a′. The two projections of the conjugation line are thus Ja and J′a′. The line J′a′ is extended to meet the line KCl-carnallite in b′ and its projection in the KCl-axis in c′. From b′, the line b′d′ is drawn parallel to the $MgCl_2$-axis and from c′, the line c′d parallel to the $CaCl_2$-axis. If now d is joined to d′, the line dd′ cuts the line Ja in one projection, e, of the point of intersection sought. The other projection is found as indicated in Fig. 5 at e′. Since e and e′ lie well within the respective projections of the triangle KCl–carnallite–$CaCl_2 \cdot 6H_2O$, it is shown that all three of these phases are in contact with the solution at I. It is to be noted that the point found graphically coincides with the point previously found analytically.

The intersection for a conjugation line originating on the line FI, along which two solid phases exist, is obtained even more simply. On FI the composition of a solution was 10.37% $MgCl_2$, 21.13% $CaCl_2$ and 2.10% KCl and of the corresponding residue sample 14.56% $MgCl_2$, 12.89% $CaCl_2$ and 21.91% KCl. The projections of the point for the solution are f and f′ and for the residue g and g′. The projections of the conjugation line are the lines fg and f′g′. The line f′g′ is extended to meet the line carnallite–KCl in h′ and the line fg to meet its projection in the KCl-axis in h. But h is the projection in the KCl-axis of the point h′. This is readily seen because the line hh′ lies parallel to the $MgCl_2$-axis. The conjugation line thus meets the line KCl–carnallite and shows the presence of both of these solid phases and absence of the third phase $CaCl_2 \cdot 6H_2O$.

The application of the Schreinemakers method of residues to other systems whose phases, in addition to the vapor phase, are all liquids, all solids, or combinations of liquids and solids, differs only in the details of application. It may further be extended, although it never has been, to systems containing metathetical elements. A quaternary isotherm of this type is commonly represented in a regular pyramid with a square base. If the diagonal planes of this pyramid are made the projection planes, the foregoing methods are readily applied.

Summary

1. The isotherm for the quaternary system $MgCl_2$–$CaCl_2$–KCl–H_2O has been determined at 0°.

2. The solid phases occurring in the quaternary isotherm are KCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$ and the double-salt hydrate carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$.

3. The isotherm at 0° is characterized by the extreme insolubility of potassium chloride and of carnallite in solutions saturated for magnesium chloride. This was noted previously[1] in studying the 0° isotherm of the system $MgCl_2$–KCl–H_2O. Both potassium chloride and carnallite are more soluble, within a restricted concentration range, in magnesium chloride solutions containing calcium chloride. Carnallite, however, cannot exist at 0° in contact with solutions containing less than 3.3% magnesium chloride or more than 33.4% calcium chloride.

4. All quaternary solutions saturated for carnallite are incongruently saturated.

5. Schreinemakers' method of residues was used for identification of the solid phases in this isotherm.

6. A method is suggested for extending the method of residues to quaternary systems containing metathetical components.

SEATTLE, WASHINGTON RECEIVED APRIL 23, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Solubility of Cupric Oxide in Alkali and the Second Dissociation Constant of Cupric Acid. The Analysis of Very Small Amounts of Copper

BY LEON A. MCDOWELL AND HERRICK L. JOHNSTON

The blue solutions produced when either cupric oxide or cupric hydroxide is treated with alkali have been objects of investigation[1-3] for more than a century. They were thought by some investigators[2] to be colloidal but have been shown, more recently, to represent true cases of chemical solution.[3] The most decisive work in support of this conclusion is that of Müller,[3] who obtained reproducible values of solubility and determined solubility curves, both for the oxide and for the hydroxide, between five normal and about twenty normal sodium hydroxide concentrations. At about fifteen normal alkali maxima were obtained in the solubility curves and at concentrations above these maxima the stable solid phase consisted of dark blue crystals whose analysis corresponded to the formula Na_2CuO_2. Aldridge and Applebey[4] have identified similar copper salts of the alkaline earths.

Müller observed that the solubility of the hydroxide exceeds that of the oxide several fold, which represents a case of metastable equilibrium since the hydroxide solubility diminishes with time and, simultaneously, the solid phase is converted to what appears to be a solid solution of hydroxide with oxide. The oxide solubility does not change with time. An apparently permanent difference between the solubility of the oxide and that attained, after several days, by the hydroxide is not explained.

The present investigation, at lower alkalinities than those employed by Müller, was carried out to obtain additional information on the nature of the copper-bearing ions present in solution and to determine dissociation constants of cupric acid.

Experimental

The method employed was similar to that followed by Johnston, Cuta and Garrett[5] in a similar study with silver oxide, and the solubility apparatus and general manipulations were the same.

Cupric oxide was prepared by dropping 0.06 *N* solutions of copper sulfate and of potassium hydroxide, simultaneously, into an initial 500 cc. of boiling conductivity water in a Pyrex reaction vessel. The entire process including subsequent washings (15 to 20 in number) was carried out in an atmosphere of nitrogen. The wash water gave no test for sulfate ion (barium chloride test) after seven or eight washings and the final product gave no test for sulfate when dissolved in nitric acid and the solution diluted.

Potassium hydroxide at concentrations below 1 *N* was prepared from pure amalgams in the manner described by Johnston, Cuta and Garrett. Potassium and sodium hydroxides at concentrations above 1 *N* were prepared from solutions of the reagent quality hydroxides by the addition

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(1) Proust, *J. Phys.*, **59**, 395 (1804); Low, *Z. anal. Chem.*, **9**, 463 (1870); Donath, *ibid.*, **40**, 137 (1901).

(2) Fischer, *Z. anorg. Chem.*, **40**, 39 (1904); Chatterji and Dhar, *Chem. News.*, **121**, 253 (1920).

(3) (a) Creighton, THIS JOURNAL, **45**, 1237 (1923); (b) Melbye, *Vetenskapsakad, Nobelinst*, **4**, No. 8 (1922); (c) E. Müller, *Z. physik. Chem.*, **105**, 73 (1923).

(4) Aldridge and Applebey, *J. Chem. Soc.*, **121**, 238 (1922).

(5) H. L. Johnston, F. Cuta and A. B. Garrett, THIS JOURNAL, **55**, 2311 (1933).

of sufficient barium hydroxide to precipitate the carbonate.

Salts, except potassium ferrocyanide as noted later, were twice recrystallized from "reagent quality" products.

Conductivity water which even after several weeks' storage had a conductivity no higher than 2 × 10^{-6} mho was employed in the preparation of all solutions and in the washing and purification of materials.

Equilibrium was approached both from the cold and from the hot side. For approach from the cold side samples were agitated at 25 ± 0.01° for from fourteen to fifty days. For approach from the hot side samples were first agitated at 45° for four days, then transferred to the 25° thermostat for an additional fourteen days. The shorter period appeared adequate in every instance. Seven days were allowed for *sedimentation*. A portion of the clear solution was then siphoned from each flask and *filtered* through a No. 1 sintered Jena glass filter, preparatory to analysis for total alkali and for copper. The first portions of the solutions which passed through the filter were discarded.

Analytical Procedure

After testing various methods which have been used for the determination of small concentrations of copper, including colorimetric methods and the polarigraph, electrometric titration with potassium ferrocyanide as precipitant was employed.

There have been several previous attempts to determine copper electrometrically but none were entirely satisfactory for very small amounts. Dutoit and von Weisse[6] concluded that a copper electrode is unsuitable for cupric copper because of irregularities in the change of its potential. By using a polarized platinum electrode they were able to titrate 0.01 *N* copper solutions with potassium sulfide, potassium ferrocyanide or sodium thiosulfate to a precision of about 1% but the low sensitivity of the method and the deposit of some copper by the polarizing current render the method unsuitable for determinations in which the copper concentration falls as low as 1 × 10^{-6} *M*. Titration as cuprous thiocyanate, with a copper electrode,[7] or reduction with an excess of titanous chloride followed by back titration with either potassium dichromate or potassium bromate,[8] is not sufficiently accurate for our requirements.

After unsatisfactory trials of a copper electrode in titrations with either sodium sulfide or potassium ferrocyanide, in which our experience was similar to that of Dutoit and von Weisse, we substituted an electrode of platinum foil. With sodium sulfide results were still unsatisfactory due to the fact that the end-point depended to too great an extent on the *p*H value of the solution. With ferrocyanide as precipitant,[9] and a technique similar to that employed by Johnston, Cuta and Garrett, high sensitivity and good accuracy were obtained. Titration of 10 cc. of a standard copper solution 6 × 10^{-4} *M* in cupric ion with potassium ferrocyanide which had a copper equivalence of 1 × 10^{-6} mole of copper per cc. led to an inflection of from 10 to 16 mv. per drop (0.02 cc.) at the equivalence point and the end-point could usually be located to within one or two drops. It was found best to clean the electrode with pumice after each titration; otherwise the sensitivity was continuously reduced. The position of the end-point was independent of the dimensions of the platinum foil (absence of adsorption). Titrations were carried out in a 250-cc. beaker which was connected by a bridge of potassium nitrate set in agar-agar to a calomel half cell. The copper solution was made just acid to methyl orange indicator. Readings of electromotive force were taken at three-minute intervals and near the end-point the standard ferrocyanide solution was added one drop at a time from a microburet.

The ultimate standard for the determination of copper was an approximately 0.06 *M* solution of copper sulfate which was analyzed for copper by electrolytic deposition and then diluted one hundred fold. Potassium ferrocyanide solutions, of copper equivalences varying from 1 × 10^{-6} to 6 × 10^{-8} mole of copper per cc. were prepared from Baker and Adamson reagent quality potassium ferrocyanide without recrystallization. These were standardized by titration against the standard copper solutions under conditions closely identical with those employed in the analysis of samples (*i. e.*, acidity, salt concentrations, total volume, temperature, etc.).

Total alkalinity was determined by titration with standard sulfuric acid to the first sharp color change with methyl orange.

Our experience with the use of the ferro–ferricyanide couple for the titration of copper differs from that of Müller and Takegami,[10] who found no sharp inflection in the e. m. f. curve and concluded that the difficulty lay in some secondary reaction such as

$$3Cu_2Fe(CN)_6 + K_4Fe(CN)_6 = 2K_2Cu_3Fe_2(CN)_{12}$$

We found, in titrations which employed weighed amounts of the reagent quality potassium ferrocyanide, that the sharp break in the e. m. f. curve came at a position within 5% of the stoichiometric value for the assumed formation of $Cu_2Fe(CN)_6$. This approximate 5% deviation was reproducible. With our method of standardization described above, this reproducible deviation from the stoichiometric end-point did not introduce error into the analyses.

The Solubility Data

The results obtained are given in the following tables in which all concentrations are expressed in moles per 1000 g. of water. These are also illustrated in the accompanying figure. Samples were always run in pairs to obtain approach to equilibrium both from the side of undersaturation and from that of supersaturation. In the tables, the data obtained with individual samples are shown separately[11] while, in the figures, the circles

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(6) Dutoit and von Weisse, *J. chim. phys.*, **9**, 578 (1911).

(7) Treadwell and Weiss, *Helv. Chim. Acta*, **2**, 694 (1919).

(8) Zintl and Wattenberg, *Ber.*, **55**, 3366 (1922).

(9) The electromotive force of the cell depends on the ferro-ferricyanide couple. Bichowsky [*Ind. Eng. Chem.*, **9**, 668 (1917)] obtained success with the use of the ferro–ferricyanide couple in the titration of zinc. *Cf.* also Kolthoff and Verzijl, *Rec. Trav. Chim.*, **43**, 380 (1924).

(10) Müller and Takegami, *Z. anal. Chem.*, **73**, 284 (1928).

(11) Alkalinities were separately determined for each sample. When significant differences were found for the two samples constituting a pair the data were corrected to a common alkalinity.

represent the means of the results obtained from under- and from supersaturation.

TABLE I

SOLUBILITY OF CUPRIC OXIDE IN AQUEOUS POTASSIUM HYDROXIDE

Alkali molality	Moles of copper per 1000 g. $H_2O \times 10^5$ Undersaturated	Supersaturated
0.0417	0.07	0.07
.0513	.08	.08
.0586	.151	.158
.0600	.132	.241
.0741	.196	.189
.0832	.172	.162
.0932	.409	.414
.0968	.302	.282
.1027	.145	.184
.1150	.324	.308
.1175	.300	.273
.1385	.398	.371
.1608	.489	.604
.1705	.608	.563
.1772	.534	.518
.2035	1.02	.83
.2165	0.96	.73
.2238	.93	.84
.2637	1.34	1.25
.2761	...	1.56
.3163	4.04	3.72
.3244	4.66	3.44
.544	4.91	5.36
.650	4.66	3.72
.753	11.7	11.0
.860	11.2	9.8
1.000	16.1	16.2
1.337	26.1	24.4
1.633	32.4	34.3
1.963	71.0	65.7
2.333	82.7	79.6
2.495	80.1	73.1
2.848	91.8	94.1
3.180	117.2	121.4
3.380	132	87.0
4.015	171	144
4.151	144	150
4.227	164	156
5.065	184	167
5.253	203	181
6.05	297	...
8.38	...	435

TABLE II

SOLUBILITY OF CUPRIC OXIDE IN AQUEOUS SODIUM HYDROXIDE

Alkali molality	Moles copper per 1000 g. $H_2O \times 10^5$ Undersaturated	Supersaturated
2.212	70.1	71.4
3.247	92.5	...
4.227	185	176

Data obtained by Müller[3] are included in Fig. 1, in which the curve is empirical. The solid curves in Figs. 2 and 3 are calculated from equation (4). The basis of this calculation and the significance of the broken lines will be referred to later.

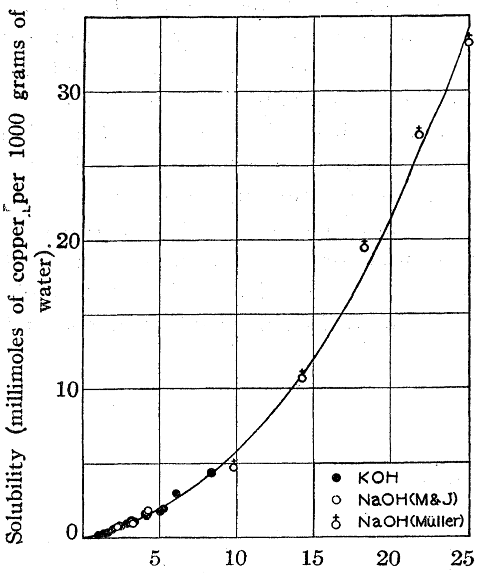

Fig. 1.—Solubility of cupric oxide in strong alkali.

We attempted to determine the solubility of the oxide in pure water and to locate accurately the position of the minimum on the solubility curve. In this we were faced with the difficulty that the solutions usually came out colloidal unless the alkalinity exceeded about 0.03 normal. It was thought best not to include data obtained for several alkalinities below 0.04 normal because of non-reproducibility. But we may conclude from the solubility product of hydroxide or oxide in pure water that the minimum on the solubility curve must lie at an alkali concentration below 0.01 normal.

We were successful in obtaining a rough value for the solubility of the oxide in pure water. This value is 2.9×10^{-5} mole/liter at 25° and is the mean of four determinations (2.5, 3.5, 3.7 and 1.7×10^{-5}, respectively) in which colloidal material was not visible. Three other samples, which were similarly handled, were definitely colloidal and were not analyzed. This result is represented by the triangle in the border of Fig. 2. While we do not regard this value as particularly accurate, we do not believe that the solubility of the oxide can be appreciably higher than this since the nature of the experimental difficulties were such as would lead to high rather than to low results. This constitutes the only value in the literature based on a direct analytical determination. Jellinek and Gordon[12] obtained 1.7 × 10^{-13} for the solubility product of the hydroxide at 20° by concentration cell measurements, in the presence of excess alkali. This result, which is not corrected for the changing activity coefficients of the ions, corresponds to a solubility about double that which we have determined. There is probably a real difference between the oxide and the hydroxide solubilities in water, as there is in alkali,[3] so that this value probably corresponds to a more soluble form than the stable oxide. Remy and Kuhlmann[13] obtained 6.7 × 10^{-5} mole/liter for the oxide at 20°, by conductimetric methods.

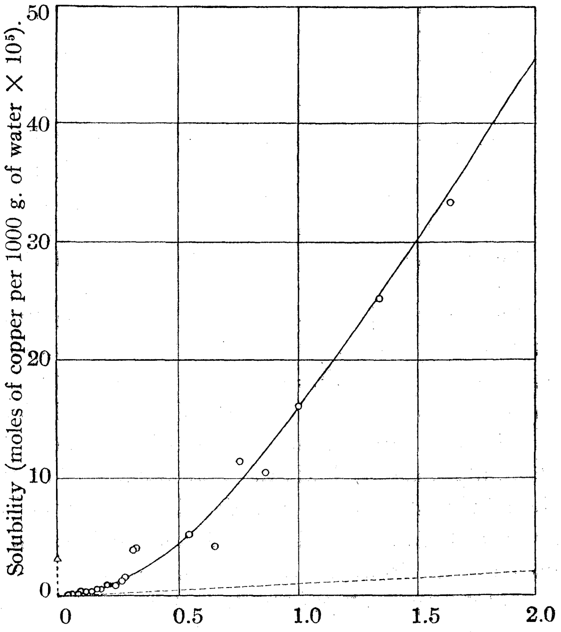

Fig. 2.—Solubility of cupric oxide in potassium hydroxide of moderate concentration: ————, total copper (calculated by Eq. 4); — — — — —, bicuprate ion concentration; Δ, water solubility.

Discussion and Interpretation of Results

Solution of copper oxide in alkali may be represented by the reactions

$$CuO + OH^- = HCuO_2^- \qquad (1)$$

$$K_1 = (m_{HCuO_2^-}/m_{OH^-})\,(\gamma_{HCuO_2^-}/\gamma_{OH^-})$$

$$CuO + 2OH^- = CuO_2^{=} + H_2O \qquad (2)$$

$$K_2 = (m_{CuO_2^{=}}/m^2_{OH^-})\,(\gamma_{CuO_2^{=}}/\gamma^2_{OH^-})a_{H_2O}$$

with their corresponding equilibrium constants. In these equations the m's represent stoichiometrical molalities of the ions; the γ's their corresponding activity coefficients and a_{H_2O} the activity of water from the solutions. For practical purposes this latter may be replaced by p/p^0, the ratio of the vapor pressure to that of pure water.[14] The total solubility of copper at concentrations of alkali too great to permit the existence of Cu^{++} ions is thus given by the relationship

$$S_{Cu} = m_{Cu(OH)_2} + K_1 m_{OH^-}(\gamma_{OH^-}/\gamma_{HCuO_2^-}) + K_2 m^2_{OH^-}(\gamma^2_{OH^-}/\gamma_{CuO_2^{=}})(p^0/p) \qquad (3)$$

in which $m_{Cu(OH)_2}$ is included to represent a probable low concentration of undissociated hydroxide in equilibrium with the solid phase. This might ordinarily be evaluated from the intercept of the solubility curve on the solubility axis but in this case, as is evident from Fig. 3, the value of this term must be quite low and the data do not permit its evaluation. For this reason we

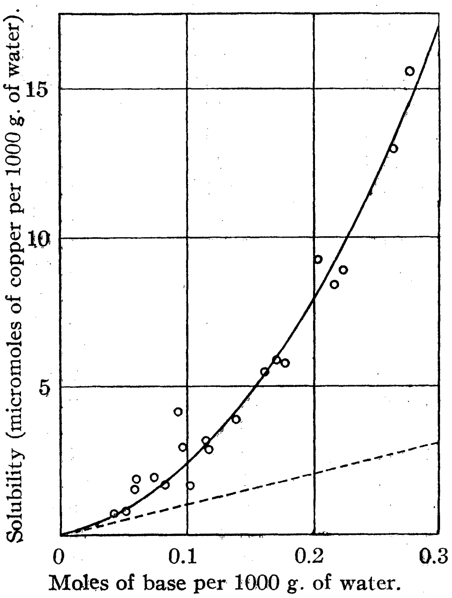

Fig. 3.—Solubility of cupric oxide in dilute potassium hydroxide: ————, total copper (calculated by Eq. 4); — — — — —, concentration of bicuprate ion.

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(12) Jellinek and Gordon, *Z. physik. Chem.*, **112**, 207 (1924).

(13) Remy and Kuhlmann, *Z. anal. Chem.*, **65**, 161 (1925).

(14) These expressions represent cupric oxide as the solid phase in equilibrium with the saturated solutions. If, in reality, this phase is a solid solution of cupric hydroxide in cupric oxide, as the data of Müller seem to indicate, reactions (1) and (2) may be rewritten

$$(XCuO, yCu(OH(_2)\text{ solid} + OH^- = HCuO_2 + yH_2O \qquad (1a)$$

$$K_{1a} = K_1 a^y_{H_2O}$$

$$(XCuO, yCu(OH)_2)\text{ solid} + 2OH^- = CuO_2^{=} + (1 + y)\,H_2O \qquad (2a)$$

$$K_{2a} = K_2 a^y_{H_2O}$$

Since Müller's data show that the mole fraction of the hydroxide cannot exceed 0.1 at most (*i. e.*, y cannot exceed 0.1) K_{1a} and K_{2a} will not differ from K_1 and K_2 by more than 1% even in 3 N alkali. It should be noted also that the solid solution, rather than pure copper oxide, is taken as the standard state in defining K_{1a} and K_{2a}. This defines the significance of the standard free energy change computed from these constants.

have chosen to neglect it. This will introduce no appreciable error into the evaluation of the constants K_1 and K_2.

At low and moderate ionic strengths, equation (3) may be considerably simplified, since the several activity coefficients will approach the values given by the Debye–Hückel interionic attraction theory and the ratio $(\gamma_{OH^-}/\gamma_{HCuO_2^-})$ may be expected to remain near unity even in solutions for which the theory no longer correctly evaluates the separate activities. In the analogous case of silver oxide dissolved in alkali it was found[5] that the ratio $(\gamma_{OH^-}/\gamma_{AgO^-})$ did not depart appreciably from unity even in 1 N alkali. A further simplification comes in the final term. Here $(\gamma^2_{OH^-}/\gamma_{CuO_2^=})$ may be accurately replaced by $(\gamma^4_{KOH}/\gamma^3_{K_2CuO_2})$ and $\gamma^3_{K_2CuO_2}$ may be, in turn, replaced[15] by $\gamma^6_{KHCuO_2}$. Introduction of unit ratio between hydroxide and bicuprate ions now completes the simplification in this term and we have

$$S_{Cu} = K_1 m_{OH^-} + K_2 m^2_{OH^-}(p^0/p\gamma^2_{KOH}) \qquad (4)$$

The parenthetical expression in the last term of (4) is easily evaluated from reliable data.[16] On the assumption that equation (4) remains valid to an ionic strength of unity we have evaluated the two constants of this equation, by an empirical "best fit" to the data recorded in Table I. We have obtained for these constants: $K_1 = 10.3 \times 10^{-6}$, $K_2 = 81 \times 10^{-6}$. The solid lines in Figs. 2 and 3 are calculated with these constants in equation (4). The excellent agreement with the experimental results both at high and low concentrations of alkali is regarded as confirmation both of the assumptions on which (4) is based and on the reliability of the chosen constants. The constants cannot be varied more than a few per cent. without destroying this agreement.

The broken lines in the figures were computed with the final term in (4) omitted and so represent the concentration of bicuprate ion alone. It is clear from these curves that even at low concentrations of alkali a considerable portion of the dissolved copper exists as the divalent acid ion. Other authors[17] have considered the divalent ion concentration as negligible in dilute alkali, in their interpretation of other cases similar to this. It appears from this work that such interpretations will warrant further investigation.

Dissociation Constants of Cupric Acid

The first dissociation constant of cupric acid cannot be determined without more information on the concentration of undissociated hydroxide (*i. e.*, a more reliable basis for extrapolation of the solubility curve to zero alkalinity). But the present data permit the evaluation of the constant for the second step in the acid dissociation

$$HCuO_2^- = H^+ + CuO_2^=$$
$$K_5 = (a_{H^+}a_{CuO_2^=})/a_{HCuO_2^-} \qquad (5)$$

by substituting for a_{H^+} its equivalent $K_w(a_{H_2O}/a_{OH^-})$, and substituting for $a_{CuO_2^=}$ and $a_{HCuO_2^-}$ from equations (1) and (2). This gives

$$K_5 = K_w(K_2/K_1) = 7.9 \times 10^{-14} \qquad (6)$$

with K_w taken to be 1.01×10^{-14} at 25°.[18]

We may estimate the first dissociation constant of cupric acid to be of the order of magnitude of 10^{-10} from the generalization that the first and second constants of di- and tri-basic acids of this approximate strength ordinarily differ by a factor of 10^3 or 10^4. This would make the concentration of undissociated hydroxide of the order of magnitude of 10^{-9} mole per liter, which we could not hope to determine by extrapolation of solubility data even if the colloidal difficulties at low alkalinities were entirely avoided.

Summary

The solubilities of cupric oxide in aqueous potassium hydroxide have been determined for the alkaline range 0.04 normal to about 8 normal, and for a few concentrations of sodium hydroxide. The data at high concentrations are in good agreement with the results obtained, in strong alkali, by Müller.[3c] Up to 2 normal alkali the solubility is well reproduced by the relationship

$$S_{Cu} = 10.3 \times 10^{-6} m_{OH^-} + 81 \times 10^{-6} m^2_{OH^-}/(a_{H_2O}\gamma^2_{KOH})$$

which is derived by application of the interionic attraction theory. The two constants in this equation are the thermodynamic equilibrium constants for the respective reactions

$$CuO + OH^- = HCuO_2^-$$
$$CuO + 2OH^- = H_2O + CuO_2^=$$

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(15) This follows from the fact that at low ionic strengths, where the Debye–Hückel limiting law is obeyed, the activity coefficient of a 1–2 electrolyte is the square of that of a 1–1 electrolyte at the same ionic strength and that where ions are of nearly the same size, as must be true with cuprate and bicuprate ions since they only differ by a proton, this relationship will continue to hold when the limiting law has broken down and terms for the ionic radius are included. This relationship was first called to attention by Walker, Bray and Johnston [THIS JOURNAL, **49**, 1235 (1927)] and shown by them to hold quite accurately for carbonate and bicarbonate solutions even to ionic strengths of 2.

(16) (a) Scatchard, *ibid.*, **47**, 648 (1925); Knobel, *ibid.*, **45**, 70 (1923); Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926). (b) "The International Critical Tables," Vol. III, p. 373.

(17) Randall and Spencer, THIS JOURNAL, **50**, 1572 (1928); Fuseya, *ibid.*, **42**, 368 (1920); Piater, *Z. anorg. allgem. Chem.*, **174**, 321 (1928).

(18) "International Critical Tables," Vol. VI, p. 152.

From these data we obtain 7.9×10^{-14} for the second acid dissociation constant of copper hydroxide

$$HCuO_2^- = H^+ CuO_2^=$$

The relative proportions of bicuprate ($HCuO_2^-$) and cuprate ($CuO_2^=$) ions in the solutions are evaluated and it is shown that the second of these predominates even below 0.1 normal alkali.

The solubility of the oxide in pure water is found to be approximately 3×10^{-5} mole per liter, which is somewhat lower than values now in the literature.

An accurate potentiometric method of determining copper in low concentrations is described.

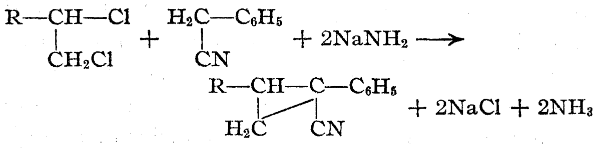
COLUMBUS, OHIO RECEIVED JULY 10, 1936

[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

Alkylene and Alkylidene Phenylacetonitriles and Derivatives. 1-Phenyl-2-ethylcyclopropanecarbonitrile, α-Phenyl-β-ethylacrylonitrile and α-Phenyl-β-isopropylacrylonitrile[1]

BY JAMES V. MURRAY AND JOHN B. CLOKE

It has been shown that 1-phenylcyclopropanecarbonitrile and its 2-methyl homolog can be prepared by the alkylenation of phenylacetonitrile with suitable dihalide derivatives, such as ethylene chloride and propylene chloride, in the presence of sodium amide, according to the reaction[2]

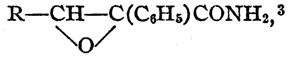


Directions have also appeared for the condensation of acetaldehyde[2] and *n*-butyraldehyde[3] with phenylacetonitrile by the action of sodium ethoxide as generalized below

$$RCHO + H_2C(CN)C_6H_5 = RCH{=}C(CN)C_6H_5 + H_2O$$

This work constitutes an extension of the work of Meyer and Frost[4] on the aromatic aldehydes to the aliphatic group.

The present paper describes the preparation of one alkylene phenylacetonitrile, 1-phenyl-2-ethylcyclopropanecarbonitrile, and two alkylidene phenylacetonitriles, *viz.*, α-phenyl-β-ethylacrylonitrile and α-phenyl-β-isopropylacrylonitrile, together with some of their derivatives.

The proof of the structures of the alkylidene phenylacetonitriles follows from (1) their method of preparation, if aldehydes are used, (2) their reaction with alkaline hydrogen peroxide to give glycidamides, [3] although not all α,β-ethylenic nitriles react, and (3) their oxidation with potassium permanganate. On the other hand, the isomeric cyclopropanecarbonitriles may be recognized (1) by their reaction with hydrogen peroxide to give simple amides, if they react at all, and (2) by their stability in the presence of permanganate. In addition, molecular refractivities have been useful in the differentiation of the cyclopropane and ethylenic isomers, although they are less reliable than the chemical methods.

1 - Phenyl - 2 - ethylcyclopropanecarbonitrile.—This nitrile was obtained in yields up to 40% by the interaction of phenylacetonitrile (I), 1,2-dichlorobutane and sodium amide, as indicated in the accompanying flow sheet. In this reaction it is advantageous to deviate from the original procedure of Knowles and Cloke by preparing the sodium amide in liquid ammonia, according to the method of Vaughn, Vogt and Nieuwland,[5] and using this solution in the initial stages of the reaction.

In passing, it may be pointed out that the glycidamide and Radziszewski reactions may be employed for the removal of phenylacetonitrile and α,β-ethylenic nitrile from the 1-phenyl-2-alkylcyclopropanecarbonitriles, since the latter are quite inert to the reagent.

Following the synthesis of 1-phenyl-2-ethylcyclopropanecarbonitrile (VI), it was essential to produce evidence for the presence of the cyclo-

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(1) This paper is based upon a thesis presented by James Vincent Murray, Jr., to the Graduate School of the Rensselaer Polytechnic Institute in June, 1935, in partial fulfilment of the requirements for the degree of Master of Science.

(2) Knowles and Cloke, THIS JOURNAL, **54**, 2028 (1932).

(3) Murray and Cloke, *ibid.*, **56**, 2751 (1934).

(4) Meyer and Frost, *Ann.*, **250**, 157 (1889).

(5) Vaughn, Vogt and Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

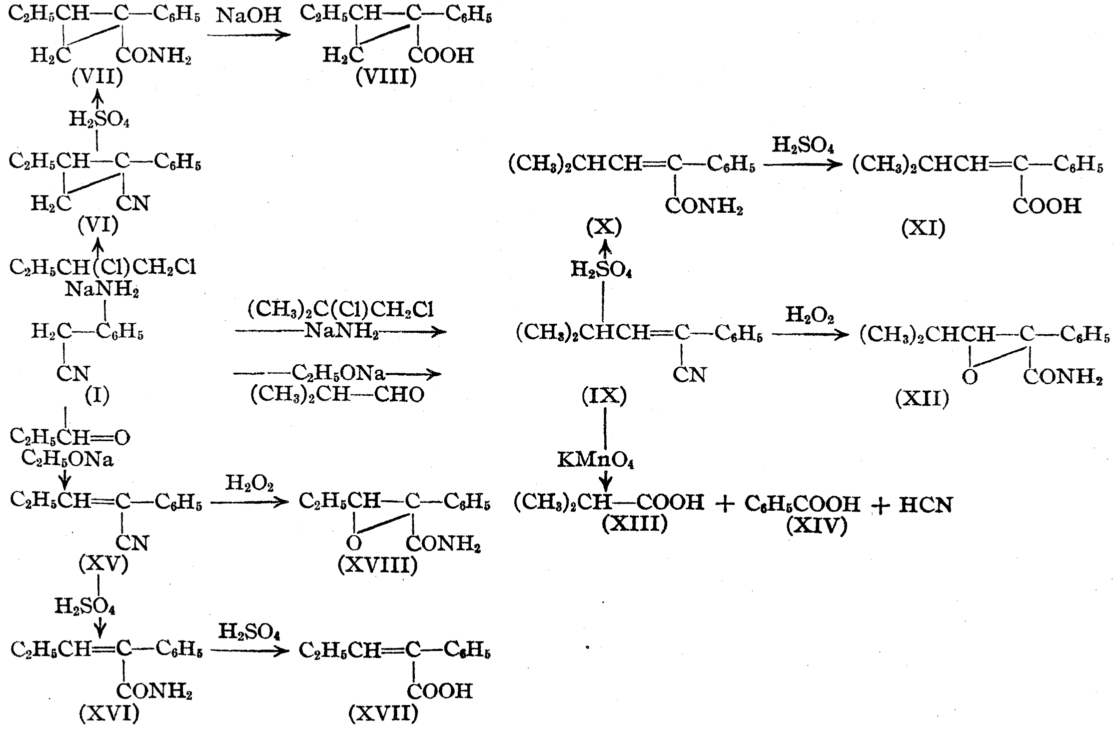
propane ring, since it appeared possible that the reaction might have given the isomeric 2-phenyl-3-hexenonitrile, which in the presence of alkali would be expected to rearrange to give an α-phenyl-β-*n*-propylacrylonitrile (V). The formation of a second series of nitriles is also possible if the secondary halogen atom of the 1,2-dichlorobutane were to react with the monosodium salt of (I).

Several lines of evidence point unquestionably to the cyclopropane structure for the nitrile (VI). In the first place, the nitrile (VI) differs widely from the isomeric ethylenic derivative (V).[3] Thus, the amide (VII) and the acid (VIII) derived from (VI) by hydrolysis are distinct from those obtained from (V). Furthermore, the molecular refractivities of the nitriles are different. In addition, the failure of (VI) to give a glycidamide with alkaline hydrogen peroxide, as well as its stability toward cleavage by alkaline potassium permanganate, definitely excludes the ethylenic structure. Moreover, its striking resistance toward hydrolysis and the ease with which it is altered by cold, concentrated sulfuric acid closely parallel the behavior of 1-phenyl-2-methylcyclopropanecarbonitrile (III), the next lower homolog. Finally, the good agreement between the observed molecular refractivity and that calculated on the basis of the cyclic structure indicates the presence of the cyclopropane nucleus in (VI).

α-Phenyl-β-isopropylacrylonitrile (IX).—With the expectation of obtaining 1-phenyl-2,2-dimethylcyclopropanecarbonitrile, phenylacetonitrile (I) was allowed to react with 1,2-dichloroisobutane and sodium amide. The resulting nitrile was obtained in yields up to 38%.

In the early stages of this work the cyclic structure for the nitrile was inferred on the basis of the method of preparation. However, consistently high values observed for the molecular refractivity cast considerable doubt on the cyclic structure, but were in harmony with the value computed for the ethylenic structure (IX). The cyclopropane structure was definitely excluded when it was found that the nitrile (IX) gave the glycidamide (XII), when it was subjected to the action of alkaline hydrogen peroxide. Still further confirmation of the ethylenic structure was obtained when it was observed that the nitrile (IX), upon oxidation with potassium permanganate in alkaline solution, absorbed three atoms of oxygen with the formation of isobutyric acid (XIII), benzoic acid (XIV), and hydrogen cyanide. This oxidation will be discussed more fully in a future communication.

Synthetic proof for the ethylenic structure (IX)



was also secured by the preparation of the nitrile in an 85% yield by the alkylidenation of phenylacetonitrile with isobutyraldehyde in the presence of dilute sodium ethoxide. The complete identity of the two nitriles was established by the fact that both yield the same amide (X), acid (XI), and glycidamide (XII) as shown by mixed melting point determinations.

It will be noted that the formation of the α-phenyl-β-isopropylacrylonitrile (IX) by the condensation of the 1,2-dichloroisobutane with phenylacetonitrile by the action of sodium amide involves a rearrangement. It is clear that the primary halogen atom of the dichloride must react with the phenylacetonitrile. This reaction is probably accompanied by the elimination of the remaining halogen atom with an adjacent hydrogen atom to give the β,γ-nitrile, $(CH_3)_2C=CH-CH(C_6H_5)CN$, which then rearranges to give the α,β-nitrile (IX), although other paths are possible.

α-Phenyl-β-ethylacrylonitrile (XV).—This nitrile, which may also be called propylidenephenylacetonitrile, was obtained in a 60% yield by the condensation of propionaldehyde with phenylacetonitrile by the use of sodium ethoxide. The structure is established by its method of preparation; the formation of the glycidamide, when it is treated with alkaline hydrogen peroxide; its instability toward alkaline potassium permanganate; and its refractivity. On hydrolysis, it yields the corresponding amide (XVI) and acid (XVII).

Experimental Part

Preparation of 1-Phenyl-2-ethylcyclopropanecarbonitrile (VI).—A two-liter, three-necked, round-bottomed flask was fitted with a dropping funnel, a reflux condenser provided with a lime tower, and an efficient mechanical stirrer which operated through a mercury seal.

One and one-half liters of liquid ammonia was placed in the reaction flask followed by 2 g. of bright sodium. The stirrer was set in motion and 1.5 g. of $Fe(NO_3)_3 \cdot 6H_2O$[5] (in later runs the hydrated chloride was used) was introduced and then 46 g. (2 atoms) of sodium in the form of small chips was added over the course of twenty minutes. The reaction mixture was then allowed to stand until the initial deep blue color had faded, denoting the completion of the reaction.

At this point, 117 g. (1 mole) of freshly distilled phenylacetonitrile[6] was cautiously added to the sodium amide solution during a period of one hour. The mixture in the flask was then stirred while 700 cc. of anhydrous ether was added at about the same rate at which the liquid ammonia evaporated. When the reaction mixture attained room temperature, it was refluxed gently for one hour.

At the end of this first stage, the sodium phenylacetonitrile mixture was cooled to −5° in an ice-salt bath and 127 g. (1 mole) of 1,2-dichloro-*n*-butane was added slowly over the course of one hour. Stirring was continued overnight while the bath came to room temperature. Following this, the reaction mixture was refluxed gently for two hours. Finally water was added to dissolve the solid precipitate and the mixture was acidified with acetic acid. The ether layer was removed and dried over anhydrous sodium sulfate. The fractionation of the dried ether extract gave 35 g. of a fraction boiling at 77–80° at less than 1 mm., which was mainly unchanged phenylacetonitrile, and a 68 g. fraction boiling at 93–94° at the same pressure. This corresponds to a 40% yield on the basis of the starting quantity of phenylacetonitrile. The nitrile possessed the following properties: d^{20}_4 0.9921; n^{20}_D 1.52457; MR_D (obsd.), 52.70; MR_D (calcd.), 52.29.[7] *Anal.* (micro.) Calcd. for $C_{12}H_{13}N$: N, 8.18. Found: N, 8.17, 8.25.

The foregoing procedure was varied in several runs by using commercial sodium amide or the specially prepared salt with ether exclusively as the reaction medium. These variations, however, markedly decreased the yield. Low yields were likewise obtained when liquid ammonia was used throughout as the reaction solvent, no provision being made for reflux periods.

1-Phenyl-2-ethylcyclopropanecarbonamide (VII).—In a 125-cc. acetylation flask were placed 10 cc. of water, 10 cc. of concentrated sulfuric acid, 10 cc. of glacial acetic acid, and 2 g. of 1-phenyl-2-ethylcyclopropanecarbonitrile. The mixture was refluxed for five hours and then poured into ice water. The aqueous solution was extracted with ether and this extract was then washed with 10% sodium carbonate solution. Evaporation of the ether solution gave the crude amide, which after decolorization and recrystallization from hot water yielded the pure amide as needles which melted at 84°.

The same amide was also obtained by hydrolysis of the nitrile with alcoholic potassium hydroxide. This method however, requires a reflux period of about sixty hours. Attempts to hydrolyze the nitrile by means of 100% phosphoric acid or by alkaline hydrogen peroxide were unsuccessful. *Anal.* Calcd. for $C_{12}H_{15}ON$: N, 7.41. Found: N, 7.35, 7.43.

1-Phenyl-2-ethylcyclopropanecarboxylic Acid (VIII).—A weight of 2 g. of the 1-phenyl-2-ethylcyclopropanecarbonamide was refluxed for fifty hours with *N* alcoholic potassium hydroxide. The crude acid was isolated in the usual manner and after recrystallization from hot water the pure acid melted at 105–105.5° (corr.).

Preparation of α-Phenyl-β-isopropylacrylonitrile (IX).—This nitrile was prepared by two different methods.

Method 1.—When phenylacetonitrile (1 mole) was allowed to react with 1,2-dichloroisobutane (1 mole) and sodium amide (2 moles) according to the procedure described for the preparation of (VI), the nitrile (IX) was obtained in yields up to 38%. After repeated fractiona-

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[6] Adams and Thal, "Organic Syntheses," Coll. Vol. I, p. 101.

[7] The molecular refractivities were calculated on the basis of Eisenlohr's data. Ostling's value of 0.7 unit is added for the cyclopropane ring. Corrections for conjugation, distribution of groups, etc., have not been included.

tion of the reaction product, the nitrile boiled at 94.5–95° at less than 1 mm.

Method 2.—A solution of 58.5 g. (0.5 mole) of phenylacetonitrile and 54 g. (0.75 mole) of isobutyraldehyde in 120 cc. of absolute alcohol was cooled to −10° and a volume of 10 cc. of 20% sodium ethylate was added at such a rate that the temperature did not rise above −5°. The resulting solution, contained in a tightly stoppered flask, was allowed to stand in the refrigerator for one week. The reaction mixture was then poured into 700 cc. of ice water and was neutralized with acetic acid. The oily layer was taken up in an equal volume of ether and the resulting solution washed with water and dried over sodium sulfate. Fractionation of the dried product gave 73 g. of the nitrile boiling at 95–95.2° at less than 1 mm. which corresponds to a yield of 85%. The nitrile possessed the following properties: d^{20}_4 0.9613; n^{20}_D 1.53530; MR_D (obsd.) 55.41; MR_D (calcd.) 53.32.[8] *Anal.* Calcd. for $C_{12}H_{13}N$: N, 8.18. Found: N, 8.25, 8.19, 8.22, 8.20.

α-Phenyl-β-isopropylacrylamide (X).—A weight of 2 g. of the nitrile (IX) was hydrolyzed by the acetic acid–sulfuric acid method utilized in the case of the nitrile (VI). The ether solution, after extraction with 10% sodium carbonate, deposited the impure amide upon evaporation. Recrystallization of the crude product from boiling water gave the pure amide melting at 123–124° (corr.).

Anal. Calcd. for $C_{12}H_{15}ON$: N, 7.41. Found: N, 7.45, 7.52.

α-Phenyl-β-isopropylacrylic Acid (XI).—The sodium carbonate extract from the foregoing hydrolysis was acidified with dilute sulfuric acid and the impure α-phenyl-β-isopropylacrylic acid precipitated. Recrystallization of the crude product from hot water gave the pure acid as fine, white needles melting at 133–134° (corr.).

Hydrolysis of the α-phenyl-β-isopropylacrylonitrile prepared by either of the two methods resulted in the same products. The identity of the derivatives from the two nitriles was established by mixed melting point determinations.

α-Phenyl-β-isopropylglycidamide (XII).—Following the procedure of Murray and Cloke,[3] 2 g. of α-phenyl-β-isopropylacrylonitrile and 25 cc. of 10% hydrogen peroxide were dissolved in acetone and enough 10% sodium carbonate added to make the solution definitely alkaline. After standing for one day, the acetone was evaporated and the residue was recrystallized from boiling water. The resulting α-phenyl-β-isopropylglycidamide melted at 148–149° (corr.). *Anal.* Calcd. for $C_{12}H_{15}O_2N$: N, 6.82. Found: N, 6.72, 6.86.

The Oxidation of α-Phenyl-β-isopropylacrylonitrile.—A weight of 30 g. of α-phenyl-β-isopropylacrylonitrile was placed in a glass-stoppered Pyrex bottle containing 5 cc. of 10% sodium carbonate solution and 100 cc. of water. Solid potassium permanganate was added in small portions with shaking until the purple color persisted. This required 54.2 g. of permanganate and corresponds to the absorption of three gram atoms of oxygen per mole of nitrile.

Extraction of the alkaline solution with petroleum ether showed no unreacted nitrile. Acidification of the filtered aqueous solution gave a precipitate of benzoic acid (XIV), which was identified by a mixed melting point determination with a known sample of the acid. After the removal of the benzoic acid, the filtrate was made alkaline and evaporated to dryness. From the residue isobutyric acid was isolated and identified as the anilide. The presence of cyanide ion was demonstrated by the Prussian blue test.

Preparation of α-Phenyl-β-ethylacrylonitrile (XV).—A solution of phenylacetonitrile (0.4 mole) and propionaldehyde (0.5 mole) in 100 cc. of absolute alcohol was treated with 9 cc. of 20% sodium ethylate according to the procedure used for the preparation of the nitrile (IX) by method 2. Purification of the nitrile gave a 55% yield of the desired product boiling at 112–112.5° at 3 mm. The nitrile possessed the following properties: d^{20}_4 0.9897; n^{20}_D 1.54300; MR_D (obsd.), 50.00; MR_D (calcd.), 48.69.[8] *Anal.* Calcd. for $C_{11}H_{11}N$: N, 8.92. Found: N, 8.97, 9.00.

An earlier run of the nitrile, originally started by Rogers[9] and allowed to stand for one year, was found on purification to give a somewhat lower yield. A considerable amount of a brown, tarry material appeared during the distillation. Rogers' first run, which was allowed to stand for three days only at a temperature not far from 0°, gave a low yield, which was difficult to separate.

α-Phenyl-β-ethylacrylamide (XVI).—Hydrolysis of the α-phenyl-β-ethylacrylonitrile by the acetic acid–sulfuric acid method gave the amide, which after recrystallization from water melted at 130° (corr.). *Anal.* Calcd. for $C_{11}H_{13}ON$: N, 8.00. Found: N, 7.93, 8.06.

α-Phenyl-β-ethylacrylic Acid (XVII).—Following the usual procedure, the α-phenyl-β-ethylacrylic acid was isolated from the foregoing hydrolysis mixture. The pure acid after recrystallization from hot water melted at 67.5–68.5°.

α-Phenyl-β-ethylglycidamide (XVIII).—The glycidamide,[9] obtained in the usual manner by the action of alkaline hydrogen peroxide on the nitrile (XV), was recrystallized from boiling water and found to melt at 155° (corr.). *Anal.* Calcd. for $C_{11}H_{13}O_2N$: N, 7.33. Found: N, 7.26, 7.30.

Summary

1. 1 - Phenyl - 2 - ethylcyclopropanecarbonitrile has been prepared in yields up to 40%. Several derivatives and reactions of this nitrile have been discussed in connection with the proof of its cyclic structure.

2. α-Phenyl-β-isopropylacrylonitrile was prepared by two different methods in yields of 38 and 95%. Proof for the ethylenic structure is given and several derivatives of the nitrile are described.

3. The preparation of α-phenyl-β-ethylacrylonitrile is described together with a number of its derivatives.

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[8] These abnormally high exaltations (not included in the calculations) have been observed in all of the alkylidene-phenylacetonitriles so far prepared. The exaltation apparently arises from a combination of conjugation of multiple linkages and distribution of groups about the ethylenic bond. Further, the anomaly appears to depend also upon the nature of the hydrocarbon residue in the β-position.

[9] D. T. Rogers, Master's Thesis, Rensselaer Polytechnic Institute, 1934.

4. Some preliminary work on the oxidation of α,β-ethylenic nitriles is described.

5. Whereas the condensation of ethylene, propylene and α-butylene dichlorides with phenylacetonitrile gives cyclopropanecarbonitriles, the use of isobutylene dichloride under the same conditions leads to the formation of an ethylenic nitrile.

TROY, NEW YORK RECEIVED JULY 28, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF MINERALOGY, OXFORD UNIVERSITY, AND THE LABORATORY FOR ENDOCRINE RESEARCH, THE JOHNS HOPKINS UNIVERSITY]

The Molecular Weight of Cinobufagin

BY DOROTHY CROWFOOT AND H. JENSEN

It has been suggested[1] that cinobufagin ($C_{25}H_{32}O_6$) can be considered as the acetyl derivative of an unsaturated hydroxylactone, $C_{23}H_{30}O_5$, and apparently is closely related chemically to certain plant aglucones which are also C_{23} derivatives.[1] The x-ray crystallographic examination of this principle by Crowfoot[2] has given values, however, which do not agree with the proposed formula $C_{25}H_{32}O_6$ and which indicate that the compound probably contains twenty-six carbon atoms.

In order to check these results, x-ray measurements have now been made on two derivatives of cinobufagin, namely, acetylcinobufagin and cinobufagone. The measurements obtained on these compounds provide two independent determinations of the molecular weight of cinobufagin and both more nearly agree with the formulas derived from C_{26}. Thus the molecular weight of acetylcinobufagin was found to be 487 ± 10, the calculated values for the acetyl derivatives of $C_{26}H_{34}O_6$ and $C_{25}H_{32}O_6$ being, respectively, 484 and 470. Cinobufagone has a molecular weight of 443 ± 10 which is in agreement with the formula $C_{26}H_{32}O_6$, 440, and not $C_{25}H_{30}O_6$, 426. Details of the crystallographic measurements are given below.

The analytical values previously reported for cinobufagin and certain of its derivatives[3] agree with the formula $C_{26}H_{34}O_6$. This new formula would bring cinobufagin into very close relationship to bufotalin (present in the secretion of *Bufo vulgaris*) to which Wieland and co-workers[4] assigned the formula $C_{26}H_{36}O_6$ and which they showed can be considered as an acetyl derivative of an unsaturated hydroxylactone ($C_{24}H_{34}O_5$). It might be mentioned, in connection with this, that the results of the pharmacological studies by Chen and Chen[5] on the action of the various animal cardiac principles indicate that their physiological properties show more resemblance to the physiological action of scillaridin than of other plant aglucones. Chemical researches by Stoll and co-workers[6] have shown that scillaridin is a C_{24} derivative, while most other plant aglucones have been found to be C_{23} derivatives. The investigation of Wieland and co-workers[4] on bufotalin indicates that the lactone ring in the animal cardiac principles is a six-membered ring probably similar to that found by Stoll and co-workers[6] for scillaridin. In view of our findings on the molecular weight of cinobufagin, it appears that arenobufagin and regularobufagin are also probably C_{24} rather than C_{23} derivatives as originally suggested by Jensen.[7] Further research on the exact chemical composition of these two principles has been undertaken in order to answer this question.

It should be added that the crystallographic examination of cinobufagone and acetylcinobufagin alone would not exclude molecular weights of twice the magnitude deduced since the asymmetric unit in each case contains two C_{26} molecules. This possibility, however, is excluded by the original measurements on cinobufagin itself in which the single molecule is the asymmetric unit.

The actual crystal structures indicated by the measurements for cinobufagin, acetylcinobufagin and cinobufagone do not seem to bear very simple relation to one another or to those of any of the compounds in the cardiac aglucone series so far examined. This is not surprising since the introduction of many hydroxyl groups is known to produce considerable variation in the crystallo-

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(1) Jensen, *Science*, **75**, 53 (1932).

(2) Crowfoot, *Chemistry & Industry*, **54**, 568 (1935).

(3) Jensen and Evans, Jr., *J. Biol. Chem.*, **104**, 307 (1934).

(4) Wieland and Hesse, *Ann.*, **517**, 22 (1935).

(5) Chen and Chen, *J. Pharmacol.*, **49**, 561 (1933).

(6) Stoll, Hofmann and Peyer, *Helv. Chim. Acta*, **18**, 1247 (1935).

(7) Jensen, THIS JOURNAL, **57**, 1765 (1935).

CRYSTALLOGRAPHIC DATA

Compound	Space group	*a*	*b*	*c*	No. in cell	No. asymmetric unit	Density	Mol. wt.
Cinobufagin	$P2_12_12_1$	7.61 α	15.79 γ	19.45 β	4	1	1.261	447 ± 10
Acetylcinobufagin	$C222_1$	28.74 γ	8.14 β	44.76 α	16	2	1.229	487 ± 10
Cinobufagone	$P2_12_12_1$	21.79 β	8.62 γ	24.22 α	8	2	1.280	443 ± 10

Acetylcinobufagin: fine orthorhombic needles elongated along (010), (001) dominating. Birefringence low.

Cinobufagone: small orthorhombic needles elongated along (010) and growing least on (001). The crystals appear partly redissolved and show curved surfaces instead of the *c* face. Birefringence low.

The densities of both compounds were determined by flotation in zinc sulfate solutions, the centrifuge being used to hasten equilibrium. These are correct to ±0.4%. The probable error on the x-ray dimensions is not more than ±0.5%.

graphic arrangement of the molecules as is found, for example, in the study of the sugars. Both the presence of the hydroxyl groups and the orthorhombic symmetry shown by the crystals of these cinobufagin compounds render it impossible to make deductions in regard to the molecular arrangement and molecular dimensions from the combination of the optical with the crystallographic data. One can only state that the data are not incompatible with formulas of the cardiac aglucone type and for comparison reference may be made to the complex crystal structures assumed by strophanthidin and certain of its derivatives.

Summary

The determinations of molecular weights of cinobufagin and two of its derivatives, acetylcinobufagin and cinobufagone, indicate that cinobufagin has the composition $C_{26}H_{34}O_6$. The analytical data previously reported for cinobufagin and certain of its derivatives agree with this new formula.

OXFORD, ENGLAND
BALTIMORE, MARYLAND

RECEIVED JULY 27, 1936

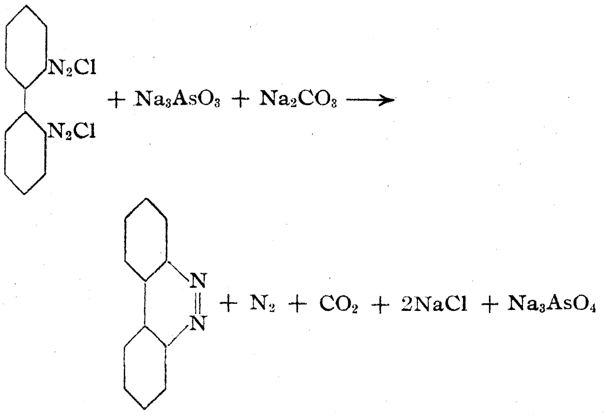
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ALBERTA]

The Formation of Cyclic Azo Compounds from 2,2′-Diaminodiphenyls

BY R. B. SANDIN AND T. L. CAIRNS

The compound 4,4′-diarsonodiphenyl[1,2] has been prepared from benzidine, according to the method of Bart. In an attempt to prepare the isomeric 2,2′-diarsonodiphenyl by an analogous procedure, the authors of this paper have found that when tetrazotized 2,2′-diaminodiphenyl is treated with arsenious oxide in sodium carbonate solution, a considerable part of the tetrazotized compound is converted into *o,o′*-azodiphenyl.[3] The authors believe it to be a general reaction. It is also believed that the arsenite functions as a reducing agent instead of proceeding according to the typical Bart reaction.

The proposed equation for this reaction is



Experimental

Cyclic *o,o′*-Azodiphenyl.—In a mixture of 250 cc. of 2 *N* hydrochloric acid and 150 cc. of water, 18.4 g. of 2,2′-diaminodiphenyl was dissolved. The solution was cooled to 0°, and to it was added gradually 100 cc. of 2 *N* sodium nitrite and an excess of nitrite was maintained for thirty minutes. The clear solution of the tetrazotized compound

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(1) Bauer and Adams, THIS JOURNAL, **46**, 1925 (1924).

(2) Hill, *ibid.*, **46**, 1855 (1924).

(3) This compound is also called phenazone and *o*-diphenyleneazone [Täuber, *Ber.*, **24**, 3081 (1891)]. Bigelow [*Chem. Rev.*, **9**, 117 (1931)] has suggested the name cyclic *o,o*-azoxydiphenyl, in place of diphenazonoxyd. For that reason it might, perhaps, be better to call phenazone or *o*-diphenyleneazone, cyclic *o,o*-azodiphenyl.

was made neutral to Congo red by the addition of 50 cc. of 2 *N* sodium carbonate which had been diluted to 100 cc. A solution of sodium arsenite was prepared by dissolving 30 g. of arsenious oxide in 300 cc. of 2 *N* sodium carbonate, and to it was added 2 g. of copper sulfate to serve as a catalyst. After this had been cooled to 0°, the tetrazotized diaminodiphenyl solution was siphoned into the arsenite solution during fifteen to twenty minutes. During this procedure there was much gas evolved and there was considerable foaming, which was very difficult to get rid of. An olive-green precipitate was produced, which was filtered by suction and washed with water. The precipitate was extracted with hot 10% hydrochloric acid and the extract was neutralized with ammonia or sodium hydroxide. This gave a precipitate of crude cyclic *o,o'*-azodiphenyl. The yield was 7.5 g. or 45% of the theoretical amount. The crude material melted at 153–154°. It was crystallized from alcohol and gave yellow crystals melting at 155°. A mixed melting point carried out with a sample of the cyclic azo compound prepared according to Täuber,[3] showed no depression of the melting point. It also gave a picrate melting at 191°.

Cyclic Azo Compound from 2,2'-Diamino-4,4'-dimethyldiphenyl.[4]—This compound was prepared in a manner similar to the above, from 2,2'-diamino-4,4'-dimethyldiphenyl. It consisted of yellow needles, soluble in dilute hydrochloric acid, and melted at 184–185°. A mixed melting point carried out with this sample and the compound produced by the sodium amalgam and methanol reduction of 2,2'-dinitro-4,4'-dimethyldiphenyl showed no depression of the melting point.

Acknowledgment.—The authors wish to thank the Carnegie Corporation Research Fund Committee for a grant which enabled the purchase of certain chemicals.

Summary

Tetrazotized diaminodiphenyls, when treated with arsenious oxide in sodium carbonate solution, are in part converted into cyclic azo compounds.

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[4] Ullmann and Dieterle, *Ber.*, **37**, 24 (1904).

Edmonton, Alberta, Canada Received June 2, 1936

[Contribution from the Department of Biological Chemistry, Columbia University]

Carboxymethoxylamine

By E. Borek[1] and H. T. Clarke

In the course of experiments on the synthesis of canaline and analogous compounds, the need arose for a convenient process for preparing carboxymethoxylamine (hydroxylamineacetic acid). In view of the recent report by Anchel and Schoenheimer[2] of the use of this substance as a reagent for the isolation of ketones from natural sources, an early description of our method of preparation seems advisable.

Carboxymethoxylamine was first prepared by Werner[3,4] by the hydrolysis of ethylbenzhydroximinoacetic acid; it has also very recently been prepared by Kitagawa and Takani[5] by condensation of benzhydroxamic acid and ethyl bromoacetate, with subsequent hydrolysis by hydrochloric acid.

The method here described consists in condensing the sodium derivative of acetoxime with ethyl chloroacetate, followed by successive alkaline and acid hydrolysis of the condensation product. The intermediate acetone carboxymethoxime may also be prepared, though in somewhat smaller yields, by condensing acetoxime with sodium chloroacetate in alkaline solution by a modification of the method of Hantzsch and Wild.[6]

The carboxymethoxylamine is isolated in the form of its hydrochloride, which melts at 151°. This product in our hands has invariably proved to consist of the hemihydrochloride; that prepared by Werner was reported to melt at 147-148°[3] and at 156°[4,5] and to give analytical figures agreeing satisfactorily with the normal hydrochloride. We are unable to account for this discrepancy.

Experimental

A solution of 24.4 g. of acetoxime in 250 cc. of absolute alcohol was added to a solution of 7.7 g. of sodium in 150 cc. of absolute alcohol. The alcohol was removed by distillation under diminished pressure and the white crystalline residue was dried *in vacuo* over phosphorus pentoxide. To the dry salt 100 cc. of ethyl chloroacetate was added and the mixture refluxed for thirty minutes. When cool, the salt was filtered off and well washed with absolute alcohol. The alcohol and the unreacted ethyl chloroacetate were removed under diminished pressure, the fraction distilling up to 52° under 28 mm. being discarded.

The sirupy residue, which consisted mainly of acetone carbethoxymethoxime, together with the corresponding

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[1] This report is from a dissertation submitted by Ernest Borek in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] Anchel and Schoenheimer, *J. Biol. Chem.*, **114**, 539 (1936).

[3] Werner, *Ber.*, **26**, 1567 (1893).

[4] Werner and Sonnenfeld, *ibid.*, **27**, 3350 (1894).

[5] Kitagawa and Takani, *J. Biochem.* (*Tokio*), **23**, 181 (1936).

[6] Hantzsch and Wild, *Ann.*, **289**, 285 (1896).

free acid, acetoxime and other contaminants such as ethyl glycolate, was heated for one hour at 100° with 125 cc. of 11.4% sodium hydroxide. When cool, the alkaline solution was extracted five times with one-fourth its volume of ether; the ether solution, which contained slight amounts of unreacted acetoxime and unsaponified ester, was discarded. The aqueous solution was acidified to Congo red with concentrated hydrochloric acid, saturated with sodium chloride and extracted with three times its volume of ether in six portions. The ether solution was dried with sodium sulfate, and the ether removed by distillation. After the last traces of ether had been removed under diminished pressure, acetone carboxymethoxime crystallized. The weight of the crude preparation was 25 g. (58% of the theoretical).

Acetone carboxymethoxime can also be prepared in aqueous solution: a solution of sodium chloroacetate prepared by neutralizing 212 g. of chloroacetic acid with 450 g. of 20% sodium hydroxide was added to a solution of 146 g. of acetoxime in 450 cc. of water; 200 g. of 40% aqueous sodium hydroxide solution was then added and the whole refluxed for one hour. When cold, the alkaline solution was four times extracted with one-fourth of its volume of ether; the ether solution, which contained some unreacted acetoxime, was discarded. The aqueous layer was acidified with hydrochloric acid to Congo red, saturated with sodium chloride and six times extracted with one-half its volume of ether. The ether solution was dried with sodium sulfate, and the ether removed on the steam-bath, finally under diminished pressure. The crude acetone carboxymethoxime which crystallized weighed 128 g. (49%). By the original method of Hantzsch and Wild[6] the yield was 46%.

The crude acetone carboxymethoxime from either preparation can be purified by distillation; b. p. 110–118° (1 mm.). It solidifies in the receiver in long needles. There is considerable carbonization and hydrogen cyanide is formed. It can be crystallized from a hot concentrated solution of acetone by the addition of ligroin. The resulting plates, the odor of which is not unlike that of phenylacetic acid, melt at 76–76.5° (uncorr.).

Anal. Calcd. for $C_5H_9O_3N$: C, 45.80; H, 6.87; N, 10.69; neut. equiv., 131. Found: C, 46.12; H, 6.49; N, 10.92; neut. equiv., 131.5.

For the preparation of carboxymethoxylamine hemihydrochloride 10 g. of the crude acetone carboxymethoxime in 100 cc. of 6 *N* hydrochloric acid was refluxed for three hours; the solution was then treated with charcoal and concentrated to about 10 cc. under diminished pressure. To the sirup was added 200 cc. of a solution of 1:1 ether and ethyl alcohol, and the cloudy solution was placed in an ice box. Four grams of crystals deposited. The mother liquor was again concentrated to a sirup and ether and alcohol solution added. One gram more of the crystals was thus obtained. The melting point of the crystals after one recrystallization from water, ether–alcohol solution is 151°.[7]

Anal. Calcd. for $(C_2H_5O_3N)_2HCl$: C, 21.95; H, 5.03; N, 12.81; Cl, 16.23. Found: C, 22.26; H, 5.45; N, 12.54; Cl, 16.29.

Acetophenone carboxymethoxime was prepared by adding a solution of 150 mg. of carboxymethoxylamine hemihydrochloride in 4 cc. of water to a solution of 0.2 cc. of acetophenone in 4 cc. of ethyl alcohol. After the solution was made alkaline to litmus with *N* sodium hydroxide, it was warmed on the steam-bath for one hour. The cool, alkaline solution was extracted five times with ether and the ether solution discarded. The aqueous solution was acidified to Congo red and placed in the ice box. The large plates that formed were filtered and recrystallized from alcohol–water solution; colorless plates, m. p. 97–97.5°, soluble in ether and alcohol; almost insoluble in water.

Anal. Calcd. for $C_{10}H_{11}O_3N$: C, 62.15; H, 5.74; N, 7.25. Found: C, 62.07; H, 5.66; N, 7.12.

Benzaldehyde carboxymethoxime was prepared in the same way as the above; it melted at 96°. Hantzsch and Wild,[6] who prepared this compound by condensing sodium chloroacetate with benzaldoxime, report a melting point of 98°.

Pyruvic acid carboxymethoxime was prepared the same way, but since it is water-soluble the solution, after acidification, was five times extracted with one-half its volume of ether, the ether solution dried with sodium sulfate and the ether distilled. The crystals which were obtained were recrystallized from ether and chloroform; m. p. 129° (Hantzsch and Wild[6] report 130–132°).

Summary

Directions are given for the preparation of carboxymethoxylamine hemihydrochloride, a reagent of use for the isolation of ketones.

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[7] As hydroxylamine hydrochloride also melts at 151°, a mixed melting point should be performed.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

Adsorption of Vapors on Glass Spheres. I. The Adsorption of Nitrogen

BY J. L. SHERESHEFSKY AND CHARLES E. WEIR

Introduction

In a previous investigation[1] of the adsorption of oxygen by glass spheres, it was observed that the amount of adsorption at corresponding pressures increased with the number of contacts per sphere. As this effect could also be due to differences in the degree of activation of the surface resulting from unequal periods of the degassing process, it was considered essential to obtain reproducible isotherms under the same conditions of treatment and packing before any definite conclusions as to the effect of the number of contacts on the adsorption could be reached.

Inasmuch as every oxygen isotherm exhibited a peculiar pressure reversal apparently connected with a discontinuity or break in the isotherm it was considered desirable to use nitrogen in place of oxygen in order to ascertain whether the peculiarity was characteristic of oxygen or was more general in nature. Nitrogen has the added advantage of being more strongly adsorbed while very similar to oxygen in its physical properties. The experiments were carried out at the temperature of liquid air where the nitrogen, as well as the oxygen previously investigated, may be classed as a vapor.

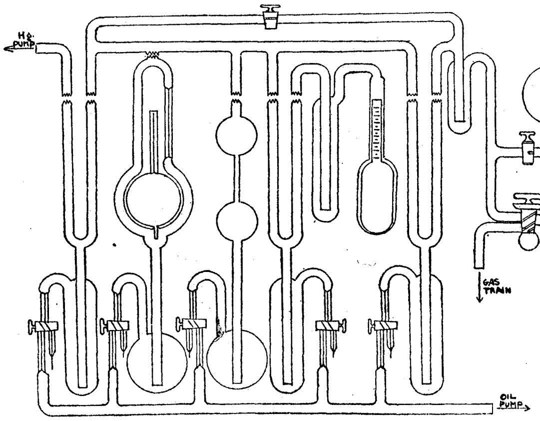

Fig. 1.—Apparatus.

Apparatus

A schematic representation of the apparatus is shown in Fig. 1. As may be seen the adsorption system proper is the conventional arrangement used when adsorption is to be calculated from pressure measurements. The McLeod gage was calibrated in three ranges, from 1×10^{-6} to 1×10^{-4}, from 1×10^{-5} to 1×10^{-3}, and from 1×10^{-4} to 5×10^{-3} cm. of mercury. F is a gas reservoir, D is a dosing stopcock, and C_1 and C_2 are auxiliary stopcocks. By varying the pressure in F, or by repetitive use of stopcock D, any desired quantity of gas could be introduced into the adsorption system by filling the bore of the dosing stopcock from the reservoir and then discharging this gas into the adsorption apparatus through mercury stop S_3.

The volumes of the various parts of the apparatus were determined with hydrogen at pressures ranging from 2 to 20 cm. of mercury. In these determinations we made use of the calibrated bulbs B_1 and B_2. All pressures were read on the mercury stop S_3 with a cathetometer reading to 0.01 mm. The pre-expansion volume extending from X_2 to X_3 was found to be 981 cc.; the total volume consisting of the pre-expansion volume and the adsorption chamber and extending from X_2 to A was 1599 cc.

Preparation of Materials

Tank hydrogen containing water and oxygen as possible impurities was purified by passage through activated charcoal at liquid air temperature.

Commercial helium containing hydrocarbons as possible impurities was likewise purified[2] by passage through activated charcoal at liquid air temperature.

Nitrogen was prepared from pure ammonium hydroxide and bromine water in a manner described by Waran.[3] The nitrogen was stored over phosphorus pentoxide for forty-eight hours before being used.

The spheres 3 mm. in diameter and of soft glass were cleaned with chromic and nitric acids and washed with distilled water. The actual surface was obtained by measuring the adsorption of methylene blue in accordance with the method of Paneth.[4] The isotherms thus obtained showed a well-defined maximum at about 1.53 mg. of the dye. Using the value given by Paneth of 1 mg. of methylene blue per square meter, the actual surface of 1000 spheres was found to be 15,380 sq. cm. as compared with the 283 sq. cm. of apparent surface calculated from the dimensions of the spheres.

Results and Discussion

Thermal Flow.—In view of the phenomenon of thermal flow observed by Knudsen[5] at low temperatures and pressures, it was necessary to establish a correction curve relating the equilibrium pressure in the apparatus at room temperature with the equilibrium pressure in the cooled portion of the system. Using a gas which is not

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[1] Unpublished.

[2] Lang, *Trans. Roy. Soc., Can.*, **17**, III, 181 (1923).

[3] Waran, *Phil. Mag.*, **42**, 246 (1921).

[4] Paneth and Radu, *Ber.*, **57B**, 1221 (1924).

[5] Knudsen, *Ann. Physik*, **31**, 205, 633 (1910).

adsorbed, the pressure in the cooled portion can be calculated from the equation

$$P_1V_1/RT_1 = P_2V_2/RT_1 + P_3V_3/RT_3 \qquad (1)$$

where P_1 is the calculated pressure obtained from a knowledge of the total gas in the system and the total volume V_1 at temperature T_1, P_2 is the equilibrium pressure measured with the McLeod gage in the volume V_2 at temperature T_1, and P_3 is the equilibrium pressure in the volume V_3 kept at temperature T_3. In this equation all quantities except P_3 are measured.

Four runs were carried out, two using helium and two using hydrogen. One of the hydrogen runs was made with an empty vessel having the same volume as the voids in the chamber filled with spheres. The other runs were made with the spheres in the chamber. The results of these measurements are given in Tables I and II, and Fig. 2. The dotted line in Fig. 2 represents the values obtained from the relation

$$P_3 = P_2\sqrt{T_3/T_1} \qquad (2)$$

which is required by the theory[6] of thermal flow under conditions where the mean free path of the gas is large compared to the diameter of the tubing. It is to be observed that the experimental values approach the theoretical at low pressures, but in the region of 1×10^{-5} to 1×10^{-3} cm. of mercury the deviation is large.

TABLE I

THERMAL FLOW OF HELIUM

Run 1		Run 2	
Temperature of liquid air 93°A.		Temperature of liquid air 94°A.	
P_2, cm.	P_3, cm.	P_2, cm.	P_3, cm.
0.72×10^{-5}	0.17×10^{-5}	0.60×10^{-5}	0.17×10^{-5}
2.08	.89	.95	.69
3.30	1.77	2.25	1.31
4.84	2.56	3.35	2.47
6.59	3.87	5.03	3.29
7.95	4.72	6.40	3.99
13.5	7.96	8.95	6.88
22.5	12.37	14.7	9.64
35.5	21.84	20.1	14.89
52.5	32.10	26.1	19.38
79.7	50.20	43.4	29.3
103.3	71.50	61.3	44.2
		82.7	60.2
		102.2	76.9
		121.8	103.5

TABLE II

THERMAL FLOW OF HYDROGEN

Run 1		Run 2	
In presence of glass spheres		In blank chamber	
Temperature of liquid air 95°A.		Temperature of liquid air 94° A.	
P_2, cm.	P_3, cm.	P_2, cm.	P_3, cm.
0.90×10^{-5}	0.50×10^{-5}	0.64×10^{-5}	0.42×10^{-5}
2.14	1.18	1.85	1.88
3.33	2.07	3.21	2.45
4.79	2.74	5.24	3.11
7.00	3.85	6.40	4.25
8.00	4.65	9.12	5.94
9.83	7.91	20.5	16.9
15.60	12.78	27.6	20.1
23.00	18.23	40.3	29.3
37.2	27.4	55.5	43.7
53.7	42.4	69.0	62.9
66.7	53.1	86.0	77.0
87.0	69.3		
101.1	70.3		

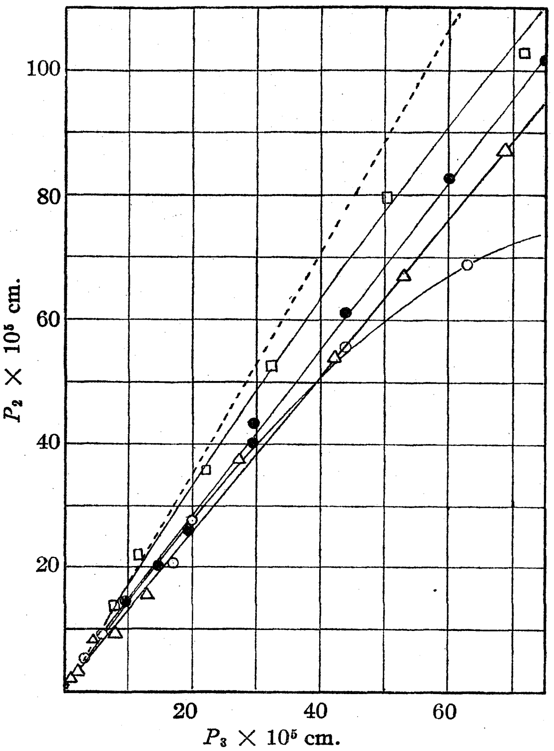

Fig. 2.—Thermal flow: □, helium Run 1; ●, helium Run 2; ○, hydrogen in blank; △, hydrogen with spheres in chamber; – – –, theoretical.

The lack of agreement between the hydrogen curves can be explained by the large adsorbing surface due to the presence of the spheres in one of the two runs. Even though the adsorption of hydrogen is negligible, the disparity in the surfaces of the two experiments is great enough to account for the difference. In the case of the helium no such explanation can be offered. However, it is in accord with observations reported by many experimenters[7] who found that repeated treatment of adsorbing surfaces with a gas enhances the adsorption of the gas.

In comparing the ratios P_3/P_2 for hydrogen in the blank chamber with corresponding ratios for the first helium run, we found them to agree with the assumption of Langmuir[8] that these ratios are

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(6) Reynolds, *Phil. Trans.*, P127 (1879).

(7) Harned, THIS JOURNAL, **42**, 372 (1920); McBain, *Nature*, **117**, 550 (1926); Chaplin, *Proc. Roy. Soc.* (London), **A121**, 344 (1925).

(8) Langmuir, THIS JOURNAL, **40**, 1378 (1918).

equal at pressures corresponding to equal mean free paths. Slight differences in these ratios, those of hydrogen always being higher, most likely indicate the presence of adsorption for hydrogen. This correspondence was taken into consideration in the adsorption calculations of nitrogen described below.

Nitrogen Adsorption.—The results of the experiments on nitrogen are presented in Tables III-IV and Figs. 3 and 4. Column 1 of each table gives the pressures of the gas in the system previous to adsorption. They were calculated from the known amount of gas introduced and the total volume of the system. The values given are all reduced to 0°. In column 2 are given the corresponding pressures reduced to 0° after adsorption has taken place and equilibrium was established. These pressures were measured with the McLeod gage at room temperature. From the measured values of this column and the calibration curve, we obtained the equilibrium pressures in the adsorption chamber which are given in column 3. The adsorption values given in column 4 were calculated by means of the equation

$$A = P_1V_1/RT_1 - (P_2V_2/RT_1 + P_3V_3/RT_3) \qquad (3)$$

where the terms have the same meaning as in equation (1).

To establish a procedure of treatment for the purpose of obtaining reproducible activation of the adsorbing surface, we first tried degassing at

TABLE III

ADSORPTION OF NITROGEN ON GLASS SPHERES

No. of Spheres, 5000. Activated at Room Temperature

Run No. 1
No. contact points per sphere—10.88
Liquid air temperature 92°A.

P_1, cm.	P_2, cm.	P_3, cm.	A, moles
0.77×10^{-5}	0.71×10^{-5}	0.48×10^{-5}	0.00×10^{-8}
1.57	1.54	1.06	.07
3.04	2.78	1.90	.04
5.39	4.71	3.31	.23
9.38	0.89	0.61	6.74
10.80	.83	.55	7.94
12.29	.83	.56	9.12
14.89	1.11	.74	10.97
17.17	1.60	1.06	12.38
19.98	1.97	1.32	14.30
23.51	2.72	1.85	15.74
29.14	4.32	3.01	19.43
38.58	6.30	4.50	25.33
46.86	8.48	6.22	30.11
57.06	13.21	10.49	33.99
68.4	17.74	14.62	38.96
78.7	22.14	18.75	43.20
94.3	30.16	26.96	46.66
108.4	36.44	34.40	53.52
127.6	45.4	45.4	60.25
142.9	53.8	53.8	64.73
173.9	63.6	63.6	80.50
200.0	87.9	87.9	78.95

Run No. 2
No. contact points per sphere—10.88
Liquid air temperature 95°A.

1.03×10^{-5}	0.86×10^{-5}	0.58×10^{-5}	0.09×10^{-8}
1.88	.45	.30	1.16
2.59	.34	.23	1.84
3.19	.34	.23	2.34
4.24	.45	.30	3.11
5.84	.55	.37	4.35
6.65	.62	.41	4.96
11.91	1.55	1.05	8.48
24.76	4.46	3.13	16.53
40.4	8.42	6.17	25.91
57.6	14.0	11.24	34.95

Run No. 3
No. contact points per sphere—10.88
Liquid air temperature 95°A.

0.77×10^{-5}	0.30×10^{-5}	0.20×10^{-5}	0.37×10^{-8}
1.29	.24	.16	.85
1.98	.16	.09	1.50
4.21	.46	.31	3.07
9.47	.92	.62	7.02
34.5	7.16	5.15	22.16
55.2	13.6	10.88	33.35
89.4	32.6	29.76	43.79
109.5	43.3	43.3	49.37
143.9	60.4	60.4	62.11

Run No. 4
No. contact points per sphere—10.92
Liquid air temperature 93°A.

0.59×10^{-5}	0.31×10^{-5}	0.21×10^{-5}	0.21×10^{-8}
1.15	.19	.12	.78
2.22	.19	.12	1.67
3.52	.30	.20	2.65
5.33	.42	.29	4.04
7.84	.65	.43	5.92
10.57	.88	.57	7.98
14.46	1.65	1.12	10.52
19.87	2.66	1.83	14.09
25.6	4.37	3.05	17.31
35.3	7.54	5.47	22.47
43.8	10.1	7.61	27.15
51.2	16.8	13.66	27.01
64.0	22.6	19.35	32.18
73.1	27.4	23.89	35.23
87.8	36.7	34.02	38.44
101.6	45.7	45.52	40.86
122.1	57.8	57.80	46.30
147.5	73.2	73.2	52.74
166.0	80.6	80.6	61.05

Run No. 5
No. contact points per sphere—10.90
Liquid air temperature 92°A.

1.21×10^{-5}	0.84×10^{-5}	0.58×10^{-5}	0.21×10^{-8}
2.02	1.48	1.01	.28
2.96	0.85	0.58	1.60
3.73	.74	.50	2.32
5.28	.82	.56	3.48
8.81	1.61	1.10	5.59
12.09	2.21	1.52	7.66
15.33	3.23	2.22	9.32
18.57	4.62	3.24	10.65
21.52	5.19	3.65	12.50
27.61	7.38	5.54	15.27
37.57	10.7	8.15	21.00
52.40	17.1	14.02	25.72
65.46	23.8	20.37	29.59
83.56	32.5	29.70	35.11
104.3	42.6	41.87	40.95
128.1	57.4	57.40	44.95
142.3	63.9	63.90	49.74
160.2	74.7	74.7	53.37
179.5	87.5	87.5	55.40
199.1	98.0	98.0	60.88
221.8	110.6	110.6	66.35
249.3	124.6	124.6	73.73

Table IV

Adsorption of Nitrogen on Glass Spheres

No. of Spheres—5000. Activated at 250°C.

P_1, cm.	P_2, cm.	P_3, cm.	A, moles
Run No. 9 No. contact points per sphere—10.73 Liquid air temperature 95°A.			
0.68×10^{-5}	0.48×10^{-5}	0.33×10^{-5}	0.09×10^{-8}
1.65	1.14	.76	.25
2.77	1.74	1.16	.62
4.35	0.63	0.42	3.39
5.35	.69	.46	4.26
6.77	.90	.61	5.36
9.19	1.28	.87	7.20
12.41	1.82	1.23	9.61
15.42	2.29	1.57	11.90
19.61	3.18	2.20	14.81
25.8	4.80	3.35	18.74
35.9	6.51	4.65	26.18
48.1	10.27	7.78	32.98
65.7	16.5	13.51	41.47
75.8	18.5	15.32	48.36
90.9	23.1	19.68	56.51
106.6	28.0	24.61	64.78
124.8	35.3	33.08	71.06
148.3	41.9	40.31	83.98
179.6	53.2	53.1	97.14
212.6	63.4	63.4	114.3
251.4	84.7	84.7	122.1
Run No. 10 No. contact points per sphere—10.73 Liquid air temperature 95°A.			
1.23×10^{-5}	0.37×10^{-5}	0.58×10^{-5}	0.16×10^{-8}
2.46	1.81	1.22	.24
3.05	0.36	0.23	2.47
4.33	.57	.38	3.43
6.37	.81	.54	5.07
9.59	1.10	.73	7.77
12.15	1.50	1.02	9.71
15.30	2.04	1.39	12.05
19.59	2.96	2.04	15.02
24.65	3.61	2.45	19.06
30.3	4.48	3.14	23.31
45.6	8.00	5.82	33.48
55.3	11.2	8.58	38.54
69.5	15.8	12.84	45.90
86.8	19.2	15.95	57.76
109.1	28.0	24.6	66.9
138.8	39.3	37.6	78.5
169.6	49.7	49.7	92.9
198.8	59.5	59.5	106.5
234.1	73.5	73.5	120.8
Run No. 11 No. contact points per sphere—11.32 Liquid air temperature 94°A.			
1.27×10^{-5}	0.96×10^{-5}	0.64×10^{-5}	0.09×10^{-8}
3.65	2.14	1.43	.97
6.12	0.82	0.55	4.82
9.52	1.72	1.16	6.98
14.7	2.94	2.01	10.43
20.6	4.39	3.07	14.27
29.6	6.72	4.82	19.94
37.8	9.22	6.83	24.62
51.6	11.6	8.95	34.45
67.6	18.1	14.95	41.0
85.5	23.1	19.66	51.2
108.5	31.7	28.7	60.8
134.6	40.4	38.9	72.7
164.2	49.5	49.5	87.1
190.5	58.6	58.6	99.5
218.9	69.2	69.2	112.2

room temperature, to eliminate the bursting of the sphere chamber on heating, until an arbitrary but fixed rate of rise of pressure in a good vacuum was obtained. This method did not prove successful as shown by the lack of agreement between the isotherms given in Table III and Fig. 3. We next studied adsorption on these spheres after they were degassed at 250° for two and one-half hours.

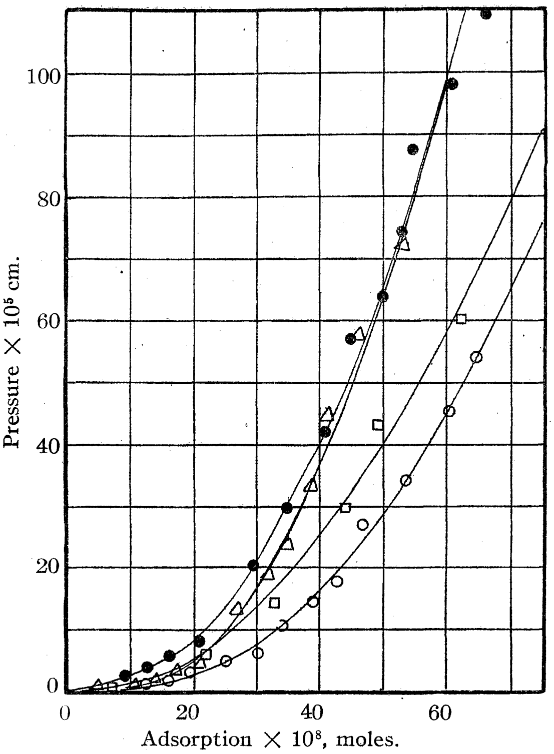

Fig. 3.—Adsorption of nitrogen on glass spheres activated at room temperature: ○, Run 1; □, Run 3; △, Run 4; ●, Run 5.

The results of these runs are given in Table IV and Fig. 4. Curves 9 and 10 are practically identical. Curve 11 shows a slight negative deviation, and is most likely due to a decrease in the adsorbing surface resulting from the greater compactness of the spheres. This higher packing was purposely brought about in order to test for the effect of capillarity. If capillarity played any role, an increase in the number of contacts per sphere should result in an increased adsorption; but since the reverse was actually observed, we must conclude that in this pressure range capillarity seems not to have influenced the adsorption of nitrogen. The observed variations in the adsorption of oxygen of a previous investigation[1] were most likely due to differences in activation of the glass spheres.

Pressure Reversal.—Similar to the results obtained with oxygen we observed pressure reversals also in the isotherms of nitrogen. As shown in Figs. 5 and 6, all isotherms show an abrupt lowering of the equilibrium pressure and a corresponding rapid rise in adsorption. The pressure at which this phenomenon sets in and the lowest pressure reached, referred to here as the reversal point, vary slightly with the isotherm.

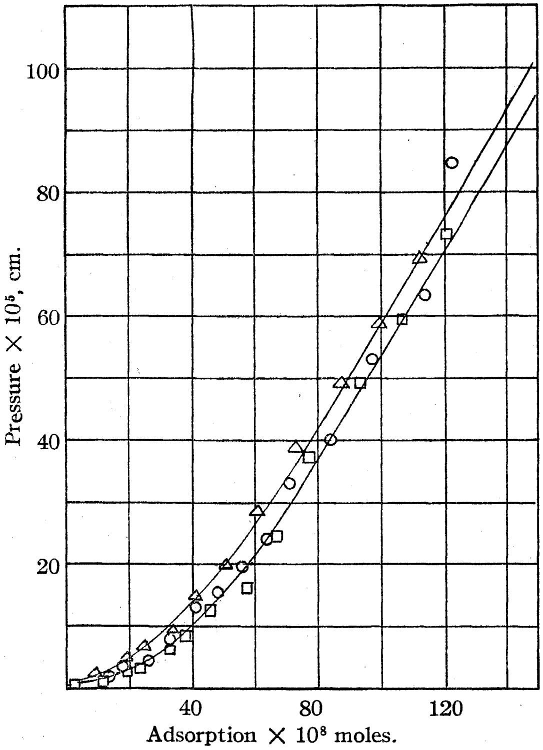

Fig. 4.—Adsorption of nitrogen on glass spheres activated at 250°: ○, Run 9; □, Run 10; △, Run 11.

It was also observed that the rates of adsorption before and after the break were at great variance. Along the linear portion of the isotherm equilibrium was established in the course of a few minutes, while in the receding portion it was established very slowly, sometimes requiring as long as forty-eight hours. It is due to this slowness of the process that curves 1, 2 and 3 show more than one equilibrium point in the receding portions of the isotherms. In all others there was observed only one equilibrium point, namely, the reversal point. Beyond this point equilibrium was attained again very rapidly, although somewhat more slowly than along the linear portion of the isotherm.

This made it evident that the rate of adsorption in the interval in which reversal took place was dependent upon some intermediate slow process which was responsible for the lowering of the equilibrium pressure.

To study the nature of this process the rates of sorption in this region of the isotherm were measured. The intervals of time over which the pressures were observed varied from ten to twenty hours, depending upon the initial pressure, *i. e.*, the quantity of gas introduced. The pressure–time curves so obtained on a number of isotherms were found to be identical in character. With the exception of the initial period of approximately five minutes where the pressure falls very rapidly and adsorption is apparently the dominating process, as shown by the typical curve in Fig. 7, each curve follows fairly closely the equation

$$\text{Ln } P/P_0 = kt \qquad (4)$$

where P is the pressure at time t, and P_0 is the initial pressure of the intermediate slow process at $t = 0$. The value of k, the specific reaction rate, was found to be the same for all isotherms studied.

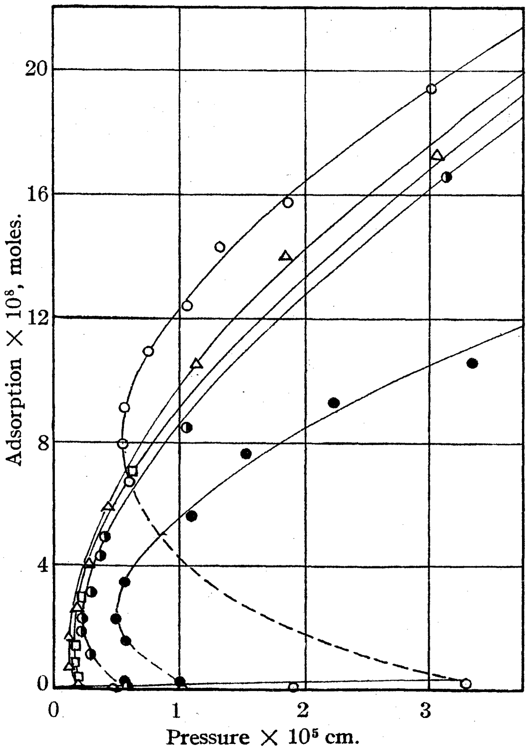

Fig. 5.—Adsorption of nitrogen at low pressures on glass spheres activated at room temperature: ○, Run 1; ◑, Run 2; □, Run 3; △, Run 4; ●, Run 5.

It might be assumed, in view of its being frequently associated with adsorption in porous bodies, that the intermediate slow process is due to absorption and the slow diffusion of the gaseous molecules through the cracks and crevices in the spheres which may have been there or have formed during the activation treatment to which the system was subjected numerous times. This seems to be supported by the consideration that theoretically absorption processes follow equation (4). However, because it was not observed after carefully testing for it at higher pressures both along the linear portion of the isotherm preceding and the portion of the isotherm following the point of reversal, absorption is most likely not the cause of the reversal phenomenon. The phenomenon is easily explained, if we assume that the adsorbed phase exists in two different states of aggregation. While there is no direct evidence to that effect, the behavior of films on liquid surfaces makes this assumption very plausible. On this basis the break in the isotherm represents the transition of the adsorbed phase from one state into the other; and the reversal in the equilibrium pressure is undoubtedly due to the tendency of the initial state toward supersaturation, as indicated by the abruptness or explosiveness of the first stage of the reversal process. The assumption is also in agreement with the measurements on the rate of the reversal process, as all transition processes follow the equation of first order reactions.

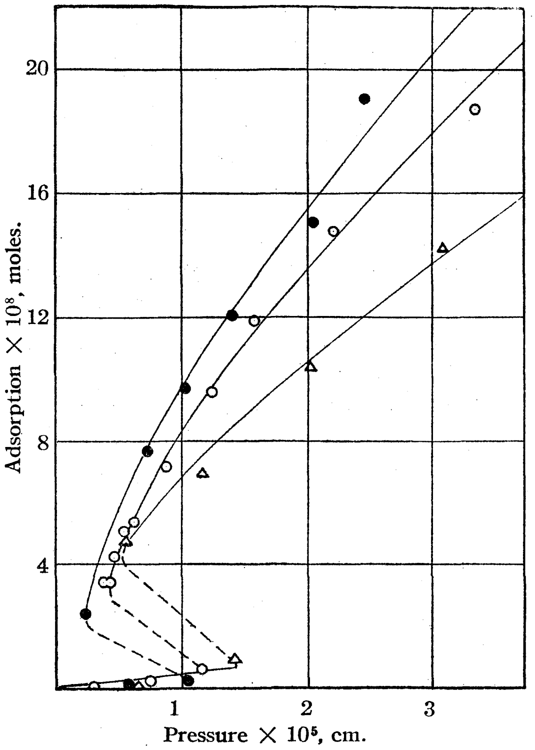

Fig. 6.—Adsorption of nitrogen at low pressures on glass spheres activated at 250°: ○, Run 9; ●, Run 10; △, Run 11.

As to the nature of the states, only the most general observations can be made. The branch of the isotherm to the left of the break seems, in view of the low pressures and the linear relationship between it and the adsorption, to represent a state in which the adsorbed gas obeys Boyle's law. In this state the van der Waals constants are either ineffective or compensating, with the result that the gas is ideal in behavior, and the adsorption isotherm follows Henry's law. In the state of the adsorbed phase described by the branch of the isotherm extending to the right of the break, the gas due to the van der Waals forces is most likely liquefied, as evidenced by the increased rise of adsorption with pressure and the abruptness of the transition. The course of adsorption in this phase seems to depend also upon the heterogeneity of the surface, as will be shown in the discussion to follow.

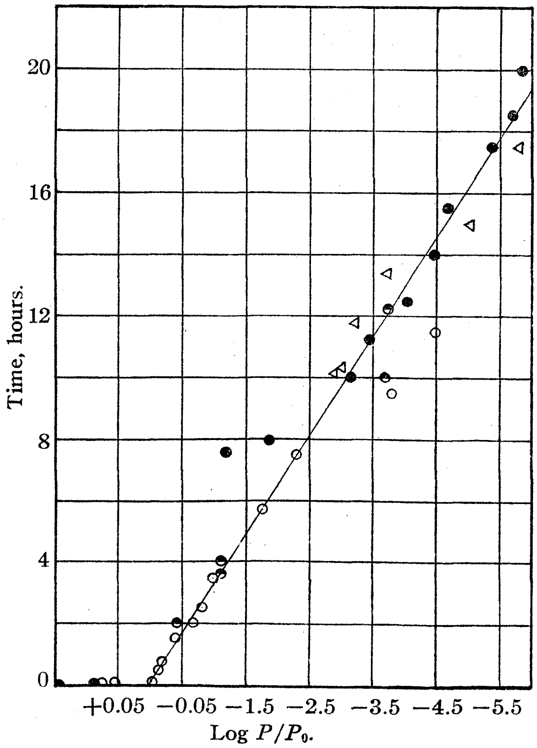

Fig. 7.—Rate of sorption at reversal point: ●, Run 1; ◑, Run 5; ○, Run 9; △, Run 10.

Adsorption Isotherm.—It is clear that no present adsorption theory will apply to the complete isotherm obtained in these experiments, and consequently in subsequent discussions reference is made only to the regular branch shown in Figs. 3 and 4.

A graphical analysis of a typical adsorption isotherm in the manner described by Cunningham[9] yielded the information that two principal types of adsorption occurred in this region. It was therefore expected that Langmuir's simple equation[10]

$$A = abP/(1 + bP) \qquad (5)$$

will not apply to these data. Such is actually the case, for graphs of P/A against P show consistently large deviations from linearity. However, an equation based on the assumption of two different elementary spaces,[10] namely

$$A = a_1b_1P/(1 + b_1P) + a_2b_2P/(1 + b_2P) \qquad (6)$$

was also found not to apply. Attempts to fit this equation to several sets of data by a few different methods, including the method of least squares, produced results which were meaningless from the point of view of Langmuir's hypotheses. Similar attempts to apply to our results the equations of Zeise[11] and of Williams–Henry[12] proved unsuccessful. On the other hand, fitting our data to the Freundlich equation[13] results in two straight lines for every isotherm, which seems to be in agreement with the two types of adsorption shown by Cunningham's method of analysis.[9]

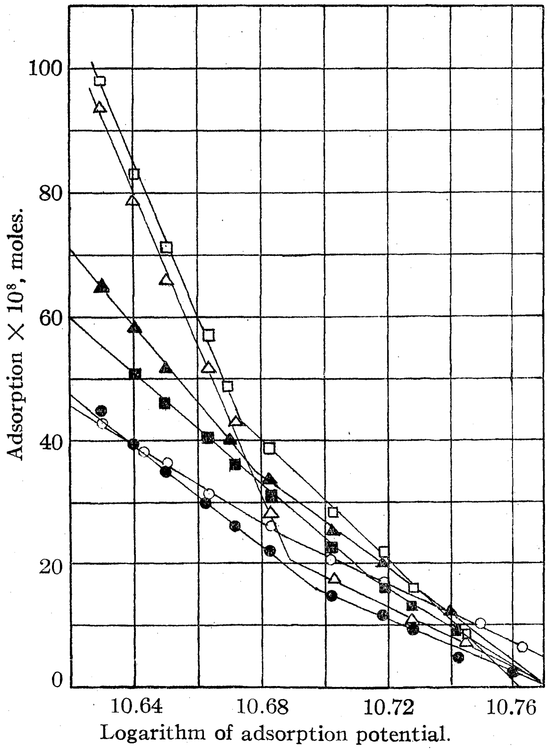

Fig. 8.—Application of equation of Palmer and Clark: ▲, Run 1; ■, Run 3; ○, Run 4; ●, Run 5; □, Runs 9 and 10; △, Run 11.

We next attempted to apply the relationship recently suggested by Palmer and Clark,[14] who assumed direct proportionality between the logarithm of the adsorption potential and the adsorption, the potential being defined in accordance with Polanyi[15] by the equation

$$\epsilon = RT \ln (P_x/P_s) \qquad (7)$$

where P_s is the saturation pressure, in this case 283 cm. of mercury,[16] and P_x is the equilibrium pressure. The plotting of our results in this manner produced two straight lines for each isotherm as shown in Fig. 8. Assuming that the two straight lines represent two different types of adsorption, we obtain by extrapolating each line to zero adsorption the maximum potential corresponding to each type. These maximum potentials correspond to the minimum pressures below which the corresponding types of adsorption cannot take place. This assumption seems to be verified by the fact that the calculated values of P_x corresponding to the maximum potentials of the upper straight line of each isotherm check fairly closely the pressures corresponding to the reversal points, which are most likely points of inflection marking the beginning of the condensed adsorption phase. This agreement is shown in Table V where the values of ϵ_m obtained by extrapolation are given in column 1; the corresponding calculated equilibrium pressures are given in column 2 and the observed pressures in column 3.

TABLE V

THE MINIMUM PRESSURES OF ADSORPTION OF NITROGEN ON GLASS

Run	ϵ_m, ergs	P (calcd.), cm.	P (meas.), cm.
9	5.81×10^{10}	0.45×10^{-5}	0.42×10^{-5}
4	6.17	.18	.12
5	5.85	.43	.50
11	5.94	.32	.55
10	5.81	.45	.23
3	6.03	.22	.09
2	6.10	.20	.23

Summary

1. The thermal flow effect of hydrogen and helium was determined and found to agree at

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(9) Cunningham, *J. Phys. Chem.*, **39**, 69 (1935).

(10) Langmuir, THIS JOURNAL, **40**, 1384 (1918).

(11) Zeise, *Z. physik. Chem.*, **136**, 397 (1928).

(12) Williams, *Proc. Roy. Soc.* (London), **A96**, 287 (1919); Henry, *Phil. Mag.*, [6] **44**, 689 (1922).

(13) Freundlich, *Z. physik. Chem.*, **57**, 385 (1906).

(14) Palmer and Clark, *Proc. Roy. Soc.* (London), **A149**, 360 (1935).

(15) Polanyi, *Verhandl. deut. physik. Ges.*, **16**, 1012 (1914).

(16) "International Critical Tables," Vol. III, p. 204.

pressures corresponding to equal mean free paths.

2. The activation of glass surfaces was studied under different conditions.

3. The adsorption of nitrogen on glass spheres at liquid air temperatures was studied. Different degrees of packing of the spheres was found to have no effect on the adsorption.

4. Similar to oxygen the adsorption isotherm of nitrogen at low pressures shows the unusual phenomenon of recession of the equilibrium pressure. A possible explanation for this behavior is suggested.

5. The application of various adsorption theories to the data is discussed.

WASHINGTON, D.C. RECEIVED AUGUST 15, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF BRITISH COLUMBIA]

The Mutual Solubilities of Hydrocarbons. I. The Freezing Point Curves of Dotriacontane (Dicetyl) in Propane and Butane

BY W. F. SEYER AND REID FORDYCE

A considerable amount of information exists concerning the mutual solubilities of hydrocarbons. Thus over thirty years ago Holde was familiar with the fact that light hydrocarbons when added to petroleum caused the asphalt portion to be precipitated. This idea was further extended by Kling[1] in 1922 and by S. V. Pilatt and M. Godlevicz[2] in 1932. This work established the fact that mutual solubility among hydrocarbons was governed largely by the molecular weights of solute and solvent. Already extensive use has been made of this knowledge to isolate and purify certain petroleum fractions by utilizing solvents of various selective powers. So far all the information which has been forthcoming has been of a qualitative nature; consequently before much more headway can be made along this line, quantitative measurements concerning the solubility relationships existing among simple systems of hydrocarbons must be made. The following pages deal with the results obtained from a study of the systems, dotriacontane (dicetyl, $C_{32}H_{66}$) and propane and dotriacontane and butane.

Materials.—The propane and butane were purchased from The Ohio Chemical & Manufacturing Company, Cleveland. These gases were listed C. P. and the butane was claimed to be free of propane but to contain a trace of isobutane, while an analysis of the propane failed to reveal any traces of either of the two isomeric butanes. The hydrocarbon, dicetyl, was synthesized from Eastman C. P. cetyl alcohol by the method first used by Kraft.[3] The hydrocarbon was recrystallized five times from ether until no change in melting point could be detected. The final melting point was 69.9° as measured by a standardized mercury thermometer. This agrees with the findings of Hildebrand and Wachter who have pointed out that the true melting point of the hydrocarbon must be in the neighborhood of 70°.[4]

Experimental Procedure

The time honored bulb method was considered the most practical one for the determination of the freezing points. In the present case this method was susceptible of considerable accuracy because of the "cloud effect"; *i. e.*, whenever a solution of dicetyl in either propane or butane was cooled beyond the limits of solubility a white suspension immediately developed. The phenomenon is apparently due to the formation of tiny crystals of the high molecular weight hydrocarbon. The point of appearance and disappearance of these crystals was extremely sharp and did not vary more than ±0.02° in any case. The difference between the two temperatures was never greater than 0.05°.

Thick-walled uniform bulbs, 2 cm. in diameter, were blown and to these were attached glass stems 9 cm. long and 2 mm. in diameter. Varying amounts of dotriacontane were introduced by first melting the hydrocarbon and then allowing it to run down a long stemmed funnel into the bulb proper. The bulbs, after weighing, were then sealed onto the apparatus outlined in Fig. 1, evacuated and the required amounts of butane or propane condensed in each. These gases were stored in two 5-liter flasks which served as gas holders and which were placed in an insulated box whose temperature could be controlled. Before allowing either of these two gases to diffuse into the systems, it was evacuated by means of a mercury vapor pump down to a pressure of the order of 0.001 mm. as measured by a McLeod gage. Knowing the volume of the apparatus and noting the pressure changes on the manometer, it was a simple matter to calculate the amounts of gases condensed in the bulbs before they were sealed and detached from the apparatus. The amounts of the hydrocarbons in each bulb were again measured by weighing the sealed bulb after the freezing point had been obtained, then breaking off the tip, allowing the gas to escape and then weighing again.

Besides the buoyancy correction one other one was con-

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[1] Kling, German Patent 362,458.

[2] S. V. Pilatt and M. Godlevicz, *Oel und Kohle*, **11**, 655 (1935).

[3] Kraft, *Ber.*, **40**, 4783 (1907).

[4] Hildebrand and Wachter, THIS JOURNAL, **51**, 2487 (1929).

sidered necessary. This was the amount of solvent present in the vapor phase. This amount of propane or butane is of course not effective in dissolving the dicetyl. Since this correction was small in any case, no great error was made in assuming the perfect gas law in the calculations. The values of the vapor pressures of butane at the various temperatures were calculated from the equation $\log_{10}p = 7.3948 - 1224.8/T$ given in the "International Critical Tables." The best values obtainable for the propane pressures over the temperature range of the investigation were those of A. W. Francis and G. W. Robbins[5] whose equation $\log_{10}p = 4.375 - 1010/T$ was used. The volume of vapor was found approximately by measuring the amount of water required to fill the vapor space in each bulb. Throughout the range of temperature covered by the investigation, the partial pressure of the dicetyl was so small it could be neglected and the total pressure was therefore sensibly equal to the vapor pressures of the low molecular weight hydrocarbons.

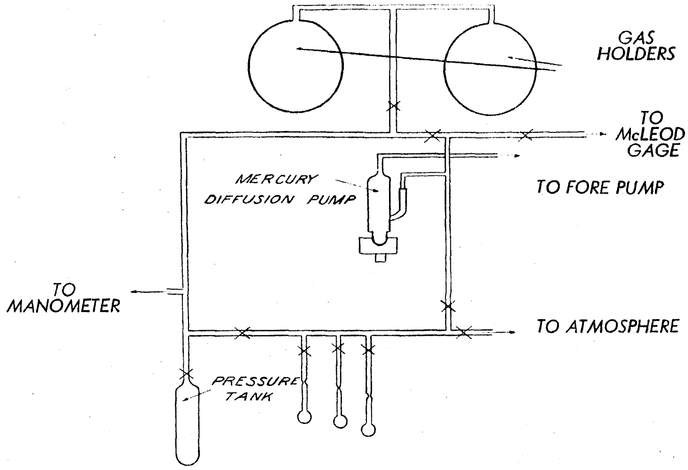

Fig. 1.—Condensing apparatus.

TABLE I

BUTANE–DOTRIACONTANE

Dotriacontane, g.	Butane, g.	Effective wt. of butane, g.	Mol. % dotriacontane	F. p., °C.
			0	−135.0[a]
0.0922	5.7882	5.7869	0.206	17.26
.0959	4.2977	4.2962	.288	20.02
.1241	4.9919	4.9902	.321	20.48
.0398	1.0640	1.0623	.482	24.09
.0447	0.6886	0.6866	.832	27.49
.1267	1.2102	1.2080	1.335	30.47
.1659	0.8931	0.8905	2.347	34.34
.2225	.8385	.8332	3.33	36.60
.3809	1.1587	1.1557	4.08	38.00
.3934	.8103	.8069	5.92	40.40
.3374	.6165	.6133	6.63	41.98
.4097	.6827	.6789	7.23	42.13
.4958	.7013	.6983	8.41	43.40
.4695	.4666	.4630	11.55	46.51
.6421	.3147	.3100	21.10	53.06
.6896	.3092	.3052	22.55	53.15
.7422	.2764	.2714	26.10	54.56
.7630	.1384	.1328	42.55	60.91
.4764	.0179	.0116	81.00	67.80
			100	69.90

[a] From "International Critical Tables."

The weights of dicetyl, of butane or propane, the effective weight, the molal concentration and the freezing points of these concentrations are given in Tables I and II.

In Fig. 1 the freezing point temperatures have been plotted against concentrations in mole per cent. It will be seen that in the neighborhood of 55° there is a slight change in curvature. From this point downward solubility changes rapidly with temperature. It would thus appear that there were two forms of the hydrocarbon and that at the above-mentioned temperature transition from one form into another takes place. Further evidence for the existence of two forms has been found by measuring the refractive index of the solid dicetyl at various temperatures below its melting point with the help of an Abbé refractometer. These figures are given in Table III.

TABLE II

PROPANE–DOTRIACONTANE

Dotriacontane, g.	Propane, g.	Effective wt. of propane, g.	Mol. % dotriacontane	F. p., °C.
			0	−189.9[a]
4.7368	4.6634	4.6581	0.16	22.30
0.1195	1.3401	1.3331	.87	34.03
.1195	1.0244	1.0181	1.136	35.70
.3107	1.1443	1.1361	2.61	39.31
.3107	0.6771	0.6688	4.36	42.13
.3661	.5434	.5374	6.27	44.13
.4769	.6398	.6309	6.92	44.30
.3661	.4381	.4289	7.72	45.80
.4769	.4628	.4543	9.28	46.81
.5617	.4180	.3831	12.54	49.72
.8449	.4895	.4895	14.46	50.53
.6388	.3309	.3207	16.45	52.63
.6583	.3222	.3113	17.15	52.90
.8449	.2393	.2272	26.70	57.90
.8527	.1663	.1545	35.0	59.88
.8787	.1135	.1015	45.80	62.42
1.2204	.1164	.1038	53.5	63.71
1.2716	.0952	.0824	60.3	64.54
			100	69.9

[a] From "International Critical Tables."

Below 55° it was extremely difficult to get accurate readings on the instruments although the temperatures were kept constant to within one-half of a degree for some hours. When, however,

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(5) Francis and Robbins, THIS JOURNAL, **55**, 4339 (1933).

TABLE III

Refractive index	Temp., °C.
1.4364 (liquid)	70
1.4738	65
1.5010	60
1.5464	57.5
1.5573	55
1.5597	50
1.5605	45
1.5632	40
1.5676	30

the figures are plotted against temperature as in Fig. 2, it is quite evident that two forms of the hydrocarbon exist and that the transition point is in the vicinity of 55°. This of course is what one should expect from the observations of Carpenter,[6] Rhodes[7] and others.

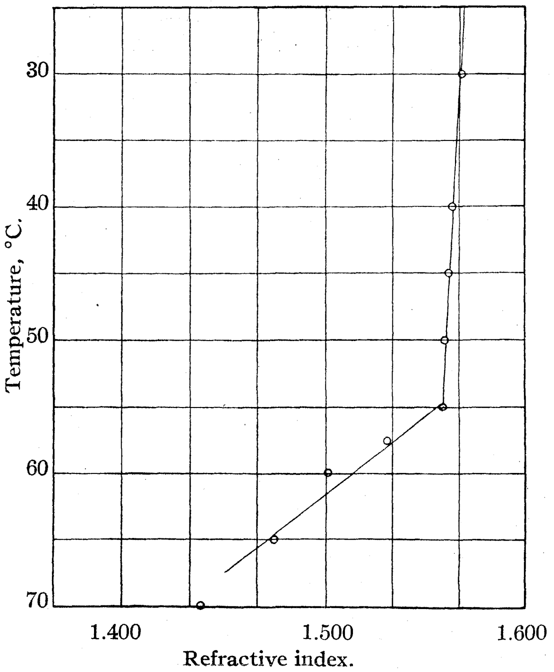

Fig. 2.

The solubility curves of the dotriacontane in propane and butane coincide until a concentration of about 50% is reached; from here on they diverge until a very low concentration is reached at temperatures below 30°. It is obvious from the shape of the curves that the solubility of the high molecular weight hydrocarbon falls off to extremely low values at low temperatures.

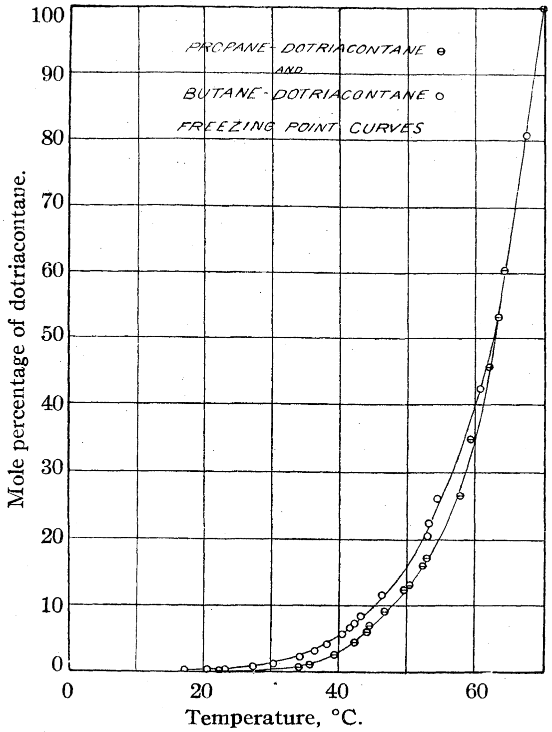

Fig. 3.—Freezing point curves: ⊖, propane–dotriacontane; ○, butane–dotriacontane.

Summary

1. The freezing points of solutions of dotriacontane (dicetyl) in propane and in butane have been found.

2. The curves constructed from the freezing point data indicate the occurrence of two forms of the high molecular weight hydrocarbon. Change of refractive index with temperature shows this to be the case and that the transition temperature is about 55°.

VANCOUVER, CANADA
RECEIVED JUNE 18, 1936

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(6) J. A. Carpenter, *J. Inst. Petroleum Tech.*, **12**, 288 (1926).

(7) F. H. Rhodes, C. W. Mason and W. R. Sutton, *Ind. Eng. Chem.*, **19**, 935 (1927).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF NEW HAMPSHIRE]

The Activity and Osmotic Coefficients of Aqueous Solutions of Lanthanum Chloride at 25°

BY CHARLES M. MASON AND GRACE L. ERNST

The present communication is concerned with the calculation of the activity and osmotic coefficients of lanthanum chloride in aqueous solution at 25°. These quantities have been calculated from the vapor pressures of the aqueous solutions obtained by the isotonic method of Robinson and Sinclair.[1]

Experimental Details

Apparatus.—The apparatus employed was the same as that described by Mason and Gardner[2] except for a few minor alterations. Six glass weighing bottles with ground-in stoppers were employed instead of the nickel crucibles. The metal tee tube was replaced by a brass needle valve to which was soldered the female half of a brass union. The male half of the union was connected by means of rubber tubing to the vacuum line. Another male half of the union interchangeable with the first was soldered shut and served to keep water out of the valve during immersion in the thermostat.

All measurements were carried out in a water thermostat at 25 ± 0.01°. The temperature was determined by thermometers checked against thermometers calibrated by the Bureau of Standards.

Lanthanum Chloride.—The lanthanum salt had been prepared carefully by repeated recrystallization. The chloride was prepared from the oxalate by ignition to the oxide and solution of this in redistilled, arsenic free hydrochloric acid. The chloride so prepared was then twice recrystallized by concentration of the aqueous solution and shaking out with hydrogen chloride gas at 0°. It was then carefully air-dried at 50° and placed for several weeks in a vacuum desiccator over potassium hydroxide. Examination of the solutions with the hand spectroscope and by chemical test showed the absence of other rare earths. The lanthanum chloride was dissolved in water to make a concentrated solution which was carefully analyzed gravimetrically for chloride content. This solution was then weighed out into the weighing bottles as needed.

Potassium Chloride.—The best C. P. grade of potassium chloride was twice recrystallized from conductivity water and then dried for twenty-four hours at 120°. This salt was weighed directly into the weighing bottles.

Results

Three samples of each concentration of lanthanum chloride solution were allowed to come to isopiestic equilibrium with three samples of the reference, potassium chloride solution. The data obtained are, therefore, in each case the mean of three determinations. These data are given in Table I.

TABLE I

CONCENTRATIONS OF ISOPIESTIC SOLUTIONS OF POTASSIUM CHLORIDE (m_1) AND LANTHANUM CHLORIDE (m_2)

m_1	m_2	m_1	m_2
0.2157	0.1091	2.5870	1.0272
.4298	.2281	2.8414	1.0967
.5697	.3063	3.2548	1.2071
.7399	.3895	3.4075	1.2472
1.0312	.5069	3.4381	1.2574
1.4362	.6603	3.5795	1.2908
1.7105	.7548	3.7674	1.3381
1.7321	.7618	3.8541	1.3595
2.0895	.8767	3.8814	1.3663
2.4924	.9985	4.1533	1.4317
		4.2776	1.4573

It was found that forty-eight hours were sufficient for equilibrium between the concentrated solutions. For the dilute solutions it was necessary to run them as long as four days to obtain equilibrium. Concentrations below 0.1 m would not come to equilibrium in any length of time. This is in accordance with the experience of Robinson and Jones[3] for higher valence types.

The data given in Table I were plotted, m_1 *vs.* m_2, on a large scale. Values of m_1 and m_2 were then obtained from this curve at round concentrations of lanthanum chloride. The vapor pressures of these isopiestic solutions were then obtained by calculation from the equation

$$R = (p_0 - p)/mp_0$$

The values of R for this calculation were obtained from a large scale plot of the values given by Robinson and Sinclair[1] for potassium chloride solutions.

The values of the activities of the water in the solutions were then calculated from the equation $a_1 = p/p_0$.

The osmotic coefficient φ was calculated by means of the equation $\varphi = (55.51/4m_2) \ln p_0/p$. These data are all given in Table II.

The activity coefficients of the lanthanum chloride in the solutions were calculated by the method of Randall and White[4] using the value 2.84 as the

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(1) Robinson and Sinclair, THIS JOURNAL, **56**, 1830 (1934).

(2) Mason and Gardner, *J. Chem. Ed.*, **13**, 188 (1936).

(3) Robinson and Jones, THIS JOURNAL, **58**, 959 (1936).

(4) Randall and White, *ibid.*, **48**, 2514 (1926).

TABLE II

VAPOR PRESSURES, OSMOTIC COEFFICIENTS AND ACTIVITY COEFFICIENTS OF LANTHANUM CHLORIDE SOLUTIONS

m_2	p, mm.	a_2	φ	γ obsd.	γ calcd.
0.0	23.756[a]	1.000	1.000	1.000	1.000
.1	23.609	0.9938	0.860	0.318	0.309
.2	23.467	.9878	.849	.269	.269
.3036	23.321	.9817	.837	.247	.254
.5	22.986	.9676	.915	.250	.249
.7	22.586	.9508	1.001	.272	
1.0	21.860	.9202	1.154	.322	
1.2	21.283	.8959	1.271	.376	
1.4	20.642	.8689	1.393	.446	
1.5	20.290	.8541	1.459	.491	

[a] "International Critical Tables," Vol. III, p. 210.

zero intercept on the $h/m_2^{1/2}$ axis, which was calculated from the value for the dielectric constant for water obtained by Wyman.[5] The calculated values are tabulated as $\gamma_{\text{obsd.}}$ in Table II. In order to provide some means of comparison with existing data the values of the activity coefficients obtained by this means have been plotted with similar values for lanthanum nitrate obtained from Landolt–Börnstein.[6] This plot, which also contains the values of the osmotic coefficients obtained, is shown in Fig. 1.

The constants A and B have been calculated for the Hückel equation[7]

$$\log \gamma = -\frac{1.068\sqrt{12c}}{1 + A\sqrt{12c}} + B(12c) - \log(1 + 0.072m)$$

A and B were found to be 1.096 and 0.02027, respectively. These values were used in the Hückel equation to calculate the activity coefficients of the lanthanum chloride solutions for which the densities had been determined by Mason and Leland.[8] The values which were obtained from the calculation are given as $\gamma_{\text{calcd.}}$ in Table II.

The value of A obtained gives a tentative value of 4.7×10^{-8} cm. for the mean distance of approach "a."

The values obtained follow the general trend noted for all electrolytes, namely, a minimum in the curve when the activity coefficient is plotted against the ionic strength. They are, of course, open to the criticism of some uncertainty due to possible variation of the graphical integration below 0.1 molal. This is, however, unavoidable with this method which is not applicable with accuracy below this concentration.

Summary

1. The vapor pressures of aqueous solutions of lanthanum chloride have been determined by the isopiestic method, using potassium chloride for the reference substance.

2. The activity and osmotic coefficients of the lanthanum chloride solutions have been calculated from the vapor pressure data.

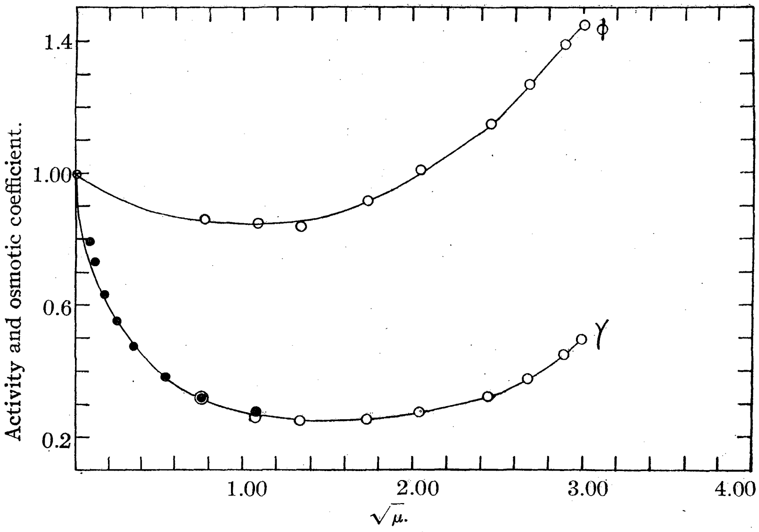

Fig. 1.—Activity and osmotic coefficients: ○, $LaCl_3$; ●, $La(NO_3)_3$.

3. The activity coefficient of lanthanum chloride in aqueous solution may be calculated by Hückel's equation, which is

$$\log \gamma = -\frac{1.068\sqrt{12c}}{1+1.096\sqrt{12c}} + 0.02027(12c) - \log(1 + 0.072m)$$

for lanthanum chloride solutions.

DURHAM, N. H.

RECEIVED JULY 18, 1936

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[5] Wyman, *Phys. Rev.*, **35**, 623 (1930).

[6] Landolt–Börnstein–Roth–Scheel, "Tabellen," (5) II Ergänzungsband, Verlag Julius Springer, Berlin, 1931, p. 1123.

[7] Hückel, *Physik. Z.*, **26**, 93 (1925).

[8] Mason and Leland, THIS JOURNAL, **57**, 1507 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Deutero-acetaldehyde (Acetaldehyde-d_4)

BY J. E. ZANETTI AND D. V. SICKMAN

The synthesis of acetaldehyde-d_4 by the hydration of acetylene-d_2 appeared to the writers as a desirable method of approach to the organic chemistry of deuterium inasmuch as the reacting materials were easily obtainable and the reaction lent itself to being carried out in a closed system.

The hydration of acetylene-d_2 with deuterium oxide was first attempted in the vapor phase by passing acetylene-d_2 and deuterium oxide vapor over a tungsten oxide catalyst at 400° but the copious formation of polymerization products made this method unsuitable for working with a comparatively expensive material. The absorption of acetylene by a deuterium oxide solution of phosphoric acid in the presence of mercuric sulfate was finally adopted and found to work very satisfactorily.

Deutero-acetaldehyde and the corresponding polymerization product, deutero-paraldehyde were thus obtained in a reasonably pure state. A preliminary notice of this work has already been published.[1]

The product obtained does not appear to differ chemically from ordinary acetaldehyde although there remains the question as to whether the reactions exhibited are due to the deutero-aldehyde group—CD=O or to an ordinary aldehyde group formed by an interchange reaction either with the solvent or the reagent. Until a set of pure deuterium reagents becomes available or it can be definitely established that such an interchange does not occur, that question cannot be answered.

The physical properties are, however, definitely changed. The densities, particularly, are considerably increased. It is to be noted that the molecular volumes—as far as they can be determined by comparing densities at equal temperatures—remain constant. The melting points of both the deutero-acetaldehyde and the corresponding paraldehyde are distinctly higher but there is little difference in the boiling points.

The Raman spectrum as determined by Professor R. W. Wood of Johns Hopkins University[2] showed the expected shift in lines.

For purposes of comparison the physical constants of acetaldehyde and of deutero-acetaldehyde are given together in Table I.

Experimental Part

Materials.—As the calcium carbide of commerce contains considerable amounts of calcium hydroxide which by exchange reactions would contaminate the deutero-acetylene made from it, the calcium carbide used in these experiments was made in an induction furnace by heating to 1800–2000° precipitated calcium carbonate mixed in proper proportions with thermatomic carbon (carbon from the thermal decomposition of natural gas). The carbonate had but traces of sulfate and no phosphate that could be detected. There were no mineral impurities in the carbon used. The crucibles were made by boring out 3″ (7.6 cm.) graphite electrodes. Every precaution was taken to prevent contamination of the carbide, which was kept in glass-stoppered bottles sealed with paraffin. The carbide for this and other experiments was made in small batches of about 250 g. as needed so as to avoid keeping any of it over long periods.

The deuterium oxide was procured from Rjukan, Norway, and was redistilled and checked for purity by the interferometer method.[3] It analyzed 99.6% deuterium oxide.

Apparatus.—In order to avoid as much as possible contamination with moisture from the air the synthesis was carried out in a closed system made entirely of Pyrex glass. The apparatus, Fig. 1, consisted of a generator A into which the carbide was dropped through a side tube and the deuterium oxide dropped on it from a small separatory funnel. The deutero-acetylene was collected over mercury in the reservoirs B and B′ each holding about one liter and from there passed into the absorption vessel C which during the reaction was shaken vigorously. This was permitted by a glass spiral in the gas line. The shaking machine was operated by a small motor D provided with an eccentric.

Operation.—About 1 g. of dry mercuric sulfate was placed in the absorption vessel. A tube containing approximately the amount of phosphorus pentoxide was sealed to one of the side tubes of the absorption vessel, the entire apparatus exhausted to dry it as completely as possible and, after letting in dry air, 25 to 30 g. of phosphorus pentoxide was volatilized into the reaction vessel in a current of dry oxygen.

A tube containing 25 g. of deuterium oxide was then sealed in and the water distilled into the reaction vessel under a pressure of less than 1 mm. Every precaution was taken at all times to prevent not only contamination with moisture from the air but with moisture from the oxygen torch employed in sealing. Stopcocks were suitably arranged so that any moisture formed could be pumped out without coming in contact with the reaction materials. The absorbing solution consisted then of a 40–50% deutero-

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(1) THIS JOURNAL, 57, 2735 (1935).

(2) A discussion of this matter will be the subject of a separate communication by Professor Wood.

(3) Crist, Murphy and Urey, *J. Chem. Phys.*, 2, 112 (1932).

phosphoric acid in deuterium oxide with 1 g. of mercuric sulfate as catalyzer. Acetylene-d_2 was then led in from one of the reservoirs, the other being used as storage for the acetylene that continued to be evolved after the deuterium oxide had been turned off. Vigorous shaking greatly facilitated the reaction.

The absorption was rapid at first, as much as 1 liter of acetylene-d_2 being absorbed in twenty minutes, but the rate gradually diminished to about 1 liter an hour. When acetylene ceased to be absorbed, the apparatus was connected with a cooling system and the contents of the vessel distilled under reduced pressure at room temperature, except toward the end when gentle heat was applied. Dissolved acetylene-d_2, acetaldehyde-d_4, deuterium oxide and paraldehyde-d_{12} came over and had to be fractionated. The fractionation was carried out entirely under a pressure of a fraction of a millimeter, using solid carbon dioxide–acetone and liquid air for obtaining the desired temperatures. Some 50 g. of the acetaldehyde and 6 g. of the paraldehyde were thus prepared.

The residue in the reaction vessel consisting of phosphoric acid, polymerization products and compounds of mercury was treated with anhydrous sodium carbonate and potassium permanganate to recover the deuterium as deuterium oxide. The residue of calcium deuteroxide from the acetylene generator was distilled at 700–800° and the deuterium oxide recovered.

Deutero-acetaldehyde.—After numerous fractionations deutero-acetaldehyde was obtained as a water white mobile liquid with a sharp odor and burning taste. The physical constants are given in Table I. Chemically it behaves, as far as could be determined, as ordinary acetaldehyde. It reduces ammoniacal silver oxide, restores the color to a fuchsine–sulfur dioxide solution and gives crystalline compounds with ammonia (small white cubes, m. p. 92–94°, dec.) and with sodium bisulfite. It resinifies when heated with alkalies.

About 2 g. was burned over copper oxide in a current of oxygen and the recovered water analyzed by the interferometer method showing 99.2% pure D_2O. This means that despite all precautions about 0.4% of ordinary water must have entered into the reaction and contaminated the deuterium.

The tendency of the acetaldehyde to polymerize is present in the deutero compound particularly after exposure to the air. Appreciable amounts of deutero-paraldehyde were found when sealed tubes in which the aldehyde was kept were opened after standing for some weeks.

Deutero-paraldehyde.—One of the fractions of the reaction consisted of deutero-paraldehyde and deuterium oxide. The same relation appears to exist between these two as between paraldehyde and water. The solubility of the paraldehyde decreases with increasing temperature. The paraldehyde layer which floated on top of the deuterium oxide was separated, dried with "drierite" and fractionally distilled. The paraldehyde was obtained as a water white oily liquid with a mint-like odor and a cooling taste. The physical properties are given in Table I. When solidified below 13°, the paraldehyde crystallizes in long prismatic needles.

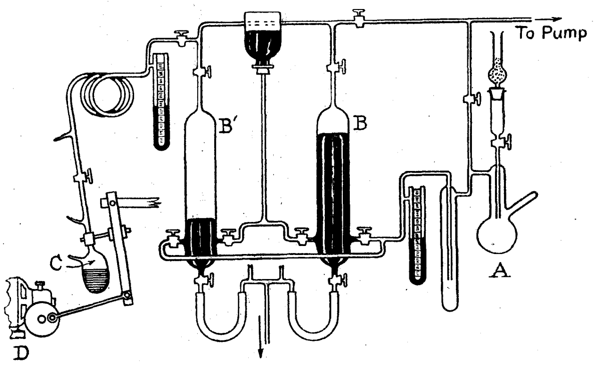

Fig. 1.

A microanalysis gave: C, 50.1, 50.3; D, 16.3, 16.5. Calcd. for $(C_2D_4O)_3$: C, 50.0; D, 16.7.

TABLE I

	Acetaldehyde	Acetaldehyde-d_4
B. p., °C.	20.2 (1 atm.)	20.5 (756 mm.)
M. p., °C.	−123.5	−121.7
D^{0}_{0}	0.806[4]	0.883
V. p., 0°C.	331 mm.[4]	327 mm.
	Paraldehyde	Paraldehyde-d_{12}
B. p., °C.	124 (1 atm.)	124–125 (753 mm.)
M. p., °C.	10.5	13.7
d^{20}_{20}	0.994	1.078

Acknowledgment.—The writers are indebted to the Chemical Foundation, Inc., of New York City, for a generous gift that made this research possible.

Summary

Acetaldehyde-d_4 and paraldehyde-d_{12} were obtained by the action of acetylene-d_2 on deuterium oxide and their properties reported.

Further work on these compounds is now in progress in this Laboratory.

NEW YORK, N. Y. RECEIVED AUGUST 8, 1936

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(4) Gilmour, *J. Soc. Chem. Ind.*, **41**, 293 (1922).

[CONTRIBUTION FROM GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 558]

The Molecular Structures of the Methyl Derivatives of Silicon, Germanium, Tin, Lead, Nitrogen, Sulfur and Mercury and the Covalent Radii of the Non-Metallic Elements

BY L. O. BROCKWAY AND H. O. JENKINS[1]

Introduction

The electron diffraction investigation of the fluorides and chlorides of carbon, silicon, germanium, tin, phosphorus and arsenic[2] showed the bond distances in most of these compounds to be shorter than the corresponding sums of the covalent radii.[3] Corrections applied to the accepted values for the radii would have removed some of the discrepancies but it was impossible to set up a single set of radii which gave agreement with all of the observed distances. It was suggested that the observed shortening could be explained on the basis of two effects: (1) an extra ionic character of the bonds which is not found in the compounds from which the table of radii was obtained and (2) the contribution of a partial double bond character due to the resonance of the molecule among several structures which have some double bonds. Since structures containing double bonds are not possible in the methyl derivatives of the elements concerned the study of the methyl compounds was proposed as a means of distinguishing between the two effects and also of testing the covalent radii. The tetramethyls of silicon, germanium, tin and lead, trimethyl nitrogen, and the dimethyls of sulfur and mercury have now been investigated by the electron diffraction method. The apparatus and the method of interpreting have recently been described in detail.[4] All of the compounds were photographed with electrons having a wave length of 0.0611 Å. with a camera distance of 10.43 cm.

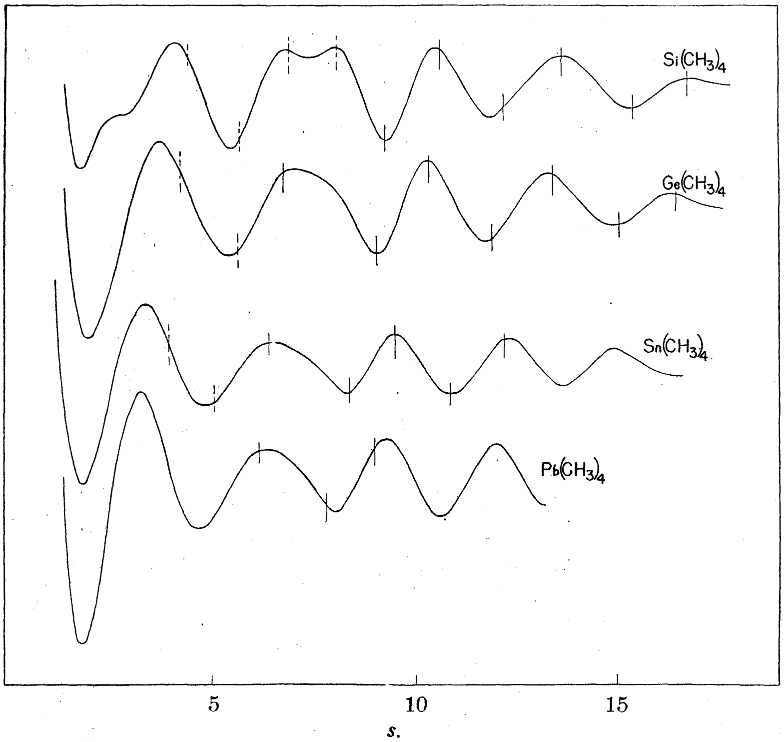

Fig. 1.—Theoretical electron diffraction curves for the tetramethyls. The observed maxima and minima are marked by the vertical lines. For $Pb(CH_3)_4$ a 3.14% shift in the s scale of the curve leads to agreement with the three observed points.

Tetramethyls.—Samples of the tetramethyls of silicon, germanium and tin were obtained from Dr. Warren C. Johnson of the University of Chicago and of lead tetramethyl from Mr. T. A. Boyd of the General Motors Research Laboratories.

Theoretical intensity curves for these compounds are reproduced in Fig. 1. For these curves the atomic scattering factors have been set equal to the respective atomic numbers. They are based on a molecular model in which the central atom is surrounded by four carbon atoms at the corners of a regular tetrahedron with three hydrogen atoms attached at tetrahedral angles to each carbon atom. In case of silicon and germanium tetramethyls an approximation to the free rotation of the methyl groups was made by averaging curves whose models differed in having successive

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(1) Fellow of the Commonwealth Foundation.

(2) L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934); L. O. Brockway, *ibid.*, **57**, 958 (1935).

(3) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

(4) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

60° rotations in the orientation of the methyl groups. The use of a smaller interval in the methyl group rotation angle would have led to the same averaged curve since this effect was tested in the case of tetramethylmethane.

The photographs show the general features of the respective curve in Fig. 1. The positions of the maxima and minima which were measured are marked by the vertical lines. In silicon tetramethyl the second maximum was observed to be a double ring. The components of this doublet were not very well resolved and visual measurements of their diameters showed wide fluctuations. Measurements of the first maximum and second minimum showed the usual displacement toward larger diameters because of their proximity to the dense central spot on the photograph. These four points, marked by dashed vertical lines in Fig. 1, were not used in the determination of the size of the molecule as given in Table I. In this table are listed the visually observed s values (equal to $4\pi(\sin\theta/2)/\lambda$), the calculated s values based on the assumed distances Si–C = 1.94 Å. and C–H = 1.06 Å., and the experimental Si–C distances. The average value taken from the more reliable ring measurements is Si–C = 1.93 ± 0.03 Å. The radial distribution function[5] was calculated with the use of the estimated intensities given in the third column of Table I. In Fig. 2 the radial distribution functions are shown for the various compounds. In each case the principal maximum corresponds to the bond distance between the central atom and the carbon atoms, and the vertical line indicates the value found for this distance by the usual method of comparing theoretical intensity curves with the photographs. The maximum for silicon tetramethyl occurs at 1.94 Å. in good agreement with the foregoing result of the usual method of interpretation, 1.93 Å.

TABLE I

SILICON TETRAMETHYL

Max.	Min.	I	s, obsd.	s, calcd. for Si–C = 1.94 Å.	Si–C, Å.
1		10	4.39	4.05	(1.790)
	2		5.66	5.45	(1.868)
2		12	(6.87)	6.84	
2a			(8.02)	7.95	
	3		9.21	9.25	1.946
3		6	10.58	10.44	1.913
	4		12.16	11.78	1.880
4		2	13.60	13.66	1.950
	5		15.36	15.30	1.932
5		1	16.72	16.83	1.952
				Average	1.929

Radial distribution function result; 1.94 Å. Final value: Si–C = 1.93 ± 0.03 Å.

TABLE II

GERMANIUM TETRAMETHYL

Max.	Min.	I	s, obsd.	s, calcd. for Ge–C = 1.99 Å.	Ge–C, Å.
1		9	4.21	3.73	(1.763)
	2		5.63	5.40	(1.909)
2		12	6.70	7.06	(2.097)
	3		9.01	9.03	1.994
3		6	10.32	10.26	1.980
	4		11.86	11.68	1.960
4		3	13.38	13.27	1.974
	5		15.04	14.92	1.975
5		1	16.43	16.31	1.976
				Average	1.977

Radial distribution function result: 2.00 Å. Final value: Ge–C = 1.98 ± 0.03 Å.

The results for germanium tetramethyl are given in Table II. The model from which the theoretical intensity curve was calculated is the tetrahedral model described above with Ge–C = 1.99 Å. and C–H = 1.06 Å. The photographs show five maxima of which the second is distinguished by the gradual decrease of intensity on its outer edge. This characteristic is also shown by the theoretical curve in Fig. 1. The first maximum and second minimum again lead to interatomic distance values which are smaller than the average. The second maximum shows the anticipated St. John effect and the corresponding interatomic distance value is too large. The average from the remaining three minima and three maxima is 1.977 Å. with a mean deviation of only 0.007 Å. The radial distribution function shown in Fig. 2 has a maximum corresponding to the Ge–C distance at 2.00 Å. The most probable value for this distance is 1.98 ± 0.03 Å.

TABLE III

TIN TETRAMETHYL

Max.	Min.	I	s, obsd.	s, calcd. for Sn–C = 2.17 Å.	Sn–C, Å.
1		6	3.95	3.37	(1.85)
	2		5.06	4.88	(2.095)
2		10	6.38	6.49	2.208
	3		8.37	8.32	2.158
3		6	9.46	9.48	2.174
	4		10.82	10.85	2.176
4		3	12.14	12.28	2.196
				Average	2.182

Radial distribution function result: 2.16 Å. Final value: Sn–C = 2.18 ± 0.03 Å.

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(5) L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

The tin tetramethyl photographs show four maxima. The theoretical intensity curve was calculated with an assumed Sn–C distance of 2.17 Å. and a C–H distance of 1.06 Å. The comparison of observed and calculated s values for three maxima and two minima leads to an average value of Sn–C of 2.18 ± 0.03 (Table III). The value 2.16 Å. given by the radial distribution function is in satisfactory agreement.

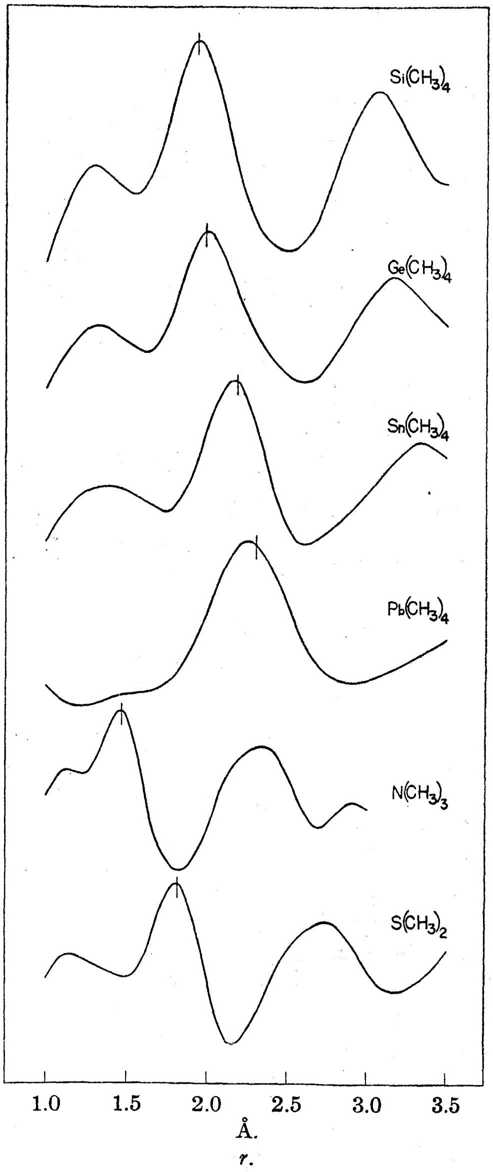

Fig. 2.—Radial distribution functions for the methyl compounds. In each case the maximum corresponding to the bond distance between the central and the carbon atoms is marked at the value for this distance as determined by the method illustrated in Fig. 1.

Good photographs of lead tetramethyl were not obtained. The heavy background on the negatives made it possible to distinguish only three rings, and of these the first was so uncertain that measurements of its diameter gave widely scattered values. Fairly consistent measurements were made on the second and third maxima and third minimum as reported in Table IV. The theoretical curve shown in Fig. 1 is based on an assumed Pb–C distance of 2.23 Å. while the experimental value is 2.30 Å. A change in the scale of the theoretical curve of 3.14% leads to excellent agreement between theory and experiment. The three term radial distribution function shows the Pb–C maximum at 2.26. Because of the relatively poor quality of the photographs, an unusually large estimate of the probable error is made; the best value for the Pb–C distance is 2.29 ± 0.05 Å.

TABLE IV

LEAD TETRAMETHYL

Max.	Min.	I	s, obsd.	s, calcd. for Pb–C = 2.23 Å.	Pb–C, Å.
1		12	(3.5)	3.26	
	2		(4.6)	4.69	
2		10	6.15	6.32	2.291
	3		7.76	8.05	2.312
3		5	8.98	9.28	2.306
				Average	2.303

Radial distribution function result: 2.26 Å. Final value: Pb–C = 2.29 ± 0.05 Å.

Comparison of the photographs of the four compounds shows the effect of the increasing size and scattering power of the central atom. The maxima occur at successively smaller angles due to the increase in the size of the molecule. This is shown in Fig. 1 by the shift toward smaller angles of the maxima on successive curves. The increase of the scattering power of the central atom is shown in the curves by the approach to a simple $(\sin x)/x$ curve; this is due to the preponderant effect of a single term in the formula for the theoretical intensity. Especially notable is the change in the appearance of the second maximum from a resolved doublet in $Si(CH_3)_4$ to an asymmetric single maximum in $Ge(CH_3)_4$ to a symmetric maximum in $Pb(CH_3)_4$.

It will be noted that the number of rings observed on the photographs of this series of compounds decreased with increasing scattering power of the central atom. This is due to the disproportionate increase of the background of atomic scattering relative to the molecular scattering

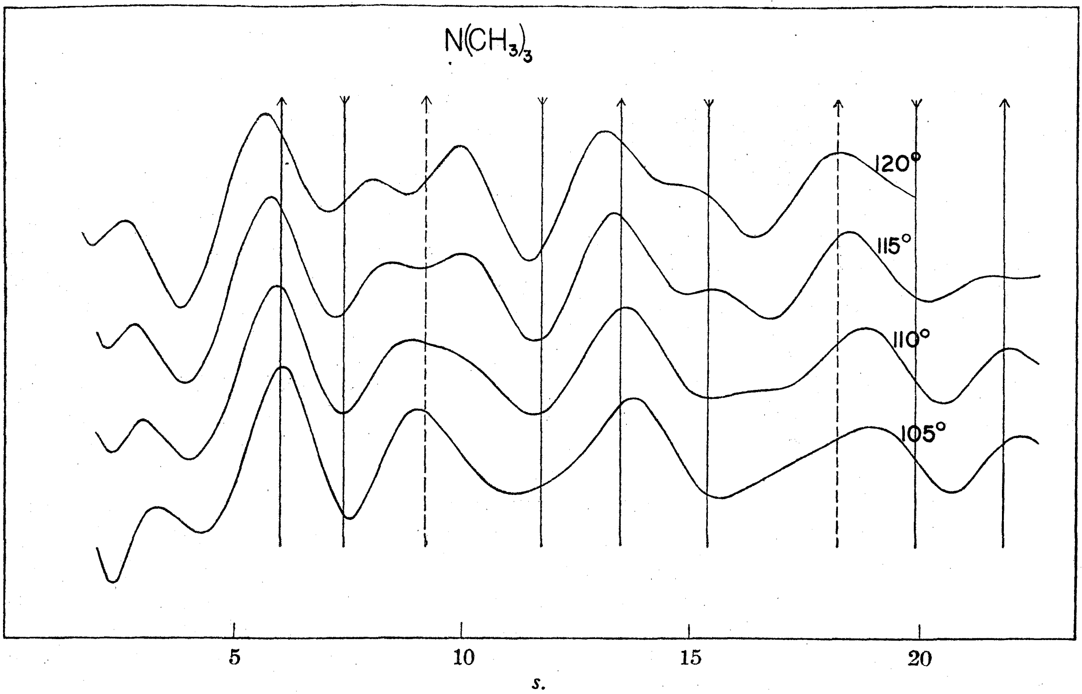

Fig. 3.—Theoretical electron diffraction curves for nitrogen trimethyl. The observed points marked by the dashed lines are not reliable for quantitative comparisons.

(*i. e.*, the part of the scattering in which the interference effects appear). Since the apparent intensity of the diffraction maxima is approximately proportional to the ratio of the molecular to the atomic scattering,[6] the relative increase of atomic scattering in a series of molecules in which one atom progressively scatters much more strongly than the others causes the maxima to become weaker and a smaller number of them to appear in the diffraction patterns of the successive molecules. On microphotometer records the fluctuations due to the interference effects become less pronounced and the intensity curve approaches that for monatomic scattering. Thus it happens that increased scattering power of a molecule results in less pronounced interference effects and poorer photographs for structure determination if the increase of scattering power occurs in only one of the atoms of the molecule.

Nitrogen Trimethyl.—The photographs of nitrogen trimethyl were obtained with the use of the Eastman product redistilled.

Theoretical intensity curves were calculated for pyramidal models having the nitrogen atom at the apex and with C–N–C bond angles of 120, 115, 110 and 105°. All terms except the H–H terms were included. Free rotation of the methyl groups was assumed and for each curve shown in Fig. 3 the scattering was averaged from a set of models which differ in having 30° intervals in the orientation of the methyl groups. The C–N distance assumed for the curves was 1.47 Å.

The measured positions of the maxima and minima are shown by the vertical lines in Fig. 3. The 120° model is eliminated since the corresponding curve shows two maxima in the region from 8 to 10 on the *s* scale where only one maximum is observed; also it shows a well-marked shelf near $s = 15$ at the position of an observed minimum. For the same reasons the 115° model is also unsatisfactory. The third ring on the photographs is broad with no well-defined maximum point and this appearance agrees better with the 110° curve than with any other. The fourth maximum is sharp whereas the fifth is indistinct on the inner edge in agreement with its appearance in the 105° curve. The general qualitative features correspond to an angle of 108 ± 4° for the C–N–C bonds.

The quantitative comparison for the 110 and 105° models is given in Table V. The wide deviations in the measurements of the third and fifth maxima make them unreliable and they are not included in the average value for the N–C distance. The five term radial distribution function

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[6] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 870 (1934).

TABLE V

NITROGEN TRIMETHYL

Max.	Min.	I	s, obsd.	s, calcd. for N–C = 1.47 Å.		N–C	
				110°	105°	110°	105°
1			Not measured	3.04	3.35		
2		10	6.00	5.92	6.07	1.450 Å.	1.487 Å.
	3		7.39	7.36	7.53	1.464	1.497
3		7	(9.20)	8.88	9.06		
	4		11.78	11.60	11.21	1.448	1.400
4		5	13.51	13.63	13.78	1.481	1.498
	5		15.43	15.45	15.67	1.477	1.492
5		3	(18.34)	18.88	18.93		
6		1	21.80	21.93	22.19	1.479	1.496
					Average	1.466	1.478
					Mean deviation	0.011	0.026

Radial distribution function result: 1.46 Å. Final values: N–C = 1.47 ± 0.02 Å., angle C–N–C = 108 ± 4°.

TABLE VI

SULFUR DIMETHYL

Max.	Min.	I	s, obsd.	s, calcd. for S–C = 1.81 Å.		S–C	
				110°	100°	110°	100°
1		12	5.07	4.06	3.92	(1.450) Å.	(1.400) Å.
	2		6.36	6.02	6.25	(1.715)	(1.780)
2		20	7.71	7.85	7.85	1.844	1.844
	3		9.71	9.79	9.69	1.825	1.805
3		12	11.16	11.24	11.32	1.823	1.834
	4		12.92	12.74	12.77	1.784	1.788
4		6	14.34	14.26	14.36	1.800	1.813
	5		16.35	16.55	16.16	1.832	1.790
5		3	18.13	18.54	18.56	1.851	1.853
					Average	1.823	1.818
					Mean deviation	0.017	0.022

Radial distribution function result: 1.81 Å. Final value: S–C = 1.82 ± 0.03 Å.

using the estimated intensities given in the table is shown in Fig. 2 with its N–C maximum at 1.46 Å. This result combined with the average value from Table V leads to an N–C distance of 1.47 ± 0.02 Å.

X-Ray diffraction photographs of nitrogen trimethyl vapor were taken by Richter,[7] who considered three models having bond angles of 60, 110 and 120° and an assumed N–C distance of 1.5 Å. Of these three the second gave the best agreement with his photographs, a conclusion which is supported by the result of the present investigation.

The observed dipole moments, 0.60 D[8] and 0.82 D,[9] also require a pyramidal structure for nitrogen trimethyl.

Sulfur Dimethyl.—Sulfur dimethyl (redistilled Eastman product) gave photographs showing five good rings. Theoretical curves for two bond angles, 110 and 100°, were calculated (Fig. 4) but no significant differences appear since the interference terms which change with the bond angle are much smaller than the unchanging term associated with the sulfur–carbon distance. This distance was taken as 1.81 Å. and the C–H as 1.06 Å. The radial distribution function (Fig. 2) shows a sharp peak at 1.81 Å. The quantitative comparison of Table VI leads to a final value of 1.82 ± 0.03 Å.

The dipole moment of sulfur dimethyl is 1.40 D.[10] The sulfur bond angle in this compound is very probably between 100 and 110°.

Mercury Dimethyl.—Photographs of mercury dimethyl were obtained from a sample supplied by Professor D. M. Yost of this Laboratory. The maxima were not well resolved from the very heavy background of atomic scattering due to the mercury atom and the measured diameters are not very reliable. For this reason the data are not given in detail; they lead to the approximate value Hg–C = 2.20 ± 0.10 Å. A determination of the bond angle in this compound by electron diffraction experiments is not possible.

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(7) H. Richter, *Physik. Z.*, **36**, 85 (1935).

(8) O. Steiger, *Helv. Phys. Acta*, **3**, 161 (1930).

(9) P. N. Ghosh and T. P. Chatterjee, *Phys. Rev.*, **37**, 427 (1931).

(10) E. C. E. Hunter and J. R. Partington, *J. Chem. Soc.*, 2819 (1932).

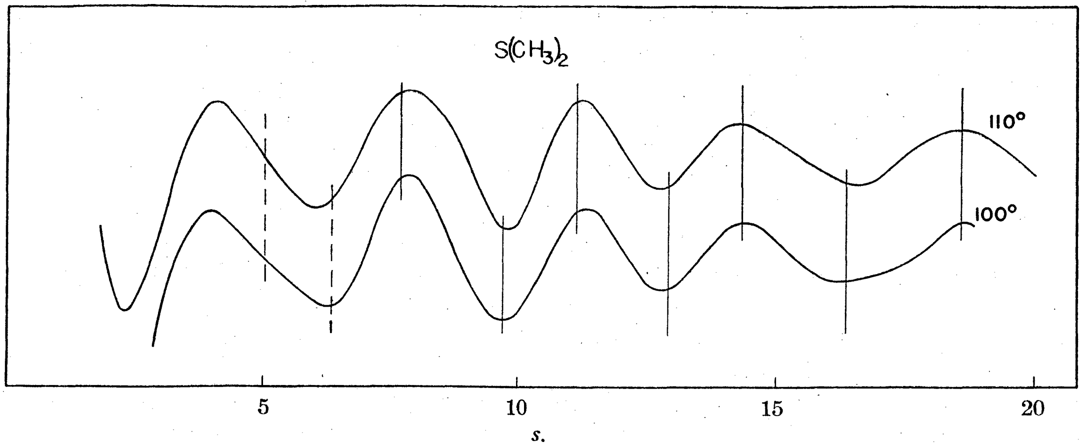

Fig. 4.—Theoretical electron diffraction curves for sulfur dimethyl.

Discussion

The data obtained from the methyl compounds are of special interest in the study of the normal covalent radii of the elements. The single bond radii proposed by Pauling and Huggins[3] for the non-metals are as follows:

C	N	O	F
0.77	0.70	0.66	0.64
Si	P	S	Cl
1.17	1.10	1.04	0.99
Ge	As	Se	Br
1.22	1.21	1.17	1.14
Sn	Sb	Te	I
1.40	1.41	1.37	1.33

These values for the carbon and halogen groups are half of the observed interatomic distances in the elements; the intermediate values were obtained by interpolation with the aid of crystal structure data. Radius sums taken from this table are intended to represent interatomic distances for single bonds when the elements have their normal valence, *i. e.*, four for the carbon group, three for the nitrogen group, two for the oxygen group and one for the halogens. Small corrections are to be applied for other valence states.

The observed bond distances in the methyl compounds may be compared with the corresponding radius sums. In Table VII this comparison is made for the elements whose methyl derivatives are reported in this paper (except lead and mercury) in addition to oxygen and chlorine, whose methyl derivatives were previously reported,[11] and for carbon, fluorine and bromine for which the details of the structure determinations will appear in forthcoming publications. The upper number in each case is the observed bond distance and the lower is the sum of the covalent radii.

TABLE VII

BOND DISTANCES AND RADIUS SUMS IN METHYL COMPOUNDS

C–C	N–C	O–C	F–C
1.55 ± 0.02	1.47 ± 0.02	1.42 ± 0.03	1.42 ± 0.02
1.54	1.47	1.43	1.41
Si-C		S–C	Cl–C
1.93 ± 0.03		1.82 ± 0.03	1.77 ± 0.02
1.94		1.81	1.76
Ge–C			Br–C
1.98 ± 0.03			1.91 ± 0.05
1.99			1.91
Sn–C			
2.18 ± 0.03			
2.17			

The agreement between the observed distances and the radius sums for all of these compounds is excellent, the differences being less than the experimental error. This shows that with respect to the factors affecting the distance the bond type in the methyl compounds is the same as in the elements where the bonds are formed between atoms of the same element. It may be pointed out that the existence of a dipole moment can have only a very small effect on the bond distance. In the methyl halides, which have appreciable moments, the distances are the averages of the carbon–carbon distance in diamond and aliphatic hydrocarbons and of the distances in the respective halogen molecules. For the other compounds, too, the bond between unlike atoms, with which there is associated an electric moment, has just the average distance of the two bonds between like

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[11] L. E. Sutton and L. O. Brockway, THIS JOURNAL, **57**, 473 (1935).

atoms, which have zero moments. The introduction of the moment has no appreciable effect on the distance.

It is now possible to discuss the data for the halogen derivatives. In Table VIII are shown the observed bond distances and the radius sums for the fluorides and chlorides in which the carbon group elements form four bonds to halogens, the nitrogen group form three, the oxygen group two and the halogens one. The table includes the compounds on which electron diffraction measurements have been made and the data are taken from a recent survey.[4] For Cl_2 and ICl the band spectral results are reported in preference to the electron diffraction results.

TABLE VIII

BOND DISTANCES AND RADIUS SUMS IN CHLORIDES AND FLUORIDES

C–Cl 1.755 ± 0.005 1.76 0.00		O–Cl 1.68 ± 0.03 1.65 +0.03	
Si–Cl 2.00 ± 0.02 2.16 −0.16	P–Cl 2.00 ± 0.02 2.09 −0.09		Cl–Cl 1.983 ± 0.005 1.98 +0.00
Ge–Cl 2.08 ± 0.03 2.21 −0.13	As–Cl 2.16 ± 0.03 2.20 −0.04		
Sn–Cl 2.30 ± 0.03 2.39 −0.09		Te–Cl 2.36 ± 0.03 2.36 0.00	I–Cl 2.315 ± 0.005 2.32 0.00
C–F 1.36 ± 0.02 1.41 −0.05		O–F 1.41 ± 0.05 1.30 +0.11	
Si–F 1.54 ± 0.02 1.81 −0.27	P–F 1.52 ± 0.04 1.74 −0.22		
	As–F 1.72 ± 0.02 1.85 −0.13		

Five of the chlorides have bond distances which within the experimental error are equal to the corresponding radius sums. Among these is the chlorine molecule whose bond distance determines the chlorine radius. The chlorides of silicon, germanium, tin, phosphorus and arsenic, on the other hand, have distances which are appreciably shorter than the radius sums. It was suggested in a previous paper[2] that two effects might contribute to this shortening. The first is related to the extra ionic character of the bonds due to the differences in the electronegativities of the atoms involved. The covalent radii quoted above were obtained from bonds between atoms of the same element having the same electronegativity; and the bonds in question between atoms with different electronegativities might well be expected to show an extra ionic character which would strengthen and shorten the bonds. The results on the methyl compounds, however, show that this explanation is not valid. Although the differences in electronegativity are more extreme in some of these compounds than in the chlorides, no deviations from additivity of the covalent radii are observed.

The alternative explanation for the shortening is that the bonds may have some double bond character. If one of the structures contributing to the normal state of the molecule has two atoms joined by a single bond and one of the atoms has an unshared pair of electrons while the other has an unoccupied orbital, then another structure in which a double electron pair bond is formed between two atoms may contribute to the normal state of the molecule. If this occurs the bond distance will be shorter than the single bond distance by an amount depending on the relative contributions of the various resonating structures. The maximum shortening will be ten per cent. since the ratio of double to single bond distance is 90%.

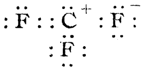
Shortening due to double bond character will not be expected when the formulation of the structure having the double bond would violate the octet rule for an atom of the first row of the periodic table. In one of these atoms the four orbitals of the L shell are filled by the four electron pairs and the higher lying levels of the M shell are not available for bond-formation. In the later rows of the periodic table, however, four electron pairs occupy the *s* and *p* orbitals with *d* orbitals of the same shell available for the formation of additional bonds.

In examining the data for the chlorine compounds we see that carbon tetrachloride could not show a double bond effect, and no shortening is observed. In chlorine monoxide the fact that no shortening occurs shows that chlorine has little or no tendency to hold five pairs. The 8% shortening observed in silicon tetrachloride indicates a considerable double bond effect. If it is the only cause of the shortening, the bonds in silicon tetrachloride have 40% double bond character according to the relation between interatomic distance and single bond–double bond resonance.[12] This requires a considerable contribution to be made by structures having two and three double bonds to silicon.

All of the shortenings observed in the chlorine compounds are compatible with the explanation on the basis of double bond character. In the methyl compounds double bonded structures are not possible because there are no unshared electrons, and no shortening is observed. Another example of shortening due to double bond character has been observed in the case of nickel carbonyl.[13]

The deviations from additivity shown in Table VIII become less in passing to the right or down through the periodic arrangement of the elements. In the second row this is inevitable since the distance in the molecule Cl_2 furnishes the standard for comparison. We have in reality measured the excess of the effect over that in Cl_2 itself. It is probable, however, that Cl_2 has very little double bond character inasmuch as the distance in carbon tetrachloride would be larger than the sum of the radii if the chlorine radius were affected by double bond character in Cl_2. The zero deviation observed for ICl also lends some significance to the apparent trend in the tendency toward double bond formation.

The bond distances of the fluorides require additional explanation. It will be noted that the C–F distance in methyl fluoride is 1.42 Å. and in carbon tetrafluoride 1.36 Å. This difference is beyond the range of experimental error. The shortening below the sum of the radii for the second compound is not due merely to ionic effects since it would also appear in some degree in the first. Professor Pauling has suggested that in addition to the single bonded structure the CF_4 molecule resonates among structures having an F^- ion bonded electrostatically to a CF_3^+ ion in which one double and two single covalent bonds are formed.



$$\begin{array}{c} :\ddot{F}: \\ :\ddot{F}::\ddot{C}^{+}\ :\ddot{F}:^{-} \\ :\underset{..}{\ddot{F}}: \end{array}$$

The quantum mechanical principle of resonance among structures having equal energies would require the four bonds to be equivalent and they would show an equal shortening. The effect could not take place in methyl fluoride and thus the difference between the two compounds is accounted for. If this explanation is correct, the effect should be observed whenever two or more fluorine atoms are attached to the same carbon or even when a fluorine and one or more chlorine atoms are bonded to carbon. It is known that the halogen derivatives of methane containing two or more halogen atoms of which fluorine is one have different chemical properties from the others. This fact is undoubtedly associated with the variations in the bond distances. A report of the electron diffraction investigation of the mixed fluorine and chlorine derivatives of methane will be published soon.

The described effect should be especially important in the fluorides on account of the pronounced electronegativity of fluorine. That the explanation is not entirely satisfactory is indicated by the magnitude of the deviations observed in silicon tetrafluoride and phosphorus trifluoride. The shortenings here are 15 and 13%, respectively, although the maximum difference observed between single and double bonds is 10%. The contribution of structures involving triple bonds is probably small in view of the slight tendency for elements of the second row to form triple bonds. If the large shortening can be explained by the combined extreme ionic-double bond character described above, then the shortening in the fluoromethanes should be greater.

As in the chlorides, the shortening for fluorides becomes less toward the right and in lower rows of the periodic system. In fluorine monoxide the bond distance is larger than the sum of the radii. No explanation of this anomaly is apparent.

Because of the agreement found for methyl compounds we believe that the covalent radii given in Pauling and Huggins' table are reliable and applicable even to bonds with considerable ionic character. The radii are also useful for predicting distances in compounds in which deviations from additivity occur due to resonance of the molecule among several electronic structures. The results for the chlorine compounds indicate the circumstances under which such deviations may be expected.

We express our indebtedness to Professor Linus Pauling for valuable discussions on the interpretation of the data on internuclear distances.

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(12) L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935).

(13) L. O. Brockway and P. C. Cross, *J. Chem. Phys.*, **3**, 828 (1935).

Summary

By electron diffraction investigation of the gases the structures of certain methyl compounds have been determined. Four tetramethyls with tetrahedral symmetry have the following bond distances: Si–C = 1.93 ± 0.03 Å., Ge–C = 1.98 ± 0.03 Å., Sn–C = 2.18 ± 0.03 Å., Pb–C = 2.29 ± 0.05 Å. Nitrogen trimethyl has a bond angle of 108 ± 4° with N–C = 1.47 ± 0.02 Å. In sulfur dimethyl and mercury dimethyl the interatomic distances are S–C = 1.82 ± 0.03 Å. and Hg–C = 2.20 ± 0.10 Å., respectively. These distances agree with the sums of covalent radii given by Pauling and Huggins.

In a discussion of previous data for the chlorides it is shown that relative electronegativities (or the existence of electric moments in the bonds) are not responsible for the shortening observed in some of the chlorides. This effect is instead probably due to the contribution of structures having double electron pair bonds. Further investigation is required to explain the observed deviations in the chlorides.

PASADENA, CALIF. RECEIVED JULY 28, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF H. S. NEWCOMB COLLEGE, TULANE UNIVERSITY]

Diazotization of Weakly Basic and Insoluble Amines. The Use of Pyridine, Quinoline and Isoquinoline as Solvents for the Amines

BY CLARA DEMILT AND GERTRUDE VAN ZANDT[1]

A series of experiments in this Laboratory on the diazotization of 4-aminobiphenyl with the use of pyridine as a solvent for the amine[2] led the authors to an investigation of the use of pyridine as a solvent for other weakly basic and insoluble amines. The success of this work led to experimentation on the use of quinoline and isoquinoline as solvents.

The use of pyridine as a solvent for the difficultly diazotizable amines has been described by Krishna and Bhatia,[3] who reported the successful diazotization of tribromoaniline, 2,6-dichloro-4-nitroaniline, dibromo-*p*-aminobenzoic acid and dibromo-*p*-aminobenzaldehyde.

The experimental work described in this paper substantiates the conclusion so often expressed that the diazotization proceeds only with the substituted ammonium salt and never with the free amine.[4,5] As groups which decrease the basicity of the amine replace the hydrogen atoms in the benzene ring, the concentration of the ammonium salt in the aqueous solution is correspondingly decreased. In order to prevent this hydrolytic action, Schoutissen[5] found that it was necessary to use a large excess of strong mineral acid or a solvent which reduces the dissociating effect of water. With the use of pyridine, quinoline and isoquinoline as solvents for the weakly basic and insoluble amines, it is possible to introduce the amine into the diazotizing mixture, namely, sulfuric acid and sodium nitrite, so that the amine is evenly distributed throughout the mixture in a very finely divided condition. The amine solution is added slowly to the cold nitrosylsulfuric acid. The solvent seems to hold the amine in solution until the sulfate is formed, which in turn reacts with the nitrous acid that is liberated by the action of the solvent on the nitrosylsulfuric acid. It is to be noted, however, that even though all other quantities and factors are the same, complete diazotization of the amine is not obtained in a reasonable length of time unless the amine is entirely dissolved in the liquid that is being used as the solvent.

The excess of mineral acid that is necessary depends upon the solubility of the amine and the nature, number and position of the groups that are present in the benzene ring. A study of the acid concentrations used in the diazotization of the substituted amines, showed that when a relatively small volume of organic solvent was used, the more dilute acid solution is satisfactory except for 4,6-dibromo-2-nitroaniline and picramide. If, however, a much larger volume of solvent is necessary to dissolve the amine, then the stronger acid solution must be

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[1] The material of this paper is from the thesis of Gertrude Van Zandt, presented in partial fulfilment of the requirements for the degree of M.S. at Tulane University, June, 1935.

[2] Carolyn Samuel, Master's Thesis, Tulane University, June, 1934.

[3] Proc. 15th Indian Sci. Cong., 152 (1928).

[4] Witt, *Ber.*, **42**, 2953 (1909).

[5] Schoutissen, THIS JOURNAL, **55**, 4531 (1933).

used, although the final concentration of the diluted acid is approximately the same. The effect of solubility is illustrated by the diazotization of 2,6-dibromo-4-nitroaniline. The amine is very soluble in quinoline and is easily diazotized with the use of this solvent. When pyridine is used as the solvent, a large volume is necessary to dissolve the amine and complete diazotization results only when a stronger acid concentration is used. It was not found possible to use dilute hydrochloric acid described by Krishna and Bhatia[3] as being satisfactory for the diazotization of difficultly diazotizable amines, when pyridine was used as the solvent for the amines. Pyridine reacts vigorously with concentrated hydrochloric acid, and weaker solutions of hydrochloric acid do not furnish the concentration of mineral acid that is necessary for the diazotization of the very weakly basic amines. For this reason, sulfuric acid has been used almost exclusively and has been found to furnish sufficient acid concentration even for the diazotization of the least basic amine, picramide.

Even though sulfuric acid is the best mineral acid to furnish the necessary acid concentration, Schoutissen[5] showed by experiment that the sulfuric acid, used alone, combines with all the nitrous acid. In order to release the nitrous acid from the nitrosylsulfuric acid, he used phosphoric acid. Glacial acetic acid was used for the same purpose by Misslin[6] in the diazotization of picramide. The addition of pyridine, quinoline or isoquinoline to a solution of nitrosylsulfuric acid was found to release the nitrous acid. Thus besides acting as a solvent for the difficultly soluble amines, these tertiary amines, which do not reduce the concentration of the sulfuric acid appreciably, have another function, that of releasing the nitrous acid from the nitrosylsulfuric acid.

Even though the three solvents have the same function in the diazotization process, each has its advantages. Much heat is generated when pyridine is added to nitrosylsulfuric acid, and it is sometimes difficult to keep the temperature as low as necessary, while little heat is evolved when quinoline or isoquinoline is used. On the other hand, pyridine shows almost no tendency to hold the azo compound formed in a coupling process in solution, while quinoline and isoquinoline do hold the coupled product in solution, especially when a proportionately large volume of the solvent has been used. Moreover, quinoline and isoquinoline cannot be used with those amines the diazonium salts of which couple with β-naphthol in alkaline solution, since they separate out as oils.

Further work on the diazotization of amines with the use of these solvents followed by the Sandmeyer reaction is in progress.

Experimental Part

1. Diazotization with Pyridine

2,6-Dichloro-4-nitroaniline.—Three grams of sodium nitrite was added to a solution of 30 cc. of concentrated sulfuric acid and 15 cc. of water, which had been cooled to 10°. To this was slowly added 4.14 g. of 2,6-dichloro-4-nitroaniline dissolved in 15 cc. of pyridine. During the addition, the mixture was stirred mechanically and the temperature was maintained below 10°. The diazonium salt solution was stirred for a half hour after the amine–pyridine solution had been added. Twice the volume (120 cc.) of ice water was then added. Finally 2 g. of urea was added to remove excess nitrous acid, and the solution was stirred until foaming had ceased. The diazonium salt solution was filtered to remove a slight residue that seemed to result on the addition of the urea. To the clear solution 2.88 g. of β-naphthol dissolved in 10 cc. of pyridine was added, and coupling took place at once. The mixture was allowed to stand for an hour, and was then diluted with 200 cc. of water. The coupled product was filtered, washed with water and digested with 150 cc. of 25% alcohol on a water-bath for a half hour to remove adhering pyridine. The yield was quantitative. Recrystallization of 2,6-dichloro-4-nitrobenzene-azo-β-naphthol from toluene gave deep red needles, m. p. 219°.

3-Nitro-4-aminobiphenyl.—The 3-nitro-4-aminobiphenyl, m. p. 165.5°, was prepared by the nitration of 4-aminobiphenyl, obtained from Eastman Kodak Co.; 4.04 g. of 3-nitro-4-aminobiphenyl dissolved in 20 cc. of pyridine was added slowly to a cold mixture of 3 g. of sodium nitrite in a solution of 30 cc. of concd. sulfuric acid and 15 cc. of water. The diazotization was carried out in the usual way. Coupling took place immediately on the addition of 2.88 g. of β-naphthol dissolved in 10 cc. of pyridine to the clear diazonium salt solution. The coupled product was filtered, washed and digested with 25% alcohol. The 2-nitro-4-phenylbenzene-azo-β-naphthol formed fine red-brown crystals from toluene, m. p. 228°.

Anal. Calcd. for $C_{22}H_{15}O_3N_3$: N, 11.38. Found: N, 10.22, 10.06.

Picramide, 2,4,6-Trinitroaniline.—A solution of 60 cc. of concd. sulfuric acid and 21 cc. of water was cooled to 10° and 3 g. of sodium nitrite was added. This mixture was heated on a water-bath until it became clear (70°) and was then cooled to 0°; 4.56 g. of picramide dissolved in 30 cc. of pyridine was added during an hour and a half to the nitrosylsulfuric acid solution. During the addition, the mixture was stirred mechanically and the temperature kept below 10°. The diazonium solution was allowed to stand for two hours. To the concentrated solution 2 g. of urea was added. Very little foaming resulted, and it was not necessary to filter the clear solution. A solution of

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[6] Misslin, *Helv. Chim. Acta*, **3**, 626 (1920); *C. A.*, **15**, 61 (1921).

2.88 g. of β-naphthol in 10 cc. of pyridine was then added, and coupling took place immediately. The coupled product was allowed to stand for an hour, diluted with 300 cc. of water and filtered. It was washed and digested with 25% alcohol; yield quantitative. Recrystallization of 2,4,6-trinitrobenzene-azo-β-naphthol from toluene gave a brick-red powder, m. p. 147°.

3-Aminophenanthrene in Sulfuric Acid.—1.93 g. of 3-aminophenanthrene (a gift from Professor W. E. Bachmann of the University of Michigan), m. p. 87.5°, dissolved in 10 cc. of pyridine was added slowly to a cold solution of 15 cc. of concd. sulfuric acid and 7 cc. of water containing 1.5 g. of sodium nitrite. The diazonium salt solution was diluted with 50 cc. of ice water and treated with 1 g. of urea. To this was added 1.44 g. of β-naphthol dissolved in 5 cc. of pyridine. Coupling took place when the solution was made alkaline with sodium hydroxide. The coupled product was filtered and washed with water. The yield of the crude product was quantitative. The phenanthrene-azo-β-naphthol recrystallized from toluene gave fine, dark red crystals, m. p. 249°.

Diazotization of 3-Aminophenanthrene in Hydrobromic Acid.—A solution of 1.93 g. of 3-aminophenanthrene in 5 cc. of pyridine was added alternately with a solution of 1.5 g. of sodium nitrite in 4 cc. of water to 18 cc. of 40% hydrobromic acid, cooled below 4°. The diazotized solution was diluted with 50 cc. of ice water and treated with 1 g. of urea. It was now added to a solution of 1.44 g. of β-naphthol in sodium hydroxide. The yield of the crude product was quantitative. The recrystallized product melted at 249°.

2. Diazotization with Quinoline[7]

4,6-Dibromo-2-nitroaniline.—A solution of 5.91 g. of 4,6-dibromo-2-nitroaniline in 15 cc. of quinoline was diazotized in a reaction mixture of 3 g. of sodium nitrite in 40 cc. of concd. sulfuric acid and 15 cc. of water. Coupling took place when to the clear diazonium salt solution a solution of 2.88 g. of β-naphthol in 10 cc. of quinoline was added. The coupled product was filtered, washed and digested with 25% alcohol. The yield was quantitative. Recrystallization of the 4,6-dibromo-2-nitrobenzene-azo-β-naphthol from toluene gave red crystals, m. p. 250°.

Anal. Calcd. for $C_{16}H_9O_3N_3Br_2$: N, 9.32. Found: N, 9.46, 9.30.

3. Diazotization with Isoquinoline

Picramide.—A mixture prepared by adding 3 g. of sodium nitrite to a cold solution of 60 cc. of concd. sulfuric acid and 21 cc. of water was heated on a water-bath to 70° until clear; 4.56 g. of picramide dissolved in 50 cc. of isoquinoline on a water-bath was added as a thick suspension to the nitrosylsulfuric acid. The mixture was stirred mechanically and the reaction carried out at room temperature. The solution was diluted with a mixture of 30 cc. of concd. sulfuric acid and 35 cc. of water and allowed to stand for an hour with stirring. Two grams of urea was added. After the foaming had ceased, the solution was clear. Water was then added until a precipitate began to form. A solution of 2.88 g. of β-naphthol in 10 cc. of isoquinoline was then added. The mixture was allowed to stand, then diluted with water. The product was filtered, washed and digested with 25% alcohol. The yield was not quantitative, apparently because the isoquinoline held some of the coupled product in solution. Recrystallization from toluene gave 2,4,6-trinitrobenzene-azo-β-naphthol as a red powder, m. p. 147°.

Summary

1. A new method for the diazotization of weakly basic and insoluble amines has been devised with the use of pyridine, quinoline and isoquinoline as solvents for the amines. The diazotization of 2,6-dichloro-4-nitroaniline, 2,4-dinitroaniline, 3-nitro-4-aminobiphenyl, 2,4,6-tribromoaniline, 2,6-dibromo-4-nitroaniline, 4,6-dibromo-2-nitroaniline, 3-aminophenanthrene and 2,4,6-trinitroaniline has been carried out with the use of these solvents.

2. Complete diazotization is not obtained in a reasonable length of time unless the amine is entirely dissolved in the liquid that is being used as the solvent.

3. Two new compounds have been prepared: 2-nitro-4-phenyl-benzene-azo-β-naphthol, m. p. 228° and 4,6-dibromo-2-nitrobenzene-azo-β-naphthol, m. p. 250°.

NEW ORLEANS, LA.

RECEIVED MAY 11, 1936

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[7] Contributed by the Barrett Co.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Polysulfones from Acetylenes and Sulfur Dioxide[1]

BY L. L. RYDEN AND C. S. MARVEL

In an earlier communication,[1] we have shown that one acetylene, 1-heptyne, combines with sulfur dioxide in a one-to-one ratio to yield a polymeric product. This reaction has now been studied with a wide variety of substituted acetylenes and it appears to be a general reaction for monosubstituted acetylenic hydrocarbons.

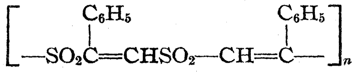
The monoalkylacetylenes, RC≡CH, in which R is a normal alkyl group containing one to five carbon atoms, have been found to combine readily with sulfur dioxide in the presence of alcohol and paraldehyde which contains peroxides. Phenylacetylene also combines readily with sulfur dioxide under the same conditions used for alkylacetylenes. Disubstituted acetylenes apparently do not enter into the reaction as shown by failure to obtain sulfur dioxide addition products from 2-butyne, 2-hexyne and methylphenylacetylene. Ethyl acetylenedicarboxylate also failed to react with sulfur dioxide. Further experiments on monosubstituted acetylenes will have to be made before the exact limits of the reaction can be set forth.

The products of the addition of sulfur dioxide to monosubstituted acetylenes are presumably polysulfones. They still contain one double bond for each hydrocarbon residue in the polymer, since oxidation gives the acid which would be expected from this structure. That the addition of sulfur

$$(\underset{|}{RC}{=}CH{-}SO_2{-})_n \xrightarrow{\text{Oxid.}} RCOOH$$

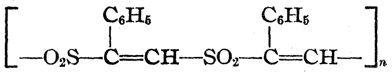
dioxide is to the acetylene and not to an allene which might result from a rearrangement of the acetylene is established by the above observation. Moreover, phenylacetylene, which could not rearrange to an allene, adds sulfur dioxide, and allene itself fails to combine with this reagent.

The polymers are readily hydrolyzed with 10% aqueous sodium hydroxide, but all of the products of this hydrolysis are not known. The phenylacetylenepolysulfone was most extensively investigated, since it was thought that the presence of the phenyl group would give products which were more readily identifiable. The products which have been isolated are benzylmethylsulfone (8%), acetophenone (trace), benzoic acid (20%) and sodium sulfite (50%). The remainder of the sulfur was present in the tarry organic products which are produced in the hydrolysis. The fact that almost exactly half of the sulfur is isolated as sulfur dioxide and half as organic sulfur compounds indicates that there is possibly the same type of alternation in the manner of combination of phenylacetylene and sulfur dioxide to give a polymer of structure I as was previously demonstrated in the case of propylenepolysulfone.[2] However, this structure does not account for the formation of benzylmethylsulfone on hydrolysis. At least a part of the polymer must have the structure shown in formula II. It seems likely that the acetophenone is produced from one end group of the polymer. Addition of water to stop the polymeric reaction would give at one end of the chain the group $C_6H_5COCH_2SO_2$-, and this would give acetophenone on alkaline hydrolysis.



$$\left[-SO_2\overset{C_6H_5}{\overset{|}{C}}{=}CHSO_2{-}CH{=}\overset{C_6H_5}{\overset{|}{C}}{-}\right]_n$$

I



$$\left[-O_2S{-}\overset{C_6H_5}{\overset{|}{C}}{=}CH{-}SO_2{-}\overset{C_6H_5}{\overset{|}{C}}{=}CH{-}\right]_n$$

II

Hydrolysis of 1-pentynepolysulfone gave a trace of methyl *n*-propyl ketone which also probably came from the end group of the molecule. About 40–50% of the sulfur was removed as sulfur dioxide. No other products of hydrolysis have been identified. An attempt was made to reduce 1-pentynepolysulfone with hydrogen over a platinum catalyst to see whether the reduction product could be shown to be identical with 1-pentenepolysulfone. No reduction occurred at room temperature in dioxane. The polymer lost sulfur dioxide when heated. Almost exactly half of the sulfur was eliminated as sulfur dioxide at the boiling point of dioxane. The only product besides sulfur dioxide which could be isolated after decomposition with heat was a crystalline material which analysis and molecular weight showed to be $C_{10}H_{16}SO_2$. The structure of this compound is yet unknown.

Pyrolysis in boiling dioxane removed approxi-

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[1] This is the fourth communication on polysulfones. For the third, see THIS JOURNAL, **57**, 2311 (1935).

[2] Hunt and Marvel, *ibid.*, **57**, 1691 (1935).

mately half of the sulfur from 1-heptynepolysulfone as sulfur dioxide. Phenylacetylenepolysulfone was insoluble in dioxane, but heating the polymer alone at 140° for the forty-five minutes liberated 62–73% of the sulfur as sulfur dioxide. No definite products could be isolated from the organic residue. When 1-pentynepolysulfone was heated to 200° until frothing ceased, only 50% of the sulfur was removed as sulfur dioxide. The evidence is as yet too meager to ascribe definite formulas to these acetylene–sulfur dioxide polymers but there is apparently considerable difference between the alkyl substituted and aryl substituted products.

No satisfactory molecular weight determinations have been made on any of the acetylene derivatives.

Experimental Part

Preparation of Polysulfones from Acetylenes.—Ten cubic centimeters each of liquid sulfur dioxide and the substituted acetylene were placed in a pressure bottle, and 5 cc. of ethyl alcohol was added. The bottles were sealed and allowed to stand overnight, then cooled and opened to permit the addition of 1 to 5 cc. of paraldehyde which contained peroxides. The amount of paraldehyde to be added varied roughly with various samples. Fresh paraldehyde was inert, but older samples which had been exposed to the air were very effective catalysts for the addition reaction. The flasks were sealed and allowed to come to room temperature. The contents of the flask were usually solid at this time. With 1-pentyne and 1-hexyne, the reaction was distinctly exothermic.

The reaction mixtures were poured into water and the products collected on a filter. The excess of sulfur dioxide and paraldehyde was removed by triturating with alcohol and ether several times. The polymer from 1-pentyne was further purified by dissolving in dioxane and reprecipitating by the addition of water. The products from 1-hexyne and 1-heptyne were purified similarly with acetone as the solvent.

The polysulfones from methyl-, ethyl- and propylacetylene were white, powdery, amorphous substances. The butyl- and amyl-acetylene derivatives were more flaky and were not easily ground to powder.

The products which have been prepared are listed in Table I.

Under the same experimental conditions which gave addition products when the monosubstituted acetylenes were used, no polysulfones could be obtained from dimethylacetylene, 2-hexyne, methylphenylacetylene, diethyl acetylenedicarboxylate or allene and sulfur dioxide. Acetylene itself was not investigated.

The polysulfones derived from methyl-, ethyl- and phenyl-acetylene were insoluble in water, alcohol, ether, acetone, carbon tetrachloride, chloroform, benzene and cold concentrated sulfuric acid. The polysulfones from *n*-propyl-, *n*-butyl- and *n*-amyl-acetylene were soluble in dioxane and could be precipitated from this solvent by the addition of water. Acetone could be substituted for dioxane when *n*-butyl- and *n*-amylacetylenes were used.

Table I

Polysulfones from Monosubstituted Acetylenes

RC≡CH R=	Yield, %	Temp. of decomp.[a] °C.	Empirical formula	S analyses, % Calcd.	Found	
Methyl	40	250–260	$C_3H_4SO_2$	30.8	29.4[b]	
Ethyl	30	210–215	$C_4H_6SO_2$	27.0	26.4	26.3
n-Propyl	60	203–208	$C_5H_8SO_2$	24.2	23.8	23.6
n-Butyl	90	195–205	$C_6H_{10}SO_2$	21.9	21.5	21.3
n-Amyl	75	164–170	[c]	..	..	..
Phenyl	50	250–275	$C_8H_6SO_2$	19.3	18.5	18.7

[a] These decomposition temperatures were determined by heating a sample in a capillary melting point tube in an oil-bath which was heated rapidly. The temperature of decomposition varies widely, depending on the rate of heating. [b] Calcd.: C, 34.6; H, 3.85. Found: C, 34.52, 34.23; H, 3.95, 3.94. [c] Analysis reported previously; see ref. 1.

All of these new polysulfones were sensitive to alkalies. The products did not dissolve in cold, aqueous, 10% sodium hydroxide, but on warming the mixture the sulfones dissolved and were hydrolyzed rapidly.

Oxidation of the Polysulfones from Acetylenes.—Five grams of 1-pentynepolysulfone was boiled for fifteen minutes with a solution of 24 g. of potassium permanganate in 500 cc. of water. The hydrated manganese dioxide was removed by filtration, and the solution was acidified with phosphoric acid. The distillate was distinctly acid. The Duclaux constants[3] for the volatile acid were 17.7, 16.0 and 14.1, whereas the values reported for *n*-butyric acid are 17.9, 15.9 and 14.6. To confirm the identification of the volatile acid the sodium salt was prepared and converted to the *p*-bromophenacyl derivative, which melted at 63°. A mixture of this product with an authentic specimen of the *p*-bromophenacyl ester of *n*-butyric acid melted at 63°.[4]

Similarly, 2 g. of 1-butynepolysulfone was oxidized with 12 g. of potassium permanganate. The product of this reaction was identified as propionic acid by the Duclaux constants, and preparation of the *p*-bromophenacyl ester which melted at 62°. There was no depression in the melting point when this ester was mixed with an authentic sample of the *p*-bromophenacyl ester of propionic acid.

When 1 g. of phenylacetylenepolysulfone was boiled with 1 g. of potassium permanganate in 20 cc. of water in a like manner, benzoic acid was obtained, m. p. 121.5°.

Hydrolysis of the Polysulfones.—Two grams of phenylacetylenepolysulfone was added to a solution of 2 g. of sodium hydroxide in 75 cc. of water, and the mixture was distilled. A very small amount of oily material came over with the water. The distillates from several such runs were combined, extracted with ether and the extract was concentrated and treated with 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazone, after crys-

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[3] Duclaux, *Ann. chim. phys.*, [5] **2**, 289 (1874); Upson, Plum and Shott, This Journal, **39**, 731 (1917); Lamb, *ibid.*, **39**, 746 (1917).

[4] Judefind and Reid, *ibid.*, **42**, 1043 (1920).

tallization from alcohol, melted at 238°, and showed no depression of melting point when mixed with an authentic specimen of the 2,4-dinitrophenylhydrazone of acetophenone.[5]

In another experiment, 4 g. of phenylacetylenepolysulfone was hydrolyzed by boiling with 60 cc. of 3% sodium hydroxide solution for thirty minutes. The volatile material was distilled with steam and the alkaline residue was extracted with ether. From this extract a solid was obtained. After recrystallization from benzene it melted at 124°, and showed no depression of melting point when mixed with an authentic specimen of benzylmethylsulfone (m. p. 124.5°).[6]

Anal. Calcd. for $C_8H_{10}SO_2$: C, 56.47; H, 5.88. Found: C, 56.38; H, 5.75.

The yield of benzylmethylsulfone was 0.28 g. (8%).

In another similar alkaline hydrolysis 2 g. of phenylacetylenepolysulfone was refluxed two hours with 50 cc. of 10% sodium hydroxide. The hydrolysate was extracted with ether to remove neutral compounds. Hydrogen peroxide was added to oxidize the sulfite, the solution was acidified with hydrochloric acid and the benzoic acid was extracted with ether. The ether was evaporated and the benzoic acid was extracted from the tarry residue with hot water and determined by titrating with 0.1 *N* sodium hydroxide. Twenty-five cubic centimers of base was used. This is equivalent to 2.5 millimoles (0.305 g.), or, roughly, 20% of the theoretical amount of benzoic acid

The amount of sulfite which had been produced in the hydrolysis was determined by oxidation with hydrogen peroxide and precipitation as the sulfate. The barium sulfate weighed 1.253 g. (5.37 millimoles). This accounts for 45% of the sulfur in the polymer.

In another experiment, analyses were run on the dried residue (after extraction with ether). This showed that 25% of the sulfur was removed by extraction with ether. An aliquot part of the dried residue was extracted with alcohol. This process removed 25% of the total sulfur, leaving a residue containing 50% of the total sulfur as sodium sulfite.

Five grams of 1-pentynepolysulfone was mixed with 100 cc. of 10% sodium hydroxide solution, and the mixture was slowly distilled. The distillate was treated with an alcohol solution of 2,4-dinitrophenylhydrazine and a small amount of the 2,4-dinitrophenylhydrazone of methyl *n*-propyl ketone, m. p. 135–137°, was obtained. This material was mixed with an authentic specimen of the methyl *n*-propyl ketone derivative (m. p. 141°),[5] and the mixture melted at 138–139°. No definite products except sodium sulfite could be identified in the alkaline residue. By making the mixture acid with phosphoric acid, and distilling the sulfur dioxide into standard alkali, it was found that between 40 and 50% of the original sulfur in the 1-pentynepolysulfone was removed as sulfite.

Pyrolysis of the Polysulfones.—A 0.2372-g. sample of 1-pentynepolysulfone was placed in a test-tube fitted with a gas delivery tube dipping into standard alkali. The test-tube was then heated to 200° until frothing in the tube ceased (thirty minutes) and the tube was swept out with air. Titration of the standard alkali showed that 50% of the sulfur of the polymer was liberated as sulfur dioxide. When the polymer was heated at 200° for one hour, 51% of the sulfur dioxide was liberated. When the polymer was heated at 205–215° for one hour, roughly 60% of the sulfur dioxide was eliminated, showing that further decomposition takes place at higher temperatures.

With phenylacetylenepolysulfone, pyrolysis at 140° for forty-five minutes liberated from 62 to 73% of the sulfur dioxide. There seemed to be no really definite stopping place in the decomposition of this derivative.

By dissolving 1-pentynepolysulfone in dioxane and heating the solution to boiling, sulfur dioxide was liberated slowly, and the amount lost approached 50% as a limiting value. 1-Heptynepolysulfone showed a similar behavior. This is shown best by the accompanying curve (Fig. 1).

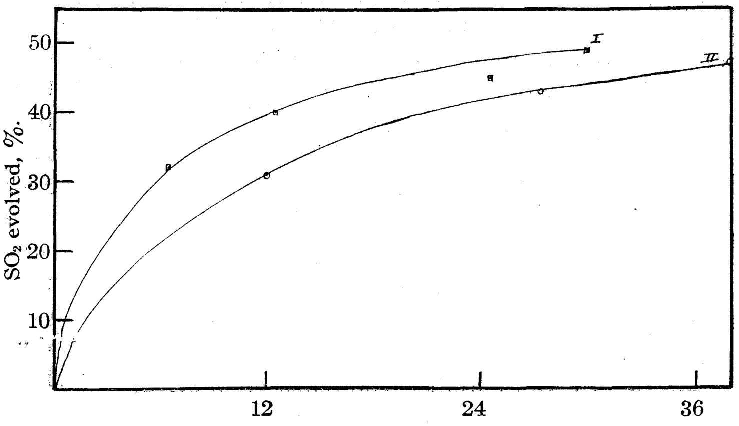

Fig. 1.—I, Pyrolyis of 1-heptynepolysulfone in dioxane; II, pyrolysis of 1-pentynepolysulfone in dioxane.

When 100 g. of 1-pentynepolysulfone was heated in 50 cc. of dioxane until approximately 50% of the sulfur dioxide was evolved and the solution evaporated and poured into ether, a small amount of the original polymer was obtained. In addition, a small amount (0.05 g.) of a crystalline compound, m. p. 88°, was obtained. This product did not add bromine, but did decolorize aqueous potassium permanganate solution.

Anal. Calcd. for $C_{10}H_{16}SO_2$: C, 60.00; H, 8.00; S, 16.00; mol. wt., 200. Found: C, 59.43; H, 7.97; S, 14.73; mol. wt. (Rast), 203.

The structure of this compound has not been determined, but its behavior toward bromine and potassium permanganate solution, together with the analysis and molecular weight, suggest that it may be a dipropylthiophenesulfone.

The polysulfones from 1-heptyne, 1-hexyne and phenylacetylene gave no product of this type.

Summary

1. A number of alkylacetylenes and phenylacetylene have been shown to combine with sul-

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[5] Allen, THIS JOURNAL, **52**, 2955 (1930).

[6] Freiman and Sugden, *J. Chem. Soc.*, 263 (1928).

fur dioxide to give polymeric products. No disubstituted acetylene has been found which gives this addition reaction.

2. Some preliminary work on the exact structure of these addition products has been described.

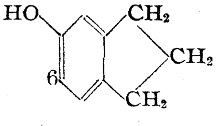
URBANA, ILLINOIS RECEIVED AUGUST 10, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

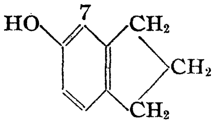
An Investigation of the Mills–Nixon Effect

BY LOUIS F. FIESER AND WARREN C. LOTHROP

In an important and much-discussed[1] paper, Mills and Nixon[2] advanced the hypothesis that hydrindene, or a given substituted hydrindene, is in a condition of less strain when it has the bond structure shown in formula I than when it exists in the alternate Kekulé form (II) in which the carbon atoms common to the two rings are connected by a double bond. As a means of testing the conclusion that I should be the more stable form of 5-hydroxyhydrindene, or the predominant isomer in the tautomeric equilibrium mixture, these investigators studied the diazo coupling of the substance and its behavior on bromination. Since these are reactions characteristic of enolic systems, substitution should occur at the ortho position joined to the hydroxylated carbon atom by a double linkage, that is, position 6 of I and position 7 of II. It was found that, although substitution does not proceed entirely in a single direction, about 90% of the reaction product is the 6-substituted isomer, indicating that I is the more stable form.

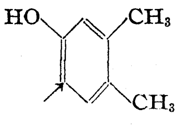


I

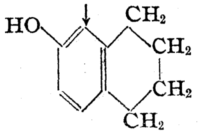


II

The observation loses some of its significance because of the fact, noted by Mills and Nixon, that *as-o*-xylenol (II) also is attacked chiefly in the 6-position (arrow), showing that in 5-hydroxyhydrindene the chemical effect of the alicyclic ring may be sufficient, without assistance from a steric factor, to control substitution largely into one of the two available ortho positions. The contrasting behavior of 6-hydroxytetralin (IV), which yields 5-substitution products, afforded the only evidence in the original work of the existence of the Mills–Nixon effect, that is, of a fixation of the bonds in one of the two Kekulé forms as the result of the stereochemical demands of an attached ring. The behavior of IV pointed to the bond structure indicated and, since the 5- and 6-membered rings must be quite similar chemically, the difference was attributed to the different spatial requirements of the two rings. From a theoretical analysis of the configuration of the tetralin molecule, Mills and Nixon concluded, albeit with less conviction than in the other case, that there should be a preference for the Kekulé structure IV.



III



IV

It seemed to us that the preferential formation of one of two possible isomers may be the result of only a moderate preponderance of one tautomeric form, or of even a very slight difference in reactivities, and that the Mills–Nixon effect may be at most a subtle one in comparison to the fixation of bonds resulting from the fusing together of two aromatic nuclei,[3] and we undertook to apply to hydrindene and to tetralin the much more severe test previously employed in investigating naphthalene,[3] anthracene,[4] and phenanthrene.[5] For this purpose phenolic derivatives in which one of the two ortho positions is blocked by an alkyl group were synthesized and tested for their ability to couple with diazotized amines. If the 5-hydroxyhydrindene derivatives V and VI exist in the stable state suggested by Mills and Nixon, coupling at the free ortho position should occur easily in the case of VI, but only following a migration of the double linkages in the case of V.

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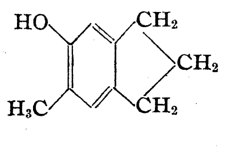
[1] Thompson, *Chemistry and Industry*, **52**, 61 (1933); Baker, *J. Chem. Soc.*, 1678, 1684 (1934); 274 (1936); Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935); Hampson and Weissberger, *J. Chem. Soc.*, 393 (1936).

[2] Mills and Nixon, *ibid.*, 2510 (1930).

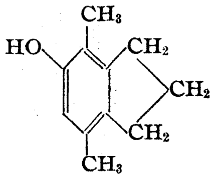
[3] Fieser and Lothrop, THIS JOURNAL, **57**, 1459 (1935).

[4] Fieser and Lothrop, *ibid.*, **58**, 749 (1936).

[5] Fieser and Young, *ibid.*, **53**, 4120 (1931).

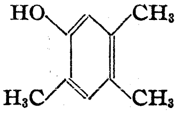


V



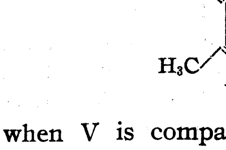
VI

Actually VI readily yielded azo derivatives whereas with V the coupling tests were entirely negative.[6] The observation is particularly striking when V is compared with pseudocumenol, VII, for the latter substance readily enters into the coupling reaction[7] and therefore is free to react in the Kekulé form shown in the formula. This evidence clearly indicates that the five-membered ring of hydrindene restricts the movement of the double linkages in the benzene nucleus exactly as supposed by Mills and Nixon and to an even greater extent than the results of these investigators would indicate.

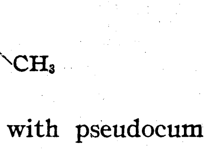


VII

In the tetralin series the situation is quite different. If the bond structure is that deduced by Mills and Nixon, and if the fixation imposed by the six-membered ring is comparable with that noted above, VIII should couple and IX should not. The first of these compounds is already known from the work of Vezelý and Štursa[8] to be capable of coupling with diazotized amines, and on examining IX we found that this substance behaves in a similar manner. Since with typical 6-hydroxytetralins both ortho positions are capable of functioning as enolic groups, it is concluded the double bonds of tetralin are at least fairly free to migrate and that if the Mills–Nixon effect is operative in this case the restriction is comparatively slight.



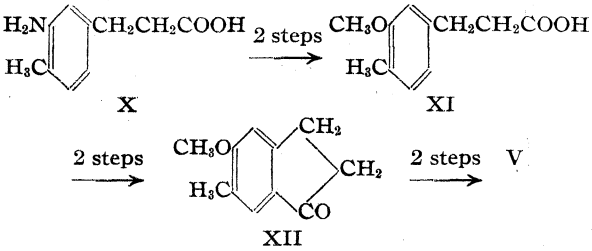
VIII



IX

Our conclusions with regard to both hydrindene and tetralin agree precisely with those recently reached by Sidgwick and Springall[9] from a study of the dipole moments of *o*-dibromo derivatives of the two hydrocarbons.

For the synthesis of 5-hydroxy-6-methylhydrindene (V), 3-amino-4-methylhydrocinnamic acid[10] (X) was prepared by known methods from 3-nitro-4-methylbenzaldehyde[11] and converted to the hydroxy compound and its ether XI.



This was cyclized through the acid chloride, and the hydrindone XII was reduced by the Clemmensen method and demethylated. That the ring closure takes the expected course is clearly indicated by the failure of V to couple with diazotized amines, for the alternate substance would have available a free para position and would surely react.

For the preparation of VI we at first investigated a synthesis from *p*-xylenol, through the aldehyde and acrylic acid derivatives, which Clemo, Haworth and Walton[12] carried as far as 6-methoxy-4,7-dimethylhydrindone-1, but as considerable difficulty was experienced in methylating the hydroxy aldehyde other methods were investigated. Since 4,7-dimethylhydrindone-1 is readily obtainable from *p*-xylene and β-chloropropionyl chloride,[13] this was reduced to 4,7-dimethylhydrindene and attempts were made to introduce a hydroxyl group through the monosulfonate or the mononitro compound. The sulfonate was obtained without difficulty, but the alkali fusion was wholly unsuccessful, and the nitration of the hydrocarbon under very moderate conditions afforded only a dinitro derivative. The hydrocarbon resembles prehnitene[14] in the latter respect. The following synthesis finally was developed. *p*-Xylyl methyl ether was condensed with β-chloropropionyl chloride in the presence of

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(6) Fisher, Furlong and Grant, THIS JOURNAL, **58**, 820 (1936), have reported the failure of the coupling reaction with a similar hydroxyhydrindene of more complicated structure.

(7) Liebermann and Kostanecki, *Ber.*, **17**, 885 (1884).

(8) Vezelý and Štursa, *Collection Czechoslov. Chem. Communications*, **6**, 137 (1934).

(9) Sidgwick and Springall, *Chemistry and Industry*, **55**, 476 (1936).

(10) Salway, *J. Chem. Soc.*, **103**, 1994 (1913).

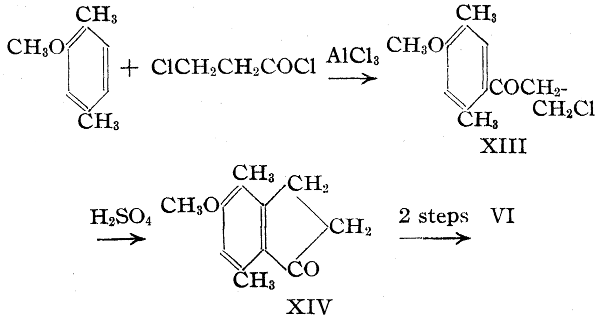
(11) Hanzlik and Bianchi, *Ber.*, **32**, 1288 (1899).

(12) Clemo, Haworth and Walton, *J. Chem. Soc.*, 2368 (1929).

(13) Mayer and Müller, *Ber.*, **60**, 2278 (1927).

(14) Smith and Hac, THIS JOURNAL, **56**, 477 (1934).

aluminum chloride, giving in good yield a crystalline chloro ketone. In analogy with other Friedel and Crafts reactions[12] and since the ring closure described below proves that the entering group is not ortho to the methoxyl group, the substance can be assigned the formula XIII. The cyclization of the chloro ketone with sulfuric acid proceeded poorly (27% yield), but gave a pure ketone, 5-methoxy-4,7-dimethylhydrindone-1 (XIV). It is interesting that this substance melts at the same temperature as the isomeric 6-methoxy compound of Clemo, Haworth and Walton,[12] for the melting points of the 5- and 6-methoxy derivatives of hydrindone-1 are within one degree of each other.[15]



The remaining compound, 6-hydroxy-5,8-dimethyltetralin (IX) was obtained from 7-methoxy-5,8-dimethyltetralone-1, synthesized according to Clemo, Haworth and Walton.[12]

Experimental Part

3-Amino-4-methylhydrocinnamic Acid.[10]—To prepare 3-nitro-4-methylbenzaldehyde[11] 120 g. of tolualdehyde was added in three to four hours to a well-stirred mixture of 600 cc. of concentrated sulfuric acid and 60 cc. of concentrated nitric acid, keeping the solution at 0-3°. After pouring the solution onto ice the pale yellow product was washed free of acid, dried in ether with calcium chloride, and vacuum distilled; yield 132 g. (80%), m. p. 43°. 3-Nitro-4-methylcinnamic acid was prepared from the aldehyde both by the Perkin reaction[11] (63% yield), and by condensation with malonic acid in the presence of pyridine and piperidine (70% yield), following the procedure given by Brand and Horn[16] for an analogous case.

The reduction of the nitro group and simultaneous saturation of the double bond was accomplished conveniently by the hydrogenation of the unsaturated acid (20.7 g.) dissolved in 95% alcohol (275 cc.) using Adams catalyst (0.2 g.). Some solid material which separated was dissolved by warming and the filtered solution was diluted with 1 liter of water and cooled well. The product separated in slightly pink crystal aggregates; yield 13.6 g. (76%), m. p. 140–141°.

3-Hydroxy-4-methylhydrocinnamic Acid.—A solution of 8.96 g. of the above amine and 2.65 g. of sodium carbonate in 100 cc. of water was cooled, treated with an aqueous solution of 3.7 g. of sodium nitrite, and poured into a mixture of 10 cc. of concentrated hydrochloric acid, 50 g. of ice and 4.7 g. of boric acid. The mixture was gradually warmed, with stirring, and finally boiled for a few minutes and clarified with Norite. After cooling, the hydroxy acid was obtained by extraction with ether as a crystalline mass, m. p. 154–156°. Recrystallization from a very small volume of water gave slightly buff colored flat needles, m. p. 156–157°; yield 5.5 g. (61%).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.63; H, 6.72. Found: C, 66.58; H, 6.95.

3-Methoxy-4-methylhydrocinnamic acid was obtained by the action of dimethyl sulfate on the above acid in warm alkaline solution. The substance crystallized from 50% alcohol as fine, colorless needles, m. p. 82–83°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.78; H, 7.35.

5-Methoxy-6-methylhydrindone-1.—The acid (9.25 g.) was warmed with thionyl chloride (4.6 cc.) and after the completion of the reaction and the removal of the excess reagent at the water pump the acid chloride was taken into 200 cc. of carbon bisulfide. Treatment with Norite gave a clear yellow solution, which was then cooled to 0° and treated with 14 g. of aluminum chloride. An oily complex separated, and after refluxing for four hours the mixture was cooled and treated with ice and hydrochloric acid. The residue remaining on removing the solvent by steam distillation was extracted with ether, which left much tarry material undissolved. On extracting the ethereal solution with sodium carbonate solution, 2.1 g. of starting material was recovered, while the residual ethereal solution yielded 2.7 g. of the hydrindone (42% conversion). The substance dissolves readily in petroleum ether and crystallizes from this solvent as lustrous, colorless needles, m. p. 114–115°.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 75.24; H, 7.05.

An attempt to demethylate the hydrindone (2.7 g.) with 48% hydrobromic acid (3.5 cc.) and glacial acetic acid (30 cc.) led to the formation of a dimer. After boiling the solution for one hour a considerable quantity of orange-red needles had deposited and the mixture was cooled and filtered. From the mother liquor 1.7 g. of unchanged hydrindone was recovered. The orange-red needles (0.65 g., m. p. 215–217°, dec.) became yellow when boiled with dilute alkali, and this material on crystallization from acetic acid formed small yellow needles, m. p. 237–240°.

Anal. Calcd. for $C_{22}H_{24}O_4$: C, 74.97; H, 6.87; mol. wt., 396. Found: C, 75.47, 75.62; H, 6.85, 6.90; mol. wt. (Rast), 346.

5-Hydroxy-6-methylhydrindene.—A mixture of 1.7 g. of the hydrindone, 13.5 g. of amalgamated zinc, 34 cc. of concentrated hydrochloric acid, 10 cc. of water and 13 cc. of toluene was refluxed for eighteen hours. After steam distillation of the solvent the product was extracted with ether, but as the crude material (1.3 g.) appeared sensitive to oxidation and turned blue, it was demethylated without

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[15] Ingold and Piggott, *J. Chem. Soc.*, **123**, 1469 (1923).

[16] Brand and Horn, *J. prakt. Chem.*, **115**, 374 (1927).

further purification by refluxing under nitrogen with 25 cc. of glacial acetic acid, 1.8 cc. of 48% hydrobromic acid and 1 cc. of 45% hydriodic acid for three and one-half hours. After pouring the solution into 200 cc. of water and neutralizing the acids with sodium carbonate, the hydroxy compound separated as large, buff colored plates, m. p. 74–76°. Recrystallization from petroleum ether gave material melting at 83–84°, but the color was not entirely removed; yield 0.7 g. (49%). The compound has an odor reminiscent of that of β-naphthol.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.02; H, 8.17. Found: C, 80.84; H, 8.37.

Coupling tests in alkaline solution with diazotized sulfanilic acid were somewhat indecisive for there was considerable discoloration. With diazotized *p*-nitroaniline test solutions remained quite clear and were hardly distinguishable from alkaline solutions containing only the diazo component.

The benzoyl derivative crystallized from dilute alcohol as small, colorless plates, m. p. 111–112°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.79; H, 6.74.

4,7 - Dimethylhydrindene.—4,7 - Dimethylhydrindone-1 (m. p. 77°) was prepared according to Mayer and Müller[13] in 71% yield. Reduction by the Clemmensen method and recovery of the product by steam distillation gave a product boiling at 223–225° at atmospheric pressure and solidifying in a freezing mixture, m. p. −1.5°, yield 73%. The substance did not form a picrate.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.00; H, 10.10.

Sodium 4,7 - Dimethylhydrindene - 5 - sulfonate.—A mixture of 6.5 g. of the hydrocarbon and 75 cc. of concentrated sulfuric acid was stirred mechanically for fifteen minutes on the steam-bath and the resulting solution was poured onto 500 cc. of ice. After neutralization with soda the solution was saturated at the boiling point with sodium chloride and on cooling the sulfonate separated as large white flakes. The yield after recrystallization was 8.7 g. (79%). For characterization and analysis the substance was converted into the *p*-toluidine salt, which formed long glistening needles from water, m. p. 248–249°, dec.

Anal. Calcd. for $C_{18}H_{23}O_3NS$: C, 64.83; H, 6.96. Found: C, 64.95; H, 7.16.

Attempted fusions of the sodium salt with potassium hydroxide gave either unchanged material or intractable tars.

5,6 - Dinitro - 4,7 - dimethylhydrindene.—To a mixture of 1.6 cc. of concentrated nitric acid and 17 cc. of concentrated sulfuric acid at 0°, 3 g. of 4,7-dimethylhydrindene was added with stirring in one-half hour. The pasty mixture was poured onto ice and the pale yellow solid obtained was crystallized twice from glacial acetic acid, giving 2.3 g. of buff colored plates, m. p. 191–192°.

Anal. Calcd. for $C_{11}H_{12}O_4N_2$: C, 55.91; H, 5.13. Found: C, 56.28; H, 5.20.

2-Methoxy-5-β-chloropropionyl-*p*-xylene (XIII).—Sodium *p*-xylene sulfonate, obtained in 85–95% yield after heating the hydrocarbon (20 g.) with concentrated sulfuric acid (100 cc.) for about fifteen minutes on the steam-bath, gave *p*-xylenol in 66% yield on fusion with potassium hydroxide at 280–290°, and the methyl ether was prepared in the usual way.[12] After several trials the following procedure was found most satisfactory for the Friedel and Crafts reaction.

To a vigorously stirred suspension of 37.2 g. of finely powdered aluminum chloride in 250 cc. of carbon bisulfide there was added over a half-hour period 35.6 g. of β-chloropropionyl chloride, a bright yellow complex separating as a solid. After cooling to 0°, 34 g. of *p*-xylyl methyl ether was added by drops with stirring in the course of forty-five minutes. On allowing the mixture to come to room temperature hydrogen chloride was evolved copiously and a dark purple complex collected as a heavy oil. After standing overnight ice and hydrochloric acid were added and the carbon bisulfide layer was separated and combined with ether extracts of the aqueous layer. After washing with dilute acid, dilute alkali and water, the solution was dried over sodium sulfate and the solvent removed by distillation. The residual yellow oil solidified on cooling and pure material was easily obtained by crystallization from petroleum ether; yield, 41.9 g. (74%). The ketone forms colorless, prismatic plates melting at 85–86°; it is volatile with steam but decomposes on attempted distillation at reduced pressure.

Anal. Calcd. for $C_{12}H_{15}O_2Cl$: C, 63.55; H, 6.66. Found: C, 63.38; H, 7.01.

A derivative, **1-phenyl-3-(2′,5′-dimethyl-3′-methoxyphenyl)-Δ²-pyrazoline,** was obtained by heating the chloro ketone (0.5 g.) in absolute alcohol (7 cc.) with phenylhydrazine (0.5 g.) on the steam-bath. The difficultly soluble product separated rapidly and was recrystallized from its faintly fluorescent solution in alcohol, giving nearly colorless small plates, m. p. 171–172°.

Anal. Calcd. for $C_{18}H_{20}ON_2$: C, 77.09; H, 7.21. Found: C, 76.69; H, 7.49.

5-Methoxy-4,7-dimethylhydrindone-1 (XIV).—In trial cyclizations of the above chloro ketone warm concentrated sulfuric acid either left the material largely unchanged or gave extensive sulfonation. Formic acid at 100° was without effect, and aluminum chloride in carbon bisulfide solution gave an alkali-soluble product. The following procedure, although far from satisfactory, was the best found. To a cold solution of 1.5 g. of the chloro ketone in 8 cc. of glacial acetic acid, 12 cc. of concentrated sulfuric acid was added and the clear red solution was warmed on the steam-bath for one hour and poured onto ice. The somewhat orange material which precipitated was collected and crystallized twice from glacial acetic acid, giving almost colorless needles, m. p. 163–165°; yield 0.35 g. (27%).

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.41. Found: C, 75.54; H, 7.25.

5-Methoxy-4,7-dimethylhydrindene.—A solution of 4 g. of the hydrindone in warm alcohol was added in small portions in one and one-half hours to a refluxing mixture of 42 g. of amalgamated zinc, 29 cc. of concentrated hydrochloric acid and 14 cc. of water, waiting after each addition until the yellow color had disappeared before adding a fresh portion. After adding 20 cc. more of the concentrated acid and refluxing for three hours, the reduction product was recovered by steam distillation as a colorless oil. Further purification was effected by steam distillation from an alkaline medium, and on cooling the distillate with ice the substance solidified to a mass of colorless needles, m. p. 25–26°; yield 3.25 g. (90%).

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.79; H, 9.14. Found: C, 81.49; H, 9.32.

5-Hydroxy-4,7-dimethylhydrindene (VI).—The above ether (3.25 g.) was refluxed with 25 cc. of glacial acetic acid and 4 cc. of 48% hydrobromic acid for three hours in a nitrogen atmosphere, and on pouring the solution into water the hydroxy compound separated as a pink solid. It was taken up in dilute alkali, the solution was clarified with Norite and acidified, and the dried product was crystallized twice from petroleum ether; yield 2 g. (66%). The substance forms fine colorless needles melting at 111–112°.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.32; H, 8.76.

The benzoyl derivative forms colorless plates, m. p. 72–73°, from dilute alcohol.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.18; H, 6.80. Found: C, 80.82; H, 6.95.

5 - Hydroxy - 4,7 - dimethyl - 6 - *p* - nitrobenzeneazohydrindene was obtained by coupling the components in 1% alkali at 0°. A red precipitate separated at once and it was unaffected by rendering the solution acidic and boiling the mixture to coagulate the material. Recrystallized from glacial acetic acid, in which it is sparingly soluble, the azo compound formed brownish-red needles, m. p. 220–222°, dec. It is insoluble in alkali.

Anal. Calcd. for $C_{17}H_{17}O_3N_3$: C, 65.58; H, 5.50. Found: C, 65.72; H, 5.85.

6-Methoxy-5,8-dimethyltetralin.—On condensing *p*-xylyl methyl ether and succinic anhydride with aluminum chloride in benzene solution as described by Clemo, Haworth and Walton,[12] the yield was even lower than that (70%) reported by these investigators, but the general procedure described by Fieser and Hershberg[17] proved very satisfactory. Using 0.2 mole of the ether, 0.21 mole of succinic anhydride, 200 cc. of tetrachloroethane, 50 cc. of nitrobenzene and 0.42 mole of aluminum chloride, stirring at 0° until solution was complete, and allowing the mixture to stand for four days at 0°, β-4-methoxy-2,5-dimethylbenzoylpropionic acid, recovered as usual and crystallized from dilute alcohol, was obtained as colorless crystals, m. p. 130–131°, in 86% yield. The reduction to γ-4-methoxy-2,5-dimethylphenylbutyric acid (m. p. 98–99°) by the Clemmensen–Martin method has been described[18] already. Cyclization was effected according to Clemo, Haworth and Walton[12] in 64% yield.

7-Methoxy-5,8-dimethyltetralone-1 (6 g.) was reduced by the ordinary Clemmensen method, refluxing for twenty-one hours, and the material extracted with ether after distillation (b. p. 116–125° at 12–13 mm.) was obtained as a solid, m. p. 36–38°; yield 4.25 g. (76%). Crystallization from petroleum ether gave colorless needles melting at 38–39°.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.52. Found: C, 82.36; H, 9.76.

6-Hydroxy-5,8-dimethyltetralin (IX).—For demethylation the ether (4.25 g.) was refluxed with glacial acetic acid (25 cc.) and 45% hydriodic acid (9.75 g.) for three hours. The crude product was precipitated from a clarified solution in dilute alkali and crystallized from petroleum ether, giving nearly colorless needles, m. p. 104–105°, yield 2.45 g. (62%). The substance dissolves in dilute alkali slowly on warming.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.79; H, 9.14. Found: C, 81.78; H, 9.48.

The benzoyl derivative forms very long, slender, colorless needles, m. p. 119–120°, from dilute alcohol.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.38; H, 7.18. Found: C, 81.44; H, 7.26.

6 - Hydroxy - 5,8 - dimethyl - 7 - *p* - nitrobenzeneazotetralin was obtained by coupling as described above and crystallized from glacial acetic acid, in which it is sparingly soluble. The substance forms bronze-red needles, m. p. 229–231°. It is insoluble in alkali and stable to acids.

Anal. Calcd. for $C_{18}H_{19}O_3N_3$: C, 66.42; H, 5.90. Found: C, 66.50; H, 6.11.

Summary

β-Hydroxy derivatives of hydrindene and of tetralin with one ortho position blocked with a methyl group and the other free have been tested in the coupling reaction to determine if both ortho positions are capable of constituting enolic groups, or if there is any fixation of the bonds in the aromatic nucleus as the result of the spatial requirements of the attached alicyclic rings (Mills–Nixon effect). This test affords a more severe criterion of fixation than that of Mills and Nixon, based upon reactivities, and the results indicate that hydrindene has a rigid bond structure comparable with that of naphthalene, but that tetralin, like all ordinary benzene derivatives, can react in both Kekulé forms.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.
RECEIVED AUGUST 12, 1936

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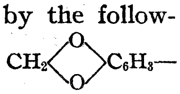
[17] Fieser and Hershberg, Part IV, in press.

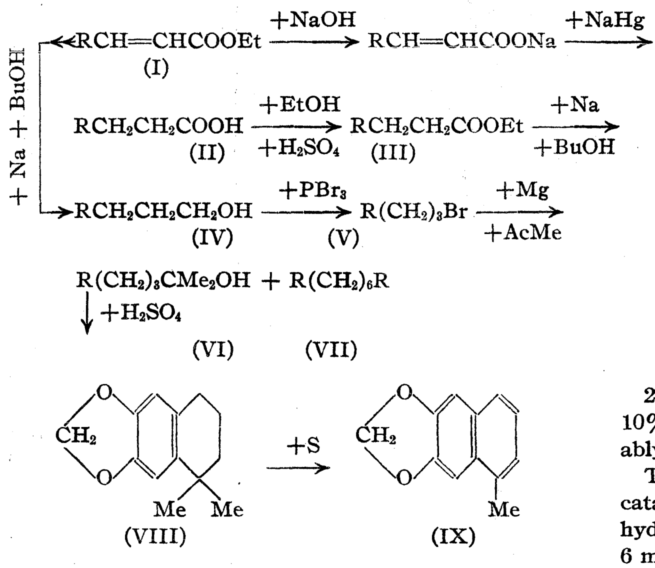
[18] Martin, THIS JOURNAL, **58**, 1438 (1936).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of 1,1-Dimethyl-6,7-methylenedioxytetralin[1]

BY RUBY MURRAY ORCUTT AND MARSTON TAYLOR BOGERT

In continuation of our investigations in the ionene field,[2] and in the cyclodehydration of aromatic alcohols,[3] we have had occasion to synthesize a methylenedioxytetralin by the following steps, in which formulas R = 



Experimental

Ethyl Piperonylacetate (III).—Ethyl piperonylideneacetate (I), prepared from piperonal and ethyl acetate, according to Hoering's directions,[4] was saponified by boiling with the calculated amount of 0.1 *N* sodium hydroxide. The solution was cooled quickly, to prevent the crystallization of the sodium salt, and a 10% excess of sodium amalgam was added slowly. When the reduction was complete, the mixture was filtered, the filtrate cooled with ice and acidified with hydrochloric acid. The precipitated piperonylacetic acid was washed, dried, and crystallized from ether, giving a colorless crystalline product, m. p. 87–90°, which did not decolorize a cooled 10% carbon tetrachloride solution of bromine; yield 75–80%.

Lorenz,[5] who prepared this acid by a similar method, differing only in certain details, gave its m. p. as 84°. Kaufmann and Radosević,[6] who obtained it by hydrolysis of its methylamide, also recorded the m. p. as 84°.

Warmed with absolute ethanol and a little sulfuric acid, the acid yielded the ethyl ester as a colorless transparent liquid, of pleasant odor, b. p. 184–185° at 14 mm., which did not decolorize a cooled 10% carbon tetrachloride solution of bromine; yield 83%.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.84; H, 6.35. Found: C, 64.94; H, 6.64.

2-Piperonylethanol (IV), prepared from the foregoing ester by reduction with sodium and *n*-butyl alcohol, formed a colorless viscous liquid, b. p. 170–172° at 8 mm., 182–183.5° at 14 mm., 184–186° at 16 mm., and 186–188° at 19 mm.; yield 87%. Cooled to −10°, it slowly congealed to a crystalline mass. When the temperature of this solid was permitted to rise slowly, it began to melt at 28° and was completely liquefied at 29°. The m. p. of 2-piperonylidene ethanol is given in the literature[7] as 78–78.8° (corr.). Hence the product cannot be the unsaturated alcohol.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.63; H, 6.72. Found: C, 66.30; H, 6.75.

2-Piperonylethanol immediately decolorized a cooled 10% carbon tetrachloride solution of bromine, presumably being promptly oxidized thereby.

This saturated alcohol has been reported[8] as one of the catalytic reduction products of piperonylidene acetaldehyde, although the b. p. recorded (149–150°, uncorr., at 6 mm.) was lower than that given above.

Phenylurethan, m. p. 98–99°.

Anal. Calcd. for $C_{17}H_{17}O_4N$: C, 68.20; H, 5.72. Found: C, 67.97; H, 5.83.

A more direct and shorter road to the same goal (IV), was the reduction of the ethyl piperonylideneacetate (I) by sodium and *n*-butyl alcohol, as follows:

A 3-necked 2-liter flask, equipped with mercury-sealed stirrer, a reflux condenser, and a dropping funnel, protected with calcium chloride guard tubes, and containing 37.8 g. of sodium and 100 cc. of dry toluene, was heated above the m. p. of the sodium and then allowed to cool during vigorous stirring, so as to obtain the sodium in a finely divided state. To this mixture, there was added, as rapidly as possible, a solution of 36.2 g. of the ester (I) in 100 cc. of *n*-butyl alcohol. There ensued a vigorous reaction, with much foaming. When this subsided, more (150 cc.) *n*-butyl alcohol was added, to dilute the mixture, to aid in keeping the alcoholate in solution, and to react with any unattacked sodium.

The mixture was hydrolyzed by addition of water, the oily layer separated from the aqueous alkaline one, the latter extracted twice with *n*-butyl alcohol and the extracts added to the oily layer. This was distilled at ordinary pressure, to remove the toluene and butyl alcohol, and then under reduced pressure, to isolate the

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(1) Presented in abstract before the Division of Organic Chemistry, at the New York meeting of the American Chemical Society, April 23, 1935.

(2) (a) Bogert and Fourman, THIS JOURNAL, **55**, 4670 (1933); (b) Bogert and Apfelbaum, *Science*, [N. S.], **79**, 280 (1934); (c) Bogert, Davidson and Apfelbaum, THIS JOURNAL, **56**, 959 (1934).

(3) (a) Bogert and Davidson, *ibid.*, **56**, 185 (1934); (b) Roblin, Davidson and Bogert, *ibid.*, **57**, 151 (1935).

(4) Hoering, *Ber.*, **40**, 2176 (1907).

(5) Lorenz, *ibid.*, **13**, 758 (1880).

(6) Kaufmann and Radosević, *ibid.*, **49**, 681 (1916).

(7) Bogert and Powell, THIS JOURNAL, **53**, 1609 (1931).

(8) Bogert and Powell, *ibid.*, **53**, 2757 (1931).

piperonylethanol (IV); b. p. 184–186° at 16 mm.; yield 62%.

From the aqueous alkaline layer there was obtained a small amount of piperonylideneacetic acid, $(CH_2O_2)C_6H_3CH{=}CHCOOH$, m. p. 237–238° (from acetic acid), agreeing with that in the literature.

Repeating the above experiment, with amyl in place of butyl alcohol, the results were much the same, except that the initial reaction was more vigorous, the yield somewhat lower (60%), and the by-product piperonylacetic acid, $(CH_2O_2)C_6H_3CH_2CH_2COOH$ (large, colorless crystals, m. p. 84°; m. p. in literature,[6] 84°).

In another series of experiments, replacing the toluene by xylene, the results were less satisfactory. The same alcohol (IV) was obtained and, as by-products, there were recovered both piperonylidene and piperonylacetic acids, in the ratio of 3:1. The former was reduced to the latter, in 80% yield, by sodium amalgam.[5]

1-Bromo-2-piperonylethane (V) could not be secured from the alcohol (IV) by the action of 48% aqueous hydrogen bromide, alone or with the addition of sulfuric acid, because of the decomposition which almost immediately ensued. It was obtained, however, by the following process.

The alcohol (28 g.), contained in a flask well protected from access of any moisture, was congealed in a freezing mixture and phosphorus tribromide (10 g.) added. After a few minutes' standing, the container was removed from the freezing mixture and allowed to come slowly to room temperature. The reaction began gradually, with evolution of hydrogen bromide, and accelerated considerably as the temperature approached that of the m. p. (28–29°) of the alcohol, so that some cooling occasionally was necessary at this point. The crude yellowish-brown product was poured into a mixture of dilute sodium bicarbonate solution and cracked ice, and the bromide (V) extracted with ether. The aqueous layer, containing some of the original alcohol as sodium alcoholate, was acidified and the alcohol recovered. The bromide obtained from the ether extracts, when freshly distilled and pure, was a colorless liquid, b. p. 163–165° at 7.5 mm., $n^{25}D$ 1.5599, but darkened rapidly on exposure to air and light; yield, 50–53%; original alcohol recovered, 20–25%.

Anal. Calcd. for $C_{10}H_{11}O_2Br$: C, 49.38; H, 4.56. Found: C, 49.41; H, 4.87.

1,4-Dipiperonylbutane (VII).—The Grignard reagent was prepared by mixing 48.8 g. of the above bromide, 8 g. of magnesium, and 50 cc. of dry ether, and adding 100 cc. more of dry ether when the reaction was well started. A final warming for an hour completed the reaction. After cooling the mixture to −5°, 14 g. of acetone in an equal volume of dry ether was slowly stirred in, and the stirring continued for a further half hour. It was then poured upon ice acidulated with the calculated quantity of sulfuric acid, extracted with ether, the ether extract dried over anhydrous potassium carbonate and the ether evaporated. As the residue cooled, crystals began to separate, and this separation was greatly hastened by the addition of some 95% ethanol. These crystals were colorless and their m. p. remained constant at 77–78.5° after six crystallizations from alcohol; b. p. about 240° at 3 mm.; yield, about 28%. Their analysis, however, indicated retention of some of the solvent alcohol. They were therefore fused for an hour at 120° and a pressure of 7.2 mm. (m. p. then 78°), and analyzed again.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.58; H, 6.79. Found: C, 73.79; H, 6.65.

2-Methyl-4-piperonylbutanol-2 (VI).—The mother liquors from the crystallization of the dipiperonylbutane (VII) were freed of solvent and distilled at 2 mm. pressure. Two fractions were thus obtained. One boiled at 65–75° and had a safrole odor. The other, b. p. 150–160°, consisted of the nearly pure tertiary alcohol (VI); yield 32%. Purified by two rectifications, it boiled at 145–148° at 2 mm. pressure.

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.23; H, 8.17. Found: C, 70.07; H, 8.50.

This alcohol was a very viscous pale yellowish liquid, which congealed to a glass, but did not crystallize, when cooled to −17°. No phenylurethan could be obtained from it, because phenyl isocyanate immediately withdrew the elements of water, with formation of carbanilide.

Attempts to isolate the olefin formed by this dehydration were not very successful, because the repeated rectifications to which it was subjected rearranged it to the tetralin, a change which takes place very easily, as shown by tests with potassium permanganate in acetone solution.

From the residue of the above distillation, more of the dipiperonylbutane was recovered.

1,1-Dimethyl-6,7-methylenedioxytetralin (VIII).—Into 5 g. of vigorously stirred 85% sulfuric acid, there was dropped slowly 4 g. of the above alcohol (VI), maintaining the temperature at 10° or below. After all the alcohol had been added, the stirring was continued for thirty minutes. The mixture was poured upon ice, extracted with ether, to free it from insoluble tarry contaminants, the ether extract washed with dilute sodium bicarbonate solution, dried over anhydrous sodium sulfate, the ether removed, and the residual liquid distilled twice over sodium. The tetralin was thus obtained as a colorless transparent liquid, of camphoraceous odor, b. p. 148–149° at 10 mm.; yield 70%.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.43; H, 7.89. Found: C, 76.38; H, 7.76.

1-Methyl-6,7-methylenedioxynaphthalene (IX).—Fusion of the tetralin (VIII) with sulfur gave such small yields of the expected naphthalene derivative (IX) that it could be satisfactorily characterized only by its *picrate*, which melted at 134–136°.

Anal. Calcd. for $C_{18}H_{13}O_9N_3$: N, 10.12. Found: N, 9.91.

Summary

Starting with ethyl piperonylideneacetate, the 1,1-dimethyl-6,7-methylenedioxytetralin has been synthesized by a series of steps analogous to those used by Bogert, Davidson and Apfelbaum[2c] for the preparation of ionene.

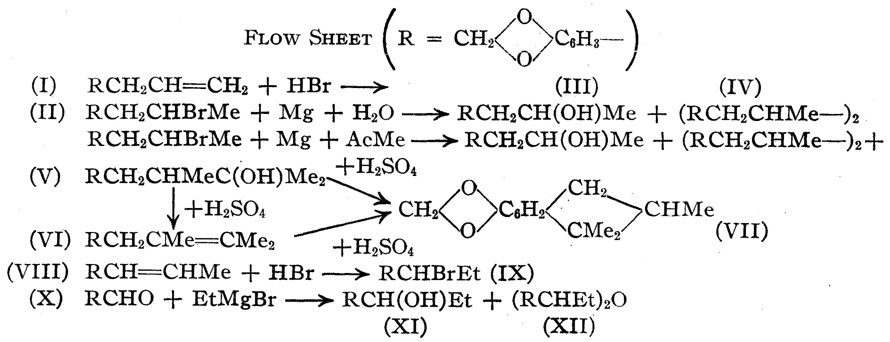
NEW YORK, N. Y. RECEIVED AUGUST 10, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of 1,1,2-Trimethyl-5,6-methylenedioxyindane from Safrole

BY RUBY MURRAY ORCUTT AND MARSTON TAYLOR BOGERT

Supplementing our previous work in the indane group,[1] some experiments have been carried out with safrole (I) and isosafrole (VIII), which have led to a simple synthesis of 1,1,2-trimethyl-5,6-methylenedioxyindane by the following steps.



Many of these compounds contain asymmetric carbon atoms and should therefore exist in optical isomers, but these stereochemical problems have not been attacked as yet.

Experimental

1-Piperonyl-1-bromoethane (II).—When a current of dry hydrogen bromide was led into carefully dried safrole, cooled to −5°, in a flask protected from access of moisture, there was a slow gain in weight up to 25% of that calculated for the addition of an equimolar quantity of hydrogen bromide. No further increase in weight occurred although the gas was passed in for several hours longer.

On working up the crude product, the yield of pure bromide (II), b. p. 145° at 9 mm., was 22%.

In another set of experiments, the safrole (25 g.) cooled to 0°, was mixed with an aqueous solution of hydrobromic acid (100 g.), saturated at 0° (or about 69% hydrogen bromide), and the mixture kept in a closed bottle at low temperature, with occasional shaking, for two or three days. The crude product was diluted with an ice-cold salt solution, the heavy bromide removed by extraction with ether, washed several times with the cold salt solution, dried over anhydrous potassium carbonate, the ether distilled off and the remainder fractionated under diminished pressure; b. p. 154–157° at 13 mm., 145° at 9 mm.; n^{25}_D 1.5614; yield 75%.

Anal. Calcd. for $C_{10}H_{11}O_2Br$: Br, 32.88. Found: Br, 32.82.

This process gave a very satisfactory product, with the by-products in the form of a decomposed residue easily eliminated. This secondary bromide was much more stable than the isomeric primary bromide, 2-piperonyl-1-bromoethane, described in a recent paper.[2]

In 1914, E. Merck took out a patent[3] for the manufacture of aromatic amines, in which this bromide, from safrole and aqueous hydrobromic acid, was an intermediate product, but was separated only in a crude state as a slightly colored heavy unstable oil, which decomposed when distilled *in vacuo* and was not analyzed.

1-Piperonylethanol-1 (III).—The bromide (II) was converted into the Grignard compound in the customary way, after activating the magnesium by a small crystal of iodine. The reaction, after starting rather slowly, proceeded satisfactorily, and the initial cloudiness disappeared as the reaction advanced. Due apparently to its sensitivity to oxygen, this Grignard compound tended to pass into the secondary alcohol (III) with surprising ease, even in a closed system from which all moisture had been carefully excluded, and this introduced complications in using it for the synthesis of other compounds as explained in the next section. No such difficulty was encountered[2] in the preparation of the isomeric $RCH_2CH_2CH_2MgBr$. At the close of the reaction, the mixture was warmed for thirty minutes, then cooled to 0°, stirred for two hours, hydrolyzed by acidulated ice water and worked up as usual. The crude product (8.5 g.) was distilled under reduced pressure, and yielded 4 g. of the alcohol (III) sought, b. p. 127–129° at 3 mm., 2.5 g. of a by-product of safrole-like odor and 0.5 g. of the butane derivative (IV).

In contradistinction to its primary isomer, 2-piperonylethanol-1, this alcohol showed no tendency whatever to crystallize.

Phenylurethan.—Colorless needles (from alcohol), m. p. 93–94° (uncorr.).

Anal. Calcd. for $C_{17}H_{17}O_4N$: C, 68.20; H, 5.72. Found: C, 67.87; H, 5.75.

2-Methyl-3-piperonylbutanol-2 (V) was prepared by the Grignard reaction from the bromide (II) and acetone. Due to the sensitivity of the $RCH_2CH(MgBr)Me$, mentioned above, the preparation proved more troublesome than expected.

When the experiments were conducted in the air, there were obtained from 46 g. of the bromide (II), 16 g. of safrole, 10.4 g. of the secondary alcohol (III), 3 g. of the tertiary alcohol (V), and 1 g. of the 2,3-dipiperonylbutane (IV). The figures for the two alcohols are only approxi-

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[1] (a) Bogert and Davidson, THIS JOURNAL, **56**, 185 (1934); (b) Roblin, Davidson and Bogert, *ibid.*, **56**, 248 (1934).

[2] Orcutt and Bogert, *ibid.*, **58**, 2055 (1936).

[3] Merck, German Patent 274,350; *Chem. Zentr.*, **85**, I, 2079 (1914).

mate, because of the difficulty of separating these alcohols quantitatively.

The secondary alcohol (III) isolated, b. p. 127–129° at 3 mm., was analyzed with the following results.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.63; H, 6.72. Found: C, 66.09; H, 6.69.

Its phenylurethan crystallized from alcohol in colorless needles, m. p. 93–94°. Mixed with the phenylurethan described in the foregoing section, the m. p. was unchanged.

Anal. Calcd. for $C_{17}H_{17}O_4N$: C, 68.20; H, 5.72. Found: C, 68.10; H, 5.77.

The tertiary alcohol (V), on account of the relatively small amount present, could not be isolated in satisfactory purity.

But when the experiments were carried out in an atmosphere of nitrogen, the same amount (46 g.) of initial bromide (II) gave 17 g. of safrole, none of the secondary alcohol (III), 11 g. of the tertiary alcohol (V), and 1.5 g. of the butane derivative (IV). From this mixture, the *tertiary alcohol* was easily isolated by fractional distillation as a colorless, very viscous liquid, b. p. 142–144° at 3 mm., which congealed in thick colorless needles, m. p. 49°, with some softening as low as 43°. The isomeric 2-methyl-4-piperonylbutanol-2 differs from it in persistently remaining liquid and refusing to crystallize.

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.23; H, 8.17. Found: C, 69.86; H, 8.37.

It did not form a phenylurethan. Phenyl isocyanate abstracted water from it, with separation of carbanilide.

2,3-Dipiperonylbutane (IV).—In the residues from the distillation of the crude products obtained in the preparation of both the secondary (III) and tertiary (V) alcohols, this by-product was found. It was purified by repeated crystallization, first from methyl and finally from ethyl alcohol, and then formed thick colorless needles or plates, m. p. 74°.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.58; H, 6.79. Found: C, 73.26; H, 6.53.

1,1,2-Trimethyl-5,6-methylenedioxyindane (VII).—To 20 g. of well-cooled (7°) 85% sulfuric acid, there was stirred in gradually 7 g. of the tertiary alcohol (V). The resultant reddish mixture was diluted with ice water, extracted with ether, the ether extracts dried over fused potassium carbonate, the ether removed and the residue fractionated thrice over sodium. The indane so obtained was a colorless oil, b. p. 137° at 11 mm., of penetrating camphoraceous odor; yield about 65%. It did not decolorize an acetone solution of potassium permanganate.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.43; H, 7.89. Found: C, 76.15; H, 8.20.

Fused with selenium for six hours at 266–270°, a strong odor of methyl mercaptan was noted, and from the tarry product there was isolated a small quantity of a clear yellow liquid, b. p. about 140° at 7 mm., which darkened rapidly and on re-distillation exhaled an odor resembling that of the original indane. It was not obtained in sufficient amount or purity for analysis or identification, nor could a picrate be prepared from it. These results are in accordance with our previous experience with indanes.[1b]

2-Methyl-3-piperonylbutene-2 (VI).—Occasionally this olefin was isolated from the crude product of the above indane synthesis, by fractional distillation of a cyclization product which was unsaturated to an acetone solution of potassium permanganate. It formed an oil, b. p. 120° at 7 mm., colorless when freshly distilled, which rapidly turned yellow, even in a tightly sealed bottle, possessed a citrous or alliaceous type of odor, quickly decolorized an acetone solution of potassium permanganate, and did not form a picrate. For analysis, it was freshly distilled.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.43; H, 7.89. Found: C, 76.21; H, 8.06.

Subjected to the further action of sulfuric acid, it was rearranged to the isomeric indane (VII).

***alpha*-Ethylpiperonyl Bromide (IX).**—This bromide appeared to be formed in good yield by the action of aqueous hydrobromic acid (69%) upon isosafrole at 0°, as described for the preparation of its isomer (II) from safrole, but it was so unstable that it decomposed when distilled at a pressure of 2 mm.

The Merck patent,[3] already mentioned, refers also to the preparation of this bromide, in an impure state, from isosafrole and hydrobromic acid, and describes it as a slightly colored heavy unstable oil, which decomposed when distilled *in vacuo*, and was not analyzed.

This patent also claims the formation of the corresponding amine when the crude bromide is treated with ammonia. When we treated our product with alcoholic ammonia, even at low temperature, a vigorous reaction ensued, with immediate separation of ammonium bromide in an amount which indicated the presence of approximately 50% of the desired bromide (IX) in the original crude.

***alpha*-Ethylpiperonyl alcohol (XI)** was prepared from piperonal (X) and ethylmagnesium bromide, as recorded by Mameli.[4] Inasmuch as the compound obtained by us (yield 50%) showed a b. p. of 126–127° at 3 mm., whereas that reported by him was 172–175° at atmospheric pressure, our product was analyzed.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.63; H, 6.72. Found: C, 66.77; H, 6.42.

No phenylurethan could be secured from this alcohol, because the phenyl isocyanate immediately withdrew from it the elements of water. In this respect it differed strikingly from the isomeric 1-piperonylethanol-1 (III). Nor could we prepare a benzoate from it, or convert it into the corresponding bromide by the action of phosphorus tribromide.

The pure alcohol, after standing for three months at laboratory temperature, turned cloudy and began to crystallize. Dried in an evacuated desiccator and analyzed, it proved to be the ether (XII); yield, equal to that calculated. Apparently this alcohol tends to split out a molecule of water on standing even at ordinary temperature. When warmed or distilled under reduced pressure, however, it loses water quite easily with formation of isosafrole, as found also by Mameli.[4]

Di-*alpha*-ethylpiperonyl Ether (XII).—The distillation residues from the preparation of the foregoing alcohol (XI), when crystallized from methyl alcohol, gave a 5% yield of this ether in colorless leaflets, m. p. 85°.

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(4) Mameli, *Rend. Accad. Lincei*, [5] 13, II, 315 (1904).

Anal. Calcd. for $C_{20}H_{22}O_5$: C, 70.14; H, 6.48; mol. wt. (Rast), 342.2. Found: C, 70.04, 69.85; H, 6.21, 6.42; mol. wt. (Rast), 336.3.

Mameli,[5] who was the first to describe this ether, found that it was formed when an ether solution of the alcohol was left for many weeks in contact with traces of inorganic salts, and gave its m. p. as 88°.

Summary

1. By the addition of hydrobromic acid to safrole, 1-piperonyl-1-bromoethane has been prepared and from this the corresponding alcohol.

2. The Grignard reaction applied to the bromide, in the presence of acetone, yielded a mixture of 1-piperonylethanol-1, 2-methyl-3-piperonylbutanol-2 and 2,3-dipiperonylbutane.

3. This butanol has been converted by the action of sulfuric acid into the corresponding butene and 1,1,2-trimethyl-5,6-methylenedioxyindane.

4. From isosafrole and hydrobromic acid, *alpha*-ethylpiperonyl bromide has been obtained. The corresponding alcohol, from piperonal and ethylmagnesium bromide, has been shown to lose water on standing, with formation of the ether.

NEW YORK, N. Y. RECEIVED AUGUST 10, 1936

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[5] Mameli, *Rend. Accad. Lincei*, [5] **13**, II, 612 (1904); *Gazz. chim. ital.*, **35**, II, 32 (1905).

[CONTRIBUTION FROM THE BURROUGHS WELLCOME AND CO., U. S. A., EXPERIMENTAL RESEARCH LABORATORIES]

Some N-Aryl Barbituric Acids. II

BY JOHANNES S. BUCK

The present work is a continuation of that described in an earlier paper.[1] Two further series of 1-aryl-5,5-dialkyl barbituric acids have been prepared, the aryl groups being, as before, phenyl, *o*-, *m*- and *p*-tolyl, *o*-, *m*- and *p*-anisyl, *o*-, *m*- and *p*-phenetyl, and α- and β-naphthyl, while the alkyl groups are now 5,5-ethyl-isobutyl and 5,5-ethyl-isoamyl. The alkyl groups were selected to allow comparison, pharmacologically, with a series of isoalkylaryl ureas at present under examination.

Since the sodium salts of the N-aryl barbituric acids show a tendency to hydrolyze in aqueous solution, a number of barbituric acids having a dialkylamino group on the phenyl ring was prepared. These compounds are soluble both in alkaline and in acid solution. The presence of the dialkylamino group should also facilitate the resolution of those barbituric acids which carry, in addition to this group, an asymmetric carbon atom.

The two phenyl compounds have been previously described by Hjort and Dox;[2] the others are new. The pharmacological data will be given later in another place.

Experimental

Ethyl isobutylethylmalonate[3] and ethyl isoamylethylmalonate[3] were prepared by the action of the isoalkyl iodide on ethyl ethylmalonate, in the presence of sodium ethylate. It was found advantageous to carry out the reaction as rapidly as possible and to shake the crude ester several times with 5% sodium hydroxide solution.[4] After fractionation under reduced pressure the isobutyl compound boiled at 128.5–130° (15 mm.) (yield 71%) and the isoamyl compound at 126–127° (7.5 mm.) (yield 64%).

The condensation of the ester with the aryl urea and the subsequent purification were carried out substantially as previously described.[1] The procedure was modified in the case of the dialkylamino compounds, the cold reaction mixture being diluted, extracted with ether when possible, and saturated with carbon dioxide to precipitate the product, which was purified by recrystallization from aqueous alcohol, and usually also from ethyl acetate–hexane. No particular trouble was encountered except with 1-*m*-phenetyl-5,5-ethyl-isoamyl barbituric acid which was very difficult to obtain crystalline.

The barbituric acids are tabulated below. They are all white, crystalline, tasteless compounds, soluble in cold 5% sodium hydroxide solution, practically insoluble in water, slightly soluble to insoluble in petroleum ether, soluble in ether, soluble in alcohol, moderately to readily soluble in benzene, and readily soluble in ethyl acetate. In addition, the dialkylamino compounds dissolve readily in 5% hydrochloric acid. The solvents used for purification are given in the order used. Three or more crystallizations were generally necessary. In the tables the appearance described is that of the bulk specimen, crystallized from the last solvent given. The appearance varies greatly with solvent, etc.

The ureas are the same as those previously used.[1] Dimethylaminophenyl urea and diethylaminophenyl urea were prepared by the action of potassium cyanate on the amine hydrochloride in aqueous solution.

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[1] Buck, THIS JOURNAL, **58**, 1284 (1936).

[2] Hjort and Dox, *J. Pharmacol.*, **35**, 155 (1929).

[3] Shonle and Moment, THIS JOURNAL, **45**, 243 (1923).

[4] *Cf.* Michael, *J. prakt. Chem.*, [2] **72**, 537 (1905).

TABLE I

1-ARYL-5,5-ETHYL-ISOBUTYL BARBITURIC ACIDS

Legend: A = alcohol; aA = aqueous alcohol; B = benzene; E = ether; Ea = ethyl acetate; H = hexane; P = petroleum ether.

Aryl radical	Appearance	M.p., °C.	Solvents recryst.	Formula	Analyses, %N Calcd.	Found
Phenyl[2]	Nodules of tiny prisms	149	aA, BP	$C_{16}H_{20}O_3N_2$	9.72	9.80
o-Tolyl	Cryst. powder (small prisms)	134	A, aA	$C_{17}H_{22}O_3N_2$	9.27	9.47
m-Tolyl	Broken cryst. crusts	138.5	aA, BP	$C_{17}H_{22}O_3N_2$	9.27	9.33
p-Tolyl	Soft crusts of prisms	149.5	A	$C_{17}H_{22}O_3N_2$	9.27	9.36
o-Anisyl	Nodules of tiny felted needles	176–177	aA, BP	$C_{17}H_{22}O_4N_2$	8.80	8.80
m-Anisyl	Bulky powder (small nodules)	139.5	aA, EaH	$C_{17}H_{22}O_4N_2$	8.80	8.94
p-Anisyl	Broken cryst. crusts	149	aA, BP	$C_{17}H_{22}O_4N_2$	8.80	8.92
o-Phenetyl	Broken crusts (tiny prisms)	142–143	aA, BH, A	$C_{18}H_{24}O_4N_2$	8.43	8.46
m-Phenetyl	Chalky powder (tiny nodules)	125.5	A, EaH	$C_{18}H_{24}O_4N_2$	8.43	8.42
p-Phenetyl	Chalky powder (clumps of needles)	145	A, BP	$C_{18}H_{24}O_4N_2$	8.43	8.38
α-Naphthyl	Finely cryst. powder	158	aA, BH, EaH	$C_{20}H_{22}O_3N_2$	8.28	8.31
β-Naphthyl	Bulky chalky powder	161–162	aA, BH	$C_{20}H_{22}O_3N_2$	8.28	8.46

TABLE II

1-ARYL-5,5-ETHYL-ISOAMYL BARBITURIC ACIDS

Aryl radical	Appearance	M.p., °C.	Solvents recryst.	Formula	Analyses, %N Calcd.	Found
Phenyl[2]	Thick friable crusts	129	aA, BH	$C_{17}H_{22}O_3N_2$	9.27	9.33
o-Tolyl	Finely cryst. powder	119	aA, EaH	$C_{18}H_{24}O_3N_2$	8.86	8.80
m-Tolyl	Finely cryst. powder	113–114	aA, EaH	$C_{18}H_{24}O_3N_2$	8.86	9.05
p-Tolyl	Chalky nodules	115	aA, BH	$C_{18}H_{24}O_3N_2$	8.86	9.06
o-Anisyl	Felted small needles	134	aA, BH, EaH	$C_{18}H_{24}O_4N_2$	8.43	8.35
m-Anisyl	Starchy cryst. powder	115–116	aA, EaH	$C_{18}H_{24}O_4N_2$	8.43	8.55
p-Anisyl	Chalky tiny nodules	120	aA, BP	$C_{18}H_{24}O_4N_2$	8.43	8.56
o-Phenetyl	Bulky nodules (tiny prisms)	162–163	aA, BP	$C_{19}H_{26}O_4N_2$	8.09	8.13
m-Phenetyl	Soft clumps of tiny nodules	72–74	EaH, EP	$C_{19}H_{26}O_4N_2$	8.09	8.40
p-Phenetyl	Coarse powder (prism nodules)	100–101	aA, BP	$C_{19}H_{26}O_4N_2$	8.09	8.25
α-Naphthyl	Bulky small nodules	193–194	BP, aA	$C_{21}H_{24}O_3N_2$	7.95	8.01
β-Naphthyl	Small nodules (clumps of prisms)	138	aA, EaH	$C_{21}H_{24}O_3N_2$	7.95	8.06

TABLE III

1-DIALKYLAMINOPHENYL-5,5-DIALKYL BARBITURIC ACIDS

Aryl radical	Alkyl radical	Appearance	M.p., °C.	Formula	Analyses, %N Calcd.	Found
p-Dimethylaminophenyl	Diethyl	Small pearly leaves	182	$C_{16}H_{21}O_3N_3$	13.85	13.80
p-Dimethylaminophenyl	Ethyl-*n*-butyl	Glitt. small flat prisms	157	$C_{18}H_{25}O_3N_3$	12.68	12.92
p-Dimethylaminophenyl	Ethyl-isobutyl	Bulky clumps of flat prisms	153	$C_{18}H_{25}O_3N_3$	12.68	12.83
p-Dimethylaminophenyl	Ethyl-isoamyl	Aggregates of small nodules	130	$C_{19}H_{27}O_3N_3$	12.16	12.17
p-Diethylaminophenyl	Diethyl	Small silky needles	175	$C_{18}H_{25}O_3N_3$	12.68	12.85
p-Diethylaminophenyl	Ethyl-*n*-butyl	Bulky fluffy powder	125.5	$C_{20}H_{29}O_3N_3$	11.69	11.83
p-Diethylaminophenyl	Ethyl-isobutyl	Broken crusts of small needles	140–141	$C_{20}H_{29}O_3N_3$	11.69	11.61
p-Diethylaminophenyl	Ethyl-isoamyl	Broken crusts (nodules)	125	$C_{21}H_{31}O_3N_3$	11.25	11.47

Dimethylaminophenyl Urea.—Slender striated needles (pale violet tint) from hot water; slightly soluble ether and benzene, soluble alcohol, insoluble petroleum ether, soluble cold 5% hydrochloric acid; no taste; m. p. 183°. *Anal.* Calcd. for $C_9H_{13}ON_3$: N, 23.45. Found: N, 23.60.

Diethylaminophenyl Urea.—Felted, slender, glittering needles (gray-violet tint) from hot water; soluble hot benzene, soluble alcohol, insoluble petroleum ether, soluble cold 5% hydrochloric acid; no taste; m. p. 136.5°. *Anal.* Calcd. for $C_{11}H_{17}ON_3$: N, 20.27. Found: N, 20.52.

The analyses (micro-Dumas) were carried out by Mr. W. S. Ide. The melting points are corrected.

Summary

1. To complete previous work, a series of 1-aryl-5,5-ethyl-isobutyl barbituric acids and a series of 1-aryl-5,5-ethyl-isoamyl barbituric acids have been prepared, the N-aryl groups in both series being phenyl, *o*-, *m*- and *p*-tolyl, *o*-, *m*- and *p*-anisyl, *o*-, *m*- and *p*-phenetyl and α- and β-naphthyl.

2. A series of acid-soluble barbituric acids was prepared in which the N-aryl groups were *p*-dimethylaminophenyl and *p*-diethylaminophenyl. The 5,5-dialkyl groups were diethyl, ethyl-*n*-butyl, ethyl-isobutyl and ethyl-isoamyl.

TUCKAHOE, NEW YORK RECEIVED JULY 30, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BUFFALO]

Oxalato Complex Compounds of Tervalent Manganese

BY G. H. CARTLEDGE AND W. P. ERICKS

Complex compounds containing manganese in the tervalent or quadrivalent state have been prepared in a few instances, but there has never been a thoroughgoing study of the field, such as has been made in the compounds of chromium and cobalt. From a consideration of the structure of the manganese atom there is every reason to expect it to form complexes readily, since the manganic ion has the combination of available *d*, *s* and *p* eigenfunctions which is required for the formation of covalent bonds, according to the theory of Pauling.[1] That so few of such possible compounds have been prepared is readily ascribed to the complicated oxidation–reduction relations of manganese. The simple manganic ion is like the cobaltic ion in its large oxidation potential, but is even more difficult to manipulate because of the readiness with which it dismutates into the manganous ion and manganese dioxide.

The oxalato complexes are of particular interest in connection with the kinetics of the reaction between potassium permanganate and oxalates.[2] Potassium trioxalatomanganiate, $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$, seems to have been prepared first by Souchay and Lenson.[3] Kehrmann[4] rediscovered the compound and isolated it in crystalline form. Meyer and Schramm[5] in 1922 attempted to prepare dioxalatodiaquomanganiates, but without success. Instead, they were able to obtain the corresponding dimalonatodiaquamanganiate, which is a fairly stable compound and readily prepared. In 1926 the same authors[6] reported that by treating cold sodium tetroxalate (in excess) with manganese dioxide they obtained an impure green material. This product was very unstable, turned yellowish-brown, and decomposed before it could be isolated for analysis. Meyer and Schramm concluded from analogy with the green sodium dimalonatodiaquomanganiate that the unstable product was the corresponding oxalato complex.

We have been able to prepare a number of pure compounds containing the trioxalatomanganiate and dioxalatodiaquomanganiate ions, as well as a difluodioxalato compound and, unexpectedly, a dioxalatodihydroxo complex of quadrivalent manganese. The oxalatomanganiates have turned out to be extremely interesting in that in aqueous solution they are easily converted one into the other, according to the reversible reaction

$$[Mn(C_2O_4)_3]^{\equiv} + 2H_2O \rightleftarrows [Mn(C_2O_4)_2(H_2O)_2]^- + C_2O_4^=$$

Using a spectrophotometric procedure we have been able to measure the equilibrium constant for this reaction, as will be shown in the following paper. The complexes are far more reactive than the corresponding chromium or cobalt compounds, but when properly isolated in pure form may be analyzed accurately and, in some instances, may be preserved indefinitely in a refrigerator.

Potassium Trioxalatomanganiate.—Our interest in the oxalato complexes arose from a need for some potassium trioxalatomanganiate of extreme purity, with particular reference to its freedom from iron. Trioxalato complexes are formed by tervalent chromium, iron and cobalt; the salts are all probably isomorphous with the manganic complex, and all of them have moderately high solubilities. Because of the instability of the manganic complex the principal purification is necessarily applied to the reagents rather than to the final product. We have accordingly devised a procedure which involves as few reagents as possible. The chief difficulty in obtaining a homogeneous product is due to the sparing solu-

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(1) Pauling, THIS JOURNAL, **53**, 1367 (1931).

(2) Schilow, *Ber.*, **36**, 2735 (1903); Skrabal, *Z. anorg. Chem.*, **42**, 73 (1904); Schröder, *Z. öffentl. Chem.*, **16**, 270 (1910); Kolthoff, *Z. anal. Chem.*, **64**, 185 (1924); Deiss, *Z. angew. Chem.*, **39**, 664 (1926); Launer, THIS JOURNAL, **55**, 865 (1933); Launer and Yost, *ibid.*, **56**, 2571 (1934); Fessenden and Redmon, *ibid.*, **57**, 2246 (1935).

(3) Souchay and Lenson, *Ann.*, **105**, 254 (1858).

(4) Kehrmann, *Ber.*, **20**, 1594 (1887).

(5) Meyer and Schramm, *Z. anorg. Chem.*, **123**, 56 (1922).

(6) Meyer and Schramm, *ibid.*, **157**, 196 (1926).

bility of the acid oxalates, and numerous procedures were investigated before a dependable one was obtained.

The method which has been developed consists in reducing potassium permanganate with oxalic acid in proper excess, followed by oxidation of the resulting manganous oxalate by a second portion of permanganate which is added along with sufficient potassium carbonate to furnish the necessary potassium and the most favorable hydrogen-ion concentration. The over-all reaction and the stoichiometric proportions actually used are expressed by the equation

$$5H_2C_2O_4 + KMnO_4 + K_2CO_3 \longrightarrow K_3[Mn(C_2O_4)_3] + 5H_2O + 5CO_2 \quad (1)$$

Preparation of Reagents.—Water was prepared by redistilling the laboratory distilled water with alkaline permanganate, using a spray trap and condenser of block tin. The middle portion of this distillate was again redistilled in an all-quartz still for conductivity water.

Oxalic acid was prepared by the hydrolysis of ethyl oxalate, Eastman ester being used in part, along with a sample prepared in this Laboratory.[7] The hydrolysis of the redistilled ester (boiling range 1°), evaporation of the alcohol and recrystallization of the resulting oxalic acid were conducted entirely in quartz.

Potassium permanganate (Baker C. P.) was dissolved in warm purified water and after digestion filtered through acid-washed asbestos. The crystals obtained by evaporation and cooling were recrystallized in quartz four times.

Potassium carbonate was prepared from potassium acid tartrate obtained from pure tartaric acid and potassium carbonate. After four recrystallizations the acid salt was decomposed at as low a temperature as possible and the carbonate formed was evaporated to crystallization in a silver dish.

Alcohol and ether were purified and dehydrated in the usual manner. Before distillation the ether was agitated with potassium hydroxide and potassium permanganate. The quartz still was used for the distillations.

Preparation of Potassium Trioxalatomanganiate.—The stoichiometric proportions represented in equation (1) were used in the reaction, which, however, was conducted in two stages. To the entire quantity of oxalic acid to be used, four-fifths of the indicated amount of potassium permanganate was added and completely reduced. After the solution had cooled to about 0° the potassium carbonate and remaining potassium permanganate were added. All operations were carried out in quartz apparatus and in a darkened room. The details were as follows.

A quarter of a mole (31.5 g.) of oxalic acid dihydrate was dissolved in 200 cc. of pure distilled water in a 500-cc. beaker. The solution was heated to 70–75° and 0.04 mole (6.32 g.) of powdered potassium permanganate was added in small portions, while agitating the solution. When the solution had become colorless, 0.05 mole (6.9 g.) of solid potassium carbonate was added in small portions, with agitation. Occasional agitation was maintained to prevent the precipitate from sticking in a solid mass. When the temperature of the mixture was about 4–5°, 150 cc. of pure water at 0–1° was added.

One one-hundredth of a mole (1.58 g.) of powdered potassium permanganate was then added in small portions; after addition of the last portion the agitation was continued for about ten minutes, and the temperature maintained at 0–2°. The formation of an intense, cherry-red color was observed. Previously, into the freezing mixture was placed a flask mounted with a Gooch crucible fitted into a rubber ring which was placed on top of the neck of the flask. The cold solution was then filtered with suction through acid-washed asbestos.

The filtrate was transferred to a cooled beaker and ice-cold alcohol, in quantity corresponding to one-half of the potassium trioxalatomanganiate solution, was added. The solution was placed in an efficient cooling mixture (ice and salt) and kept in the dark for about two hours.

The precipitated potassium trioxalatomanganiate was then filtered with suction on a cooled Büchner funnel. The precipitate was washed with ice-cold 50% (by volume) pure alcohol four times, using about 25 cc. for each wash, then with 95% alcohol, absolute alcohol and, finally, three portions of purified ether. The temperature of all solvents used for washing was in the neighborhood of 0°.

The crystals so obtained were sucked dry on a silica crucible, then removed to an evaporating dish and dried at room temperature and atmospheric pressure for twelve hours, and preserved in a colored glass bottle to prevent decomposition by light. It is important that the organic solvents evaporate completely before the bottle is stoppered.

The filtration and washing of the crystals were carried out in the shortest time possible. Based on the data of four experiments, the yield was approximately 50%.

Analysis.—Microscopic examination of the product revealed no inhomogeneity, whereas samples prepared by the other procedures investigated almost invariably contained white crystals of potassium acid oxalate. A complete analysis of the crystals was made by the following methods: (a) total manganese, by gravimetric determination as $Mn_2P_2O_7$; (b) manganese, oxidation equivalent, by liberation of iodine and titration with thiosulfate; (c) oxalate, by titration with permanganate, making allowance for the oxalate oxidized by the manganic ions, as determined in (b); (d) potassium, by decomposition of a sample with sulfuric acid and ignition to constant weight at 500°, subtracting the weight of manganous sulfate calculated from (a); (e) water, by decomposition in a combustion furnace and absorption of the water liberated. The results were as follows, the theoretical values calculated from the formula $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$ being in parentheses: potassium, 24.12 (23.92); manganese 11.19 (11.21); oxalate, 53.90 (53.85); water, 10.9 (11.02).

A sample was examined for iron spectrographically.[8] No iron lines could be detected, the test being sensitive to 0.0001%.

The density of potassium trioxalatomanganiate was determined in a pycnometer, toluene, xylene and ethyl oxalate being used as liquids in different experiments. Three determinations were made with the usual precautions to

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(7) *Organic Syntheses*, **5**, 59 (1925).

(8) We are indebted to Dr. E. Weiner for conducting this test.

displace adhering air, the results being d^{20}_4 2.148, 2.152, 2.148; mean, 2.149.

Potassium trioxalatomanganiate in the solid state has a deep reddish-purple color. Impure samples often decompose overnight at room temperature, especially if imperfectly dried. We have found that very pure samples keep well even at 20° if protected from the light, and in a refrigerator at −6° no decomposition is apparent after storage for a year or more. The salt is insoluble in alcohol, ether, acetone, toluene and xylene, but is very soluble in water, and very slightly soluble in methyl alcohol. The color of aqueous solutions varies markedly with the concentration. A 0.001 *M* solution is yellowish-brown; with increasing concentration the solution becomes cherry-red, and concentrated solutions in an oxalate–oxalic acid buffer at *p*H 5 are deep red with a purplish shade. These color changes are due to the partial replacement of an oxalate ion by water molecules, as shown by spectrophotometric studies which will be reported in the succeeding paper. When a solution is made moderately acid the color changes to a golden-yellow, but rapidly fades, owing to reduction of the manganese. A brown precipitate forms in an acetate buffer if the acidity is decreased appreciably below a *p*H of 5.

Potassium Dioxalatodiaquomanganiate.—Whereas the trioxalto complexes of cobalt and chromium are very stable with respect to dissociation of the anion, or the replacement of an oxalate group by water molecules, a number of facts made it apparent that the trioxalatomanganiate ion is decidedly less stable in this respect. Addition of silver ions or calcium ions to a solution of the pure salt produces an immediate precipitation of an oxalate, with decomposition of the red salt. Furthermore, the yellow color produced by acidifying the solution is restored to red by addition of an excess of potassium oxalate. Before we discovered the work of Meyer and Schramm we had been successful in isolating the green dioxalatodiaquomanganiate, though considerable work was required before a dependable procedure was developed. Four methods were studied, all of which gave the desired compound in varying degrees of purity.

(a) A concentrated solution of the trioxalato complex at 0° was treated with dilute sulfuric acid until the color changed to a clear golden-yellow; the green dioxalato salt crystallized out upon addition of alcohol. The salt was contaminated with colorless crystals, presumably of potassium acid oxalate.

(b) and (c) Manganous oxalate was oxidized by potassium permanganate in the presence of oxalic acid and potassium oxalate in varying proportions.

(d) The best results were obtained by a simple modification of the procedure developed for making the trioxalato complex. The total reaction is

$$4H_2C_2O_4 + KMnO_4 \longrightarrow K[Mn(H_2O)_2(C_2O_4)_2] + 4CO_2 + 2H_2O \quad (2)$$

The reaction is carried out in one step, and because of the strongly acid character of the solution during the initial stages it is necessary to control the temperature very accurately and to work rapidly according to the following procedure.

Preparation of Potassium Dioxalatodiaquomanganiate.—Eight hundredths of a mole (10.08 g.) of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) was dissolved in 200 cc. of water in a 750-cc. Erlenmeyer flask. The solution was cooled to 1° and 0.02 mole (3.16 g.) of powdered potassium permanganate was added. The mixture was thoroughly agitated for about twenty minutes and the temperature was allowed to rise to 7°, at which temperature the reaction started, as judged by the evolution of carbon dioxide. The flask was immersed quickly in an efficient cooling mixture of ice and salt. The agitation was continued and the temperature was lowered gradually to 0°. When the evolution of gas began to diminish, 25 cc. of ice-cold ethyl alcohol (95%) was added and the temperature was allowed to drop to −3°. At this stage the solution was greenish-brown in color, without any red shade. The solution was filtered very quickly through a Gooch crucible with an asbestos mat, which was previously washed and cooled. The filtrate was collected in an externally-cooled flask.

The filtrate was cooled below 0° and 200 cc. of 95% alcohol was added in portions, keeping the temperature below 0°. The solution was allowed to stand in an efficient cooling mixture for about half an hour. If no crystallization had begun at this time the inner wall of the flask was scratched slightly with a stirring rod and the solution allowed to stand at a temperature of −5 to −10° for one hour. Green, lustrous crystals were observed at this time on the bottom of the flask. They were filtered with suction and washed with ice-cold ethyl alcohol (50, 95% and absolute), followed by three washes with ice-cold dry ether. The yield was about 45% of the theoretical.

Anal. The compound was analyzed by the methods described in connection with the trioxalato complex. The results on two samples were as follows, the percentages calculated from the formula $K[Mn(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$ being in parentheses: potassium, 10.76, 10.75 (10.85); manganese, 15.16, 15.22 (15.25); oxalate, 48.70, 48.92 (48.90); water, 25.1 (25.0).

Under the microscope the green crystals appear as well-formed, thin, diamond-shaped plates. The salt dissolves readily in water, giving a golden-yellow solution which rapidly decomposes at room temperature. As the decomposition liberates oxalate ions some trioxalato salt forms in the reaction. The solution does not immediately give a precipitate of calcium oxalate when treated with calcium chloride. Addition of potassium oxalate immediately gives the trioxalato complex. Pink compounds are also formed by addition of chloride ion or fluoride ion. At room temperature the crystals decompose rapidly, as a rule, but in a refrigerator may be preserved.

In one experiment the preparation was conducted by a slight variation of the procedure described. Instead of the theoretical quantity of oxalic acid a 1% excess was used, and only 50 cc. of alcohol was used to precipitate the salt. The product consisted of golden crystals which appeared homogeneous under the microscope. Analysis gave: manganese, 15.1; oxalate, 49.0, 48.7. It is evident that the composition of the two products is identical. The dioxalatodiaquo complex may exist in isomeric *cis* and *trans* forms, and we are of the opinion that the differences observed may be accounted for in this way. The two solids give solutions of the same color, which may indicate that the solution contains both forms in equilibrium. Further work is in progress in this connection.

In a further preparation the reaction mixture was made as nearly anhydrous as would permit the reactions to occur. Eight hundredths of a mole (10.08 g.) of powdered oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) was dissolved in 200 cc. of absolute alcohol and cooled to 0°. Two hundredths of a mole (3.16 g.) of powdered potassium permanganate was added. The solution was shaken and a few pieces of ice were added until the solution turned brown and the larger portion of the permanganate went into solution. Then the solution was filtered. The precipitate consisted mainly of unreacted materials. The filtrate was brown in color; 1.12 g. of potassium hydroxide was dissolved in 50 cc. of 95% alcohol. The potassium hydroxide solution was cooled and portions of it were added until a precipitate appeared. The yellowish-green precipitate was filtered off. It was washed in the usual way and analyzed for oxalate and manganic ions. The results follow, the percentages calculated for $K[Mn(C_2O_4)_2(H_2O)_2]$ being in parentheses: manganese, 17.8 (17.91); oxalate, 56.8 (57.5).

The product was apparently the anhydrous form of potassium dioxalatodiaquomanganiate. It was more stable than the trihydrate and remained undecomposed at room temperature for several days. Other characteristics were identical with those of the hydrated form of the salt.

It is claimed by Brintzinger and Eckardt[9] that dioxalato complexes of bivalent central ions often polymerize to double ions in dilute solution. Freezing point measurements accordingly were made on 0.05 *M* solutions of yellow potassium dioxalatodiaquomanganiate by the Beckmann method.[10] The results showed an apparent degree of dissociation of the same magnitude as is commonly found for solutions of uni-univalent salts of the same concentration. The solution is weakly acidic, probably as a result of a slight dissociation according to the reaction $[Mn(C_2O_4)_2(H_2O)_2]^- \rightleftharpoons [Mn(C_2O_4)_2(OH)(H_2O)]^= + H^+$.

Complexes Containing Complex Cations

On account of the high solubility of the potassium salts obtained an effort was made to find some other cation which might give complexes of lower solubility. The alkaline earths and heavy metals are necessarily eliminated because their oxalates also are insoluble. The oxalato anions are relatively large in size, and since it is often true that the solubility of salts with large anions decreases as the cation becomes larger, it was thought likely that compounds containing a complex cation as well as the complex anion might be favorable forms in which to isolate the unstable manganese complexes.

Hexamminecobalti Trioxalatomanganiate, $[(CoNH_3)_6][Mn(C_2O_4)_3] \cdot xH_2O$.—One hundredth of a mole (2.67 g.) of hexamminecobalti chloride $[Co(NH_3)_6]Cl_3$, (yellow) was dissolved in 100 cc. of water at a temperature of 2° and 0.01 mole (4.90 g.) of potassium trioxalatomanganiate dissolved in 50 cc. of water at a temperature of 2° was added. The mixture was shaken, after which a purplish-pink precipitate was observed. The precipitate was filtered off and washed in the usual way; yield 4.8 g. The theoretical yield of anhydrous hexamminecobalti-trioxalatomanganiate is 4.80 g. Upon addition of alcohol to the filtrate, a precipitate formed in small quantity. The mixture was allowed to stand overnight in the refrigerator and the lustrous pink crystals which formed were filtered off and washed with alcohol.

A partial analysis of the first crop of crystals gave manganese 10.6 (10.29), cobalt 10.9 (11.03); oxalate 50.2 (49.44), the values in parentheses being calculated for the trihydrate. The atomic ratio found corresponds to $Co:Mn:C_2O_4 = 0.96:1.00:2.96$, the percentage values lying between those for the dihydrate and the trihydrate.

The dioxalatodiaquomanganiate anion also unites with complex cations to form sparingly soluble double complexes. With *cis*-dinitrotetrammine cobalti ion an olive-yellow precipitate was obtained. The product was heterogeneous under the microscope, however, and was not subjected to analysis.

Note on Potassium Dimalonatodiaquomanganiate

Meyer and Schramm[5] prepared their complex manganiates by using manganic hydroxide or manganese dioxide as the source of manganese. Their procedures gave impure products in many instances, and they report that they were not able to obtain potassium dimalonatodiaquomanganiate in a form suitable for analysis. We have conducted several experiments in which it was hoped that the greater stability of malonic acid toward oxidation would permit isolation of a type of hydroxo complex that we have not been able so far to obtain in pure form in the oxalate series. It was found that suitable modification of our procedure, in which potassium permanganate is used, easily produces pure crystals of the potassium salt, $K[Mn(C_3H_2O_4)_2(H_2O)_2] \cdot 2H_2O$.

Four procedures were investigated in which malonic acid, potassium permanganate and, in two cases, potassium carbonate were mixed in various proportions in aqueous solution at 0°. In all cases the same product was obtained, the yield being highest (80%) when stoichiometric proportions were used according to the equation

$$5CH_2(COOH)_2 + 2KMnO_4 \longrightarrow 2K[Mn(C_3H_2O_4)_2(H_2O)_2] + 3CO_2 + 2H_2O$$

The reactions were carried out at about 0° in solutions containing 0.01 mole of permanganate with the other reagents in 100 cc. of water. To precipitate the crystals 50 cc. of alcohol was also present. The average of four closely concordant analyses for manganese was as follows, the value calculated for the dihydrate being in parentheses: Mn, 14.85% (14.83). Potassium and water were determined on one sample: K, 10.4 (10.57); H_2O, 2.63 (2.7). The dark-green crystals dissolve readily in water to give an unstable yellow solution, as reported for the other salts by Meyer and Schramm. The salt may be recrystallized from cold 0.05 *M* malonic acid by addition of alcohol.

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(9) Brintzinger and Eckardt, *Z. anorg. allgem. Chem.*, **224**, 93 (1935).

(10) We are indebted to Mr. J. T. Grey, Jr., for making the measurements.

Summary

1. A procedure has been developed whereby potassium trioxalatomanganiate may be prepared spectroscopically free from iron.

2. Potassium dioxalatodiaquomanganiate has been prepared in the pure crystalline state. Two forms of the trihydrate have been obtained, as well as the anhydrous salt.

3. It has been shown that these manganiate ions form sparingly soluble salts with complex cations.

4. Pure potassium dimalonatodiaquomanganiate has been prepared and certain of its properties have been determined.

BUFFALO, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BUFFALO]

Equilibrium between the Trioxalatomanganiate and Dioxalatodiaquomanganiate Ions

BY G. H. CARTLEDGE AND W. P. ERICKS

In spite of the enormous number of transformations among complex compounds that have been developed in the course of the classic researches of Werner and his successors, very few of such reactions have been investigated quantitatively from the standpoint of chemical equilibrium. The complexes of the metals that have been most fully studied are, as a rule, so stable with respect to dissociation that readily measurable equilibria are comparatively rare. Such measurements as have been made concern principally the dissociation of solid ammine complexes or the instability constants of such relatively stable complexes as the silver–ammonia or silver–cyanide ions in solution. In a few cases the acidic dissociation of aquo complex ions has also been studied.[1] Investigations of affinity in the complex compounds are desirable on account of the renewed interest in the question as to the type and strength of the chemical bonds in such substances.

Meyer and Schramm[2] observed that the trioxalatomanganiate ion and the dioxalatodiaquomanganiate ion are convertible one into the other according to the equation

$$[Mn(C_2O_4)_3]^{\equiv} + 2H_2O \rightleftarrows [Mn(C_2O_4)_2(H_2O)_2]^- + C_2O_4^=$$

That a measurable equilibrium is established rapidly is evident from the color changes observed in aqueous solutions of the trioxalatomanganiates. A concentrated aqueous solution is ordinarily described as cherry-red. We have found that the color is perceptibly changed to a more purplish-red upon addition of an oxalate oxalic acid buffer at *p*H 4.5. As an aqueous solution is diluted its color changes steadily; in 0.001 *M* solution the color is brown, but may be restored to red by addition of an excess of the oxalate buffer. The dioxalatodiaquomanganiate ion reacts immediately with the oxalate ion to produce the trioxalato complex. In this respect the dioxalato ion contrasts with the dimalonato ion, which is very incompletely converted to the trimalonato ion. The dioxalatodiaquomanganiate ion itself has a golden-yellow color in cold aqueous solution, but the solution is acid and soon becomes turbid. This effect is no doubt due to an acidic ionization of the water molecules in the complex, whereby a sparingly soluble hydroxo complex is formed. We have found that the solution in 0.01 *M* nitric acid remains clear and is stable enough for our purposes. The nitric acid evidently suppresses the ionization, giving the pure color of the aquo complex ion.

The method of determining the equilibrium concentrations consisted in a spectrophotometric analysis of solutions of the trioxalatomanganiate in water at various concentrations and also in various oxalate–oxalic acid buffer mixtures. Equilibrium was also approached from the dioxalatodiaquomanganiate side of the reaction. As has been found by Uspensky and his collaborators[3] in a number of cobaltic and chromic complexes, when water molecules replace an acido group within a complex ion the maximum absorption in the visible region is displaced in the direction of shorter wave lengths. In the oxalatomanganiates

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(1) Brönsted and King, *Z. physik. Chem.*, **130**, 699 (1927).

(2) Meyer and Schramm, *Z. anorg. allgem. Chem.*, **157**, 190 (1926).

(3) Uspensky and others, *Trans. Inst. Pure Chem. Reagents, U. S. S. R.*, **13**, 1 (1933).

the same shift is observed, and is so great as to permit convenient determination of the ions in a mixture. The calculation of the concentrations depends upon a knowledge of the extinction coefficients of the pure components. In the case of the dioxalatodiaquomanganiate the extinction coefficient is relatively small in the region of most importance for our measurements. Furthermore, the values differ only slightly whether the salt is dissolved in pure water, in dilute oxalic acid or in dilute (0.01 *N*) nitric acid. We have therefore taken the measurements on this salt in 0.01 *N* nitric acid, since this concentration was found ample to prevent dissociation to a hydroxo complex; at 0° the solution does not decompose rapidly enough to interfere with the analysis.

In the case of the trioxalatomanganiate it was found that there is an appreciable replacement of an oxalate ion by water molecules even in the most favorable oxalate buffer. It is therefore impossible to determine the extinction coefficients for the pure component in these solutions. We have avoided this difficulty by making measurements at a low concentration of the complex in a pair of buffered solutions of known oxalate-ion concentration. By treating both the extinction coefficient of the trioxalato ion and the equilibrium constant as unknowns we arrive at pairs of equilibrium equations from which both quantities may be calculated. The extinction coefficients thus found at three wave lengths were then used for other solutions in which the oxalate-ion concentration was not necessarily known.

For the calculation of the concentration of the components in the equilibrium mixture the Lambert–Beer law was used in the form

$$\log (I_0/I) = lc(x_1E_1 + x_3E_3) \qquad (1)$$

in which c is the formality as to manganese, l the cell length in cm., x_1 and x_3 the fractions of the complex in the form, respectively, of the univalent dioxalato ion and the tervalent trioxalato ion, and E_1 and E_3 the molecular extinction coefficients of the corresponding ions. If the apparent extinction coefficient calculated from the measured transmittance of any mixture is E, we obtain

$$E = x_1E_1 + x_3E_3 \qquad (2)$$

The fractions of the complex in the two forms are then given by

$$x_1 = (E_3 - E)/(E_3 - E_1) \text{ and } x_3 = (E - E_1)/(E_3 - E_1) \qquad (3)$$

The extinction coefficients were measured from 440 mμ to 600 mμ in certain cases, but the three wave lengths 550, 540 and 520 mμ were selected for the equilibrium calculations. The extinction coefficients at these points were then repeatedly determined on freshly prepared solutions. A Bausch and Lomb visual spectrophotometer was used, the cells being jacketed in ice during the measurements. A jet of dry air prevented the condensation of moisture on the cells. The least stable solutions showed no alteration during the few minutes they were in use. Distilled water boiled in quartz was used for preparing the unbuffered solutions. All salts used were pure, as determined from careful analyses.

For the equilibrium equation we have

$$\frac{\gamma_1[\mathrm{Mn(C_2O_4)_2(H_2O)_2}^-]\gamma_2\mathrm{C_2O_4}^=]}{\gamma_3[\mathrm{Mn(C_2O_4)_3}]^\equiv} = K \qquad (4)$$

the γ's being the activity coefficients of the respective ions. Expressed in terms of the fractions of the two colored ions this becomes

$$\frac{\gamma_1\gamma_2}{\gamma_3} \times \frac{x_1}{1 - x_1} \times [\mathrm{C_2O_4}^=] = K \qquad (5)$$

The values of the activity coefficients were obtained from graphs of the coefficients of the chlorate, sulfate and ferricyanide ions. For the univalent ion the activity coefficient was plotted against the cube root of the ionic strength. In the case of the bivalent and tervalent ions the reciprocal of the activity coefficient was plotted against the square root of the ionic strength. Taking the numerical values from Lewis and Randall,[4] essentially linear graphs were obtained from which the required activity coefficients could be read with only moderate extrapolation to the more concentrated mixtures. In calculating the oxalate-ion concentration in the buffered solutions due regard was paid to the secondary ionization of oxalic acid in all cases where required. In terms of the individual extinction coefficients the equilibrium equation takes the form

$$\frac{\gamma_1\gamma_2}{\gamma_3}\left(\frac{E_3 - E}{E - E_1}\right)\left[c_0 + \left(\frac{E_3 - E}{E_3 - E_1}\right)c\right] = K \qquad (6)$$

when equilibrium is approached from the trioxalato side; c_0 is the concentration of oxalate ions in the buffer solution itself.

In making the calculations different values were employed for the extinction coefficient E_1 of the dioxalatodiaquomanganiate ion depending upon the acidity of the solution. In the acidic, buffered solutions the values were taken from measurements on the pure component in 0.01 *N* nitric acid as the solvent. In the more nearly neutral,

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(4) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 382.

unbuffered solutions the values obtained from a simple aqueous solution of the dioxalato salt were used, as these undoubtedly represent more closely the actual state of the substance in the equilibrium mixtures. Owing to the unavoidable uncertainty in these extinction coefficients, however, we have selected wave lengths at which the values are still relatively small in comparison with those of the trioxalato ion.

The values of the extinction coefficients of the trioxalato ion were first determined approximately from measurements on a 0.001 *M* solution of the complex in buffers consisting of 0.08 *M* potassium oxalate and 0.02 *M* potassium hydrogen oxalate, KHC_2O_4, in one case, and the same buffer diluted with an equal volume of water in the second case. In these buffers the oxalate ion contributed by the reaction of the complex ion with water is negligibly small. From the approximate results so obtained final values for the extinction coefficients of the trioxalato ion were then obtained from three series of measurements in buffers containing 0.02 *M* potassium oxalate and 0.08 *M* potassium hydrogen oxalate, or the same diluted with an equal volume of water. The approximate values of the extinction coefficients E_3 previously obtained made it possible to calculate with sufficient accuracy the amount of oxalate ion formed in the reaction. The replacement reaction proceeds further in these more acidic buffers, and the calculated extinction coefficients are consequently less sensitive to errors in the measurements.

Table I

Calculated Extinction Coefficients of the Trioxalatomanganiate Ion

Expt.	Wave lengths, mμ 550	540	520
3, 4	232	274	303
12, 13	248	276	314
16, 17	237	266	306
Average E_3	239	272	308

For the determination of the extinction coefficients of the trioxalatomanganiate ion experiments 3, 4, 12, 13, 16 and 17 (Table II) were used. The results are summarized in Table I.

The general results and calculated equilibrium constants in buffered and aqueous solutions are shown in Table II. Certain of the measured extinction coefficients are shown in Fig. 1.

Discussion of Results

From Table II it will be seen that in different experiments we have carried the replacement reaction from 10–70% toward completion in the solutions containing added oxalate ions. In simple aqueous solution the range was from 31–85%. Equilibrium has been approached from both sides, and it is evident that the reaction proceeds to equilibrium almost instantaneously, since the absorption measurements were started

Table II

Composition of Equilibrium Mixtures and Calculated Equilibrium Constants

Expt.	Solute and formality, *c*	Solvent formality $K_2C_2O_4$	KHC_2O_4	Fraction as dioxalato ion, x_1	*K*, calcd. × 10^3
1	$K_3[Mn(C_2O_4)_3]$, 0.001 *M*	0.08	0.02	0.096	5.0
2	$K_3[Mn(C_2O_4)_3]$, .001 *M*	.04	.01	.126	4.1
3	$K_3[Mn(C_2O_4)_3]$, .001 *M*	.02	.08	.159	3.0
4	$K_3[Mn(C_2O_4)_3]$, .001 *M*	.01	.04	.233	2.8
5	$K_3[Mn(C_2O_4)_3]$, .002 *M*	.08	.02	.096	5.0
6	$K_3[Mn(C_2O_4)_3]$, .002 *M*	.04	.01	.134	4.4
7	$K_3[Mn(C_2O_4)_3]$, .002 *M*	.0016	.0004	.597	3.8
8	$K_3[Mn(C_2O_4)_3]$, .001 *M*	.0008	.0002	.702	3.5
9	$K_3[Mn(C_2O_4)_3]$, .005 *M*	.0008	.0002	.568	4.1
10	$K_3[Mn(C_2O_4)_3]$, .01 *M*	.08	.02	.095	4.6
11	$K_3[Mn(C_2O_4)_3]$, .01 *M*	.04	.01	.099	3.2
12	$K_3[Mn(C_2O_4)_3]$, .01 *M*	.02	.08	.134	2.2
13	$K_3[Mn(C_2O_4)_3]$, .01 *M*	.01	.04	.197	2.3
14	$K[Mn(C_2O_4)_2(H_2O)_2]$, 0.001 *M*	.08	.02	.094	4.8
15	$K[Mn(C_2O_4)_2(H_2O)_2]$, .001 *M*	.04	.01	.145	4.7
16	$K[Mn(C_2O_4)_2(H_2O)_2]$, .001 *M*	.02	.08	.176	3.1
17	$K[Mn(C_2O_4)_2(H_2O)_2]$, .001 *M*	.01	.04	.274	3.1
18	$K_3[Mn(C_2O_4)_3]$, 0.001 *M*	.00	.00	.845	4.6
19	$K_3[Mn(C_2O_4)_3]$, .002 *M*	.00	.00	.728	3.8
20	$K_3[Mn(C_2O_4)_3]$, .010 *M*	.00	.00	.499	4.4
21	$K_3[Mn(C_2O_4)_3]$, .025 *M*	.00	.00	.309	2.4
				Average	3.8

as quickly as possible after the preparation of the solution. The range of concentrations as to the complex salt is necessarily restricted by the intensity of the absorption, but we have covered as wide a range as could be measured with any degree of precision with the visual spectrophotometer, namely, from 0.001 to 0.025 *M*. Considering the instability of the system, the necessity of approximating the activity coefficients, and the inherent difficulties in the precise determination of the extinction coefficients, the concordance of the equilibrium constants is all that could be expected.

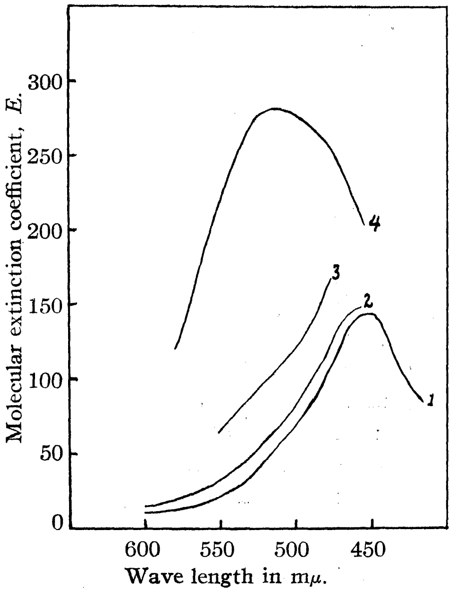

Fig. 1.—Absorption spectra: curve 1, $K[Mn(C_2O_4)_2(H_2O)_2]$, 0.01 *M* in 0.01 *M* HNO_3; curve 2, $K[Mn(C_2O_4)_2(H_2O)_2]$, 0.01 *M* in water; curve 3, $K_3[Mn(C_2O_4)_3]$, 0.001 *M* in water; curve 4, $K_3[Mn(C_2O_4)_3]$, 0.01 *M* in buffer 0.08 *M* in $K_2C_2O_4$ and 0.02 *M* in KHC_2O_4.

The absence of any trend in the calculated constants as the replacement reaction becomes extensive shows that under the prevailing conditions the dioxalato ion does not lose a second oxalate ion to an appreciable extent. The dioxalato ion may be decomposed by addition of ions that form very insoluble oxalates, but it is evident that such a reaction proceeds only at decidedly lower concentrations of oxalate ions than were present even in our most dilute solutions. The ready loss of one oxalate ion from the trioxalatomanganiate ion contrasts strongly with the behavior of the trioxalato chromiates and cobaltiates, which are not decomposed even by addition of cations which form very insoluble oxalates.

Figure 1 shows the extinction coefficients of certain of the systems measured. In the case of the dioxalatodiaquomanganiate the same absorption was observed whether the green or the yellow form of the salt was used.[5] Either form of the salt is converted immediately to the trioxalato complex by addition of potassium oxalate. When preparing the dioxalato complex we have sometimes isolated both kinds of crystals from the same solution. These results appear to indicate that in aqueous solution there is an equilibrium between the yellow and green forms, which we assume to be *cis* and *trans* isomers.

The maximum absorption of the dioxalato complex lies at about 450 mμ, whereas that of the trioxalato salt is at about 520 mμ. This shift of 70 mμ is in the same direction as observed by Uspensky and collaborators,[3] but is considerably greater in magnitude. The Russian authors have also observed that in the case of *cis-trans* isomers the *trans* isomer often has an absorption minimum at approximately the same wave length at which the *cis* isomer has a maximum. This rule was found to hold for a number of chromium and cobalt complexes, and if it applies to the manganese compounds it would indicate that our yellow dioxalato salt is the *cis* isomer. That this form predominates to such a large extent in aqueous solution is in accordance with the statistical probability, which, for the *cis* isomer, is 0.8 in such a case.

The magnetic susceptibility of potassium trioxalatomanganiate has been determined by Johnson and Mead[6] and found to correspond to four unpaired electrons. These authors therefore concluded that the complex must be held together by ionic bonds, since if there were six covalent bonds there would be only two unpaired electrons. Another possibility has to be considered, however. According to Pauling's rules for the covalent bonds in complex ions[7] tervalent manganese in its normal state should have four unpaired electrons and just the combination of available *d*, *s* and *p* eigenfunctions required for the formation of four covalent bonds directed toward the corners of a square. The readiness with which the trioxalatomanganiate ion loses its first oxalate ion, and the abnormally large shift in the absorption

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[5] Cartledge and Ericks, THIS JOURNAL, **58**, 2061 (1936).

[6] Johnson and Mead, *Trans. Faraday Soc.*, [5] **29**, 626 (1933).

[7] Pauling, THIS JOURNAL, **53**, 1367 (1931).

maximum when this occurs, suggest the hypothesis that two of the oxalate ions are covalently bound, while the third is held by the weaker ionic forces. Such a structure would agree with the observed magnetic susceptibility. Further work is in progress in an attempt to gain more insight into the structure of these complexes.

Summary

1. The extinction coefficients of aqueous and buffered solutions of potassium trioxalatomanganiate and potassium dioxalatodiaquomanganiate at various concentrations have been measured in the visible region of the spectrum. The trioxalato salt has a maximum absorption at about 520 mμ and the dioxalato salt at about 450 mμ.

2. The two salts are convertible into each other according to the reaction

$$[Mn(C_2O_4)_3]^{\equiv} + 2H_2O \rightleftarrows [Mn(C_2O_4)_2(H_2O)_2]^- + C_2O_4^{=}$$

Equilibrium is established almost instantaneously. The equilibrium constant of the reaction has been determined by spectrophotometric analysis and found to be 3.8×10^{-3} at 0°.

3. The green and yellow dioxalato salts both give a golden-yellow solution with the same absorption curve, and the solution presumably consists of an equilibrium mixture of the two isomers. The optical evidence makes it likely that the yellow form is the statistically more probable *cis* isomer.

4. It is suggested that the complex manganiates may be derived from a covalent *dsp*^{2} structure fundamentally, the fifth and sixth valence bonds being ionic or ion-dipole in character.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BUFFALO]

An Oxalato Complex of Quadrivalent Manganese

BY G. H. CARTLEDGE AND W. P. ERICKS

In the course of the investigation described in a previous paper[1] an attempt was made to prepare a hydroxo-oxalato complex compound containing tervalent manganese. In the previous experiments on the trioxalatomanganiate potassium permanganate was first reduced all the way to the manganous state by an excess of oxalic acid; the manganous ion was then oxidized by addition of a second portion of permanganate, the exact product being determined by the proportions of the reactants used. In view of the weakly acidic character of the water molecules in the dioxalatodiaquomanganiate ion, it was thought that the corresponding hydroxo ion might be obtained by suitable decrease of the hydrogen-ion concentration. Accordingly, a preparation was carried out in which part of the oxalic acid was replaced by potassium oxalate, using the proportions:

$$3.5H_2C_2O_4 : 0.5\ K_2C_2O_4 : KMnO_4$$

The materials were allowed to react at a little above 0° and the result was a mixture of two kinds of crystals. Microscopic examination showed the presence of some potassium trioxalatomanganiate along with a considerably larger proportion of dark, olive-green crystals. The experiment was repeated with further alteration in the reacting proportions until a method was finally developed which gave the green material in pure form. Although the substance is very unstable we were able to isolate it and prove that it contains quadrivalent manganese, its composition being represented accurately by the formula $K_2[Mn^{IV}(C_2O_4)_2(OH)_2]\cdot 2H_2O$. It is therefore to be called potassium dioxalatodihydroxomanganeate. So far as we have been able to discover it is the only known complex of quadrivalent manganese with the exception of the hexahalogenato complexes $[MnX_6]^{2-}$ and a diglycerol complex reported by Schottländer.[2]

Preparation.—The preparation is conducted according to the reaction

$$3.5H_2C_2O_4 + 0.65K_2C_2O_4 + KMnO_4 \longrightarrow K_2[Mn(C_2O_4)_2(OH)_2] + 0.5H_2C_2O_4 + 0.15K_2C_2O_4 + 3CO_2 + 2H_2O$$

The operations are conducted rapidly, in a cool and darkened room. Fourteen hundredths of a mole of oxalic acid (17.64 g. $H_2C_2O_4\cdot 2H_2O$) is dissolved in 250 cc. of distilled water. The solution is cooled to 0° and 0.04 mole (6.32 g.) of powdered potassium permanganate is added, followed by 0.026 mole of potassium oxalate (4.78 g. $K_2C_2O_4\cdot H_2O$). The mixture is agitated vigorously for about twenty minutes and the temperature is allowed to rise to 7°. At this point carbon dioxide begins to be

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(1) Cartledge and Ericks, THIS JOURNAL, **58**, 2061 (1936).

(2) Schottländer, *Ann.*, **155**, 230 (1870).

evolved rapidly, and the flask containing the mixture is submerged in an efficient cooling mixture to reduce the temperature quickly to 0°, the agitation being maintained meanwhile.

When the reaction is complete the solution has a dark green color. It is filtered rapidly through paper on a cold Büchner funnel, the filtrate being collected in a flask standing in a freezing mixture. Alcohol is added to the filtrate in small portions, keeping the temperature at about 0°, until 100 cc. has been added. The precipitation of the crystals begins almost at once.

The crystals are filtered rapidly and washed successively with ice-cold 50% alcohol, 95% alcohol, absolute alcohol and anhydrous ether. The filtrate from the crystals is red and upon standing often deposits the trioxalatomanganiate. The green crystals decompose rapidly at room temperature, especially in the light, but keep for some weeks if preserved in the dark at −6°.

Analysis.—The analytical procedures used were similar to those described in a preceding paper.[1] Volumetric and gravimetric determinations of manganese showed that two equivalents of iodine are liberated for each atomic weight of manganese, indicating the presence of quadrivalent manganese. In the determination of oxalate by titration with permanganate the proper allowance was made for the oxidation of a portion of the oxalate by the quadrivalent manganese. Before the final procedure had been developed as described above, five preparations were obtained which were somewhat impure but gave analyses with sufficient concordance to establish the composition. A sample prepared by the final procedure appeared to be homogeneous under the microscope and gave the following analysis:

Constituents	Found	Calculated for $K_2[Mn(C_2O_4)_2(OH)_2]\cdot 2H_2O$
K^+	20.3	20.62
Mn (gravimetric)	14.5	14.49
Mn^{4+} (volumetric)	14.3	
$C_2O_4^=$	46.2	46.42
H_2O (total)	14.2	14.26

Attempts to prepare the compound during the summer were at first unsuccessful, but the product was obtained without difficulty by the following method. The Büchner funnel was jacketed in an ice-bath, and closed at the top with a large one-holed rubber stopper. A glass tube passed from the funnel to the bottom of the reaction flask, which stood in a freezing mixture. The washing liquids were added through this flask by means of a separatory funnel; the air entering the flask and subsequently drawn through the crystals was first dried with calcium chloride and then chilled in a cooling coil. By this means the crystals were protected from the warm, humid air until completely washed and dried. Thorough and rapid drying is essential.

Although potassium dioxalatodihydroxomanganeate decomposes rapidly at room temperature, we have kept pure specimens for several weeks in a refrigerator at −6° before decomposition became apparent. The salt dissolves in water to give a clear, deep green, neutral solution which quickly becomes brown and turbid, and later changes into the red trioxalatomanganiate. The green color of a cold aqueous solution is unaffected by addition of small amounts of acids or alkalies. At 0° a solution containing a little oxalic acid remains clear and is stable enough to permit a determination of the absorption spectrum.

As obtained by the procedure described above, the product is an impalpable powder in which no distinct crystals can be seen under the microscope. The salt may be recrystallized as follows. The powder is dissolved in twenty-five times its weight of cold 0.1 *M* oxalic acid. After rapid filtration the solution, at 0°, is treated with one-sixth its volume of ice-cold 95% alcohol and placed in a freezing mixture until crystallization occurs. If the precipitation is sufficiently gradual well-defined crystalline rods are formed. A photomicrograph of one of our products is shown in Fig. 1; for this we are indebted to Professor E. Raymond Riegel. The crystals photographed were clearly seen to be of two colors, green and orange. Careful analysis showed the material to be pure, however, and it is probable that the two kinds of crystals were the *cis* and *trans* isomers theoretically possible. So far we have been unable to separate the two forms, owing to their instability.

Barium Dioxalatodihydroxomanganeate.—From the fact that our analysis indicated that we had a complex bivalent anion of rather large size, it was expected that its barium and lead salts should be sparingly soluble. Preliminary qualitative tests showed the correctness of this surmise, and the barium salt was obtained without difficulty. To 20 cc. of 5% barium chloride solution 1 cc. of concentrated hydrochloric acid was added. This mixture gives no precipitate of barium oxalate if a small quantity of oxalate ion is added. To 0.8 g. of potassium dioxalatodihydroxomanganeate dissolved in 40 cc. of ice-cold water, 13 cc. of the acidified barium chloride was added (a 25% excess). A silky precipitate appeared almost at once. The brown mixture was filtered, leaving a pale, apple-green precipitate which was washed and dried in the usual manner. The salt is sparingly soluble in water, giving a pale green color. Addition of sulfuric acid causes the color to disappear with the precipitation of barium sulfate. Analysis of the salt gave the following results:

Constituents	Found	Calculated for $Ba[Mn(C_2O_4)_2(OH)_2]\cdot 3H_2O$
Ba^{++}	29.8	30.09
Mn (gravimetric)	12.1	12.03
$C_2O_4^=$	38.6	38.56

Chloropentamminecobalti - dioxalatodihydroxomanganeate.—In qualitative tests it was found possible also to isolate the new complex ion as a sparingly soluble double complex with cobalt cations. Stoichiometrically equivalent amounts of chloropentamminecobalti chloride and potassium dioxalatodihydroxomanganeate were mixed, using 0.001 mole of each dissolved separately in the least possible quantity of water at 0°. Soon after mixing the solutions fine crystals formed, of fawn color with a greenish cast. The crystals were filtered rapidly and washed with cold alcohol and ether in the usual manner. The yield was 85%.

Microscopic examination showed that the product was homogeneous and had a needle-like structure. The crystals are sparingly soluble in water, forming a silky suspension. Upon addition of potassium oxalate the crystals gradually dissolve, giving a yellowish-green color. Sulfuric acid gives a brown solution which quickly changes to the pink of the chloropentamminecobalti ion. Qualitative tests showed the presence of cobalt and manganese. The double complex appears to be decidedly more stable than the potassium salt.

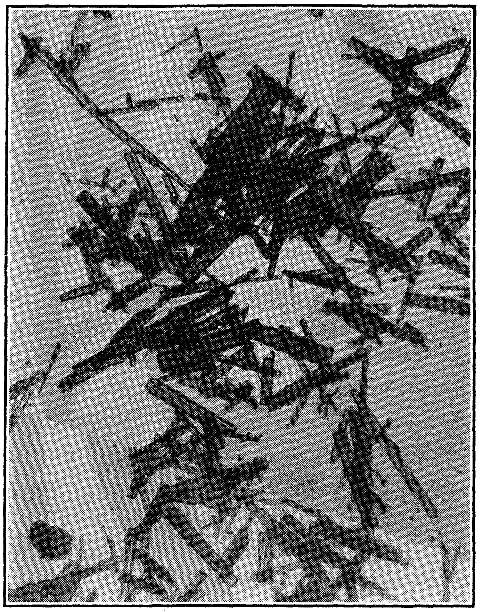

Fig. 1.—Potassium dioxalatodihydroxomanganeate, × 354.

The Absorption Spectrum of Potassium Dioxalatodihydroxomanganeate.—The absorption spectrum cannot be measured accurately in simple aqueous solution owing to the rapid appearance of a turbidity. In the presence of dilute oxalic acid, however, the solution remains clear and spectrophotometric measurements can be made with a considerable degree of accuracy, provided the solution is kept at 0° and the observations do not extend over three or four minutes on any one solution. Three series of determinations were made in 0.1 M oxalic acid, the concentration of the complex compound being 0.005, 0.01 and 0.025 M, respectively. The measurements were made with a Bausch and Lomb spectrophotometer, the precautions described in the preceding paper[3] being observed. The solutions were in all cases prepared immediately before use, and the cell was jacketed in ice during the measurements. The extinction coefficients obtained indicate that Beer's law is followed within the accuracy of the procedure over the concentration range employed. The solution has a minimum absorption at 566 mμ, with a pronounced maximum at 643 mμ, as shown in Fig. 2.

According to Pauling's theory of the bonds in complex compounds[4] quadrivalent manganese should be expected to form six equivalent octahedral bonds, since in its lowest state six d^2sp^3 eigenfunctions are available for bond formation. Magnetic susceptibility measurements cannot distinguish such a covalent structure from one involving purely ionic bonds in the present case, since both structures should give a susceptibility corresponding to three unpaired electrons. Considering the high valence of the manganese, however, it is more than likely that the covalent structure is favored.

It is noteworthy that in the case of tervalent manganese a diaquo complex forms readily and functions only very weakly as an acid, whereas with quadrivalent manganese the hypothetical aquo-ion dissociates into its corresponding hydroxo ion even in moderately acid solutions. This behavior is in accordance with the relation between the acidic strength of aquo ions and ionic potentials as developed by one of the authors.[5] From the ionic potential of quadrivalent manganese we should expect manganese dioxide to be somewhat more acidic than titanium dioxide. Although a sufficiently high hydrogen-ion concentration should theoretically convert the hydroxo ion into the aquo ion, there is no evidence from color changes that such an effect occurs in the presence of dilute acids. Higher hydrogen-ion concentrations cannot be used because of the rapid reduction of the manganese in strongly acid solutions. It is significant that Tschugajeff[6] has prepared a hydroxo complex of quad-

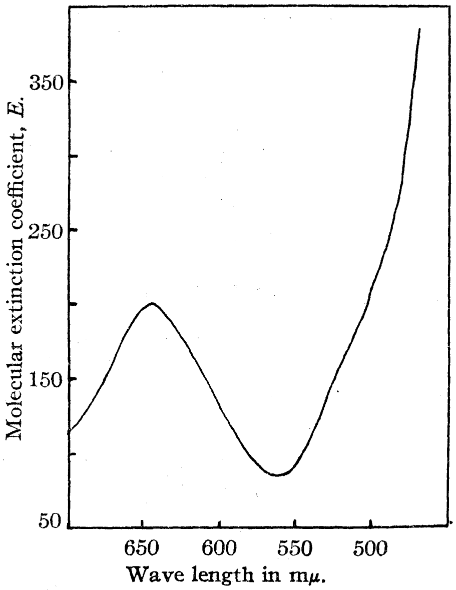

Fig. 2.—The absorption spectrum of potassium dioxalatodihydroxomanganeate in 0.1 M oxalic acid.

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(3) Cartledge and Ericks, THIS JOURNAL, **58**, 2065 (1936).

(4) Pauling, *ibid.*, **53**, 1367 (1931).

(5) Cartledge, *ibid.*, **50**, 2855, 2863 (1928).

(6) Tschugajeff, *Z. anorg. allgem. Chem.*, **137**, 1 (1924).

rivalent platinum which is not converted into an aquo compound even by concentrated hydrochloric acid.

Summary

1. A new complex compound of quadrivalent manganese has been prepared which has the composition $K_2[Mn(C_2O_4)_2(OH)_2]\cdot 2H_2O$. The barium and chloropentamminecobalti salts were also isolated.

2. The absorption spectrum was measured in the visible region.

BUFFALO, NEW YORK RECEIVED JUNE 19, 1936

NOTES

Sodium Fluorenone as a Dehydrating Agent[1]

BY H. E. BENT AND H. M. IRWIN, JR.

The most rapid method of drying an organic liquid is to dissolve in it some compound which reacts rapidly with water. For this purpose sodium benzophenone has been widely used although this involves using an alkali metal, sodium–potassium alloy or some other material which introduces considerable hazard into such work. Fluorenone has the advantage over benzophenone that it will react readily with dilute sodium amalgam to form an addition compound which has a deep green color and therefore like benzophenone gives a definite indication by its color of the absence of water. Dry solvent is then obtained by distilling from this solution.

The object of this investigation is to compare the efficiency of sodium fluorenone with the customary drying agents, magnesium perchlorate and activated alumina. Since the compound formed by the addition of sodium to fluorenone is more stable than that formed with benzophenone, it is important to be sure that the ketyl is still sufficiently reactive to be an effective drying agent.

A dilute solution of sodium fluorenone was prepared for this work by introducing 0.025 g. of fluorenone and evacuating with a mercury pump for one hour. Three to five cubic centimeters of a saturated amalgam (about 1%) was then added *in vacuo* and 50 cc. of dry ether. Shaking produced a solution which was sufficiently concentrated to react with at least one hundred times as much water as is retained by the glass on its surface.[2] A tube, connected to the reaction flask by a capillary capable of being broken and thereby opened by a magnetic hammer, carried four side-tubes. The first two were empty and used as a check on the method. The third and fourth contained activated alumina and magnesium perchlorate, respectively. The samples of alumina and magnesium perchlorate were prepared by exposing them in a thermostat to one liter of air saturated with water vapor at 25°. The quantity of water absorbed by the sample was at least one hundred times as much as was necessary to destroy the sodium fluorenone with which it came in contact, while still being small enough to give the very low vapor pressure characteristic of the dehydrating agent. The tubes containing the solid dehydrating agents were evacuated for a short time before sealing the apparatus, and immediately the capillary was broken in order to prevent diffusion from one solid to the other. The fluorenone was decolorized in the first empty tube on account of moisture on the glass and in the vapor state. In the second tube the solution retained its color. In the third and fourth tubes the solution was immediately decolorized by the alumina and by the magnesium perchlorate, indicating that the vapor pressure of water was sufficiently high to be removed by the ether solution of sodium fluorenone. A duplicate run verified the conclusion from this experiment.

The vapor pressure of water is given as 0.003 mm. for alumina and the water is given as unweighable in 210 liters for magnesium perchlorate.[3] If unweighable means less than 1 mg. this would give a vapor pressure of less than 0.005 mm. If we assume that in the presence of a small amount of water the ketyl is converted to fluorenone and fluorenole,[4] then we can estimate a mini-

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[1] This problem was studied as a reading period assignment in the first course in physical chemistry at Harvard University.

[2] Bent and Lesnick, THIS JOURNAL, **57**, 1246 (1935).

[3] Yoe, *Chem. News*, **130**, 340 (1935).

[4] Bachman, THIS JOURNAL, **55**, 1179 (1933).

mum value for the equilibrium constant for the reaction

$$NaR + H_2O = NaOH + {}^1/_2R + {}^1/_2RH_2$$

Since the sodium hydroxide is present as a solid we may express the equilibrium constant by the equation

$$K = (R)^{1/2}(RH_2)^{1/2}/(NaR)(H_2O)$$

If we assume, as a consequence of the complete destruction of the green color of the solution, that the reaction goes at least 99.9% to completion, then we obtain

$$K = 0.5 \times 999 \times 23/0.003 = 3.8 \times 10^6$$

referring the vapor pressure of water to that of pure liquid water as the standard state. This gives a value for ΔF of -9.0 kcal. These figures represent the minimum efficiency of sodium fluorenone as a drying agent. In any normal procedure a large excess of the drying agent would be used which would result in the removal of water until the pressure is at least as low as 10^{-7} mm.

CONTRIBUTION FROM THE
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RECEIVED JULY 30, 1936

The Vapor Density of Hexaphenylethane

BY H. E. BENT AND E. S. EBERS

In a recent publication the statement is made that hexaphenylethane probably does not dissociate in the vapor state.[1] In order to verify this statement an attempt was made to measure directly the vapor density of hexaphenylethane. This measurement combined with the previous data on the vapor pressure would give the molecular weight in the vapor state.

Since the vapor pressure of hexaphenylethane at 120° is only 0.004 mm. a very large volume would be necessary in order to produce a weighable amount of compound. For this purpose a ten-liter flask was attached to the fiber gage used in the previous research and to a capsule of hexaphenylethane. Ground joints controlled by electromagnets were so arranged as first to saturate the ten-liter flask with the ethane and then, closing the ethane capsule, condense the vapor in a small ampoule. The flask could then be saturated again and the vapor a second time condensed and in this way any desired amount of material obtained.

The method was checked by determining the vapor density and the molecular weight of triphenylmethane. The result was high by about 20% which we assume to be due to adsorption. As it was expected that difficulty would be encountered with hexaphenylethane on account of decomposition a procedure was adopted with triphenylmethane which would avoid this difficulty as far as possible. The ground joint to the pump was opened just enough to reduce the pressure to about three-fourths of the saturation pressure. After the pressure had become constant the valves to the pump and to the capsule of sample were closed simultaneously and the valve to the receiver opened for a time sufficiently long to condense about half of the total amount of material in the ten-liter flask. The valve to the receiver was then closed and the pressure again measured, the difference between the initial and the final pressure giving a measure of the amount of material condensed. This process was repeated about ten times and the flask then cooled and the receiver cracked off. The amount of material was determined by weight, both by difference and by evaporation of the solution of the compound to dryness in a crucible. This method of operating between three-fourths and three-eighths saturation would also be effective in avoiding condensation in the ten-liter flask or in removing adsorbed material from the surface of the glass during condensation.

When the method was applied to hexaphenylethane it was found that decomposition was too rapid to permit even an approximate determination of the vapor density. In a flask of such a large size decomposition was so great that even with the pump operating the pressure remained several times that of hexaphenylethane for a space of three hours at 120° (the valve to the solid remaining open). By this time apparently all of the ethane had decomposed for the pressure gradually decreased. However, the material in the flask was no longer hexaphenylethane but a decomposition product for on closing off the flask the pressure remained perfectly constant. Under these conditions hexaphenylethane decomposes rapidly enough to be measured easily. We concluded, therefore, that it is not possible to meas-

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[1] G. R. Cuthbertson and H. E. Bent, THIS JOURNAL, **58**, 2000 (1936).

ure the vapor density of hexaphenylethane by this method on account of rapid decomposition.

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RECEIVED AUGUST 3, 1936

Relative Reactivities of Organometallic Compounds. XIV. Orientation in Metalation

BY HENRY GILMAN AND ROBERT H. KIRBY

Schlenk and Meyer[1] have shown that Abeljanz[2] did not obtain phenylpotassium from benzene and potassium. However, Schorigin[3a] very probably had phenylpotassium in hand, despite the confusion due to the paucity of experimental data.[4] We have found that carbonation of the products resulting from interaction of benzene, diethylmercury and potassium gives benzoic acid (45% yield) as well as phthalic and terephthalic acids. The same products, in different quantities, are obtained when sodium is used in place of potassium.

The organo-alkali compounds appear to arise largely as a consequence of metalation by ethylalkali compounds

$$C_6H_6 + C_2H_5K \longrightarrow C_6H_5K + C_2H_6$$

and not by the action of the alkali metals or their amalgams on benzene, for the evolved gas consists predominantly of ethane and contains only small quantities of ethylene and hydrogen.[5] The isolation of phthalic and terephthalic acids establishes the intermediate formation of *o*- and *p*-dialkalibenzenes, and indicates that phenylsodium (or potassium) orients subsequent metalation to the *ortho* and *para* positions. Mercuration may not follow such orientation.[6] It is noteworthy that isophthalic as well as terephthalic acid has been obtained from successive interaction of benzene, diamylmercury, sodium and carbon dioxide in the interesting studies by Morton and Hechenbleikner.[7]

The results are consistent with some of the earlier generalizations on relative reactivities of organometallic compounds,[8] particularly the increase in reactivity of RM compounds with increase in atomic weight of the alkali metal. For example, Mr. R. V. Young, in a study of organoalkali compounds, has shown that ethyl-lithium does not metalate benzene during a two-month period at room temperature;[3b] the over-all metalation of benzene by ethylsodium is less than that by ethylpotassium; and ethylpotassium gives much more of the dimetalated compounds than does ethylsodium.[9]

The metalations reported are merely special cases of general metalation which may be a direct metathesis, and, when RM compounds are used, a metathesis resulting in the formation of the salt of the stronger acid. Metalation of aromatic nuclei by RM compounds may involve preliminary addition, with subsequent elimination of RH.[10] Metalation by RM compounds is, of course, possible with all compounds, saturated as well as unsaturated, for all hydrogens are acidic to varying degrees from the viewpoint of metalation. A pertinent illustration is the metalation of saturated aliphatic hydrocarbons of the R_3CH type by ethylpotassium. In such cases, it is unlikely that unsaturated compounds are intermediates, even though it has been shown that RM compounds can act as dehydrogenating agents.[11]

Experimental Part

Metalation with Ethylpotassium.—To a suspension of 3.13 g. (0.08 g. atom) of potassium shavings in 35 cc. of benzene was added 5.17 g. (0.02 mole) of diethylmercury. Reaction set in at once as was evident by amalgamation of the potassium, evolution of gas and warming of the benzene. The mixture was stirred without heating for forty-eight hours, cooled to 7° and carbonated with carbon dioxide gas. The yields of products, based on diethylmercury, were 33% benzoic acid and 14% terephthalic acid (mixed melting point of dimethyl ester). The odor of propionic acid was noticeable, and a strong fluorescein test established the presence of phthalic acid. Isophthalic acid was not isolated, but may have been present in small quantities. The gas evolved contained 8 cc. of ethylene,

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(1) Schlenk and Meyer, *Ber.*, **46**, 4060 (1913).

(2) Abeljanz, *ibid.*, **9**, 10 (1876).

(3) (a) Schorigin, *ibid.*, **43**, 1938 (1910); (b) *ibid.*, **41**, 2723 (1908).

(4) Wooster, *Chem. Rev.*, **11**, 8 (1932). See, also, Schlenk and Holtz, *Ber.*, **50**, 262 (1917).

(5) There is a possibility of some di-alkali compound being formed by self-metalation of phenylalkali compound. Incidentally, it is likely that the spontaneous transformations of some of the more reactive alkylalkali compounds involve self-metalation to give polymetalated types culminating in carbides [see ref. 12].

(6) Gilman and Kirby, *J. Org. Chem.*, **1**, 146 (1936).

(7) Morton and Hechenbleikner, THIS JOURNAL, **58**, 1024 (1936). Dr. Morton and co-workers have shown, in some unpublished studies, that phthalic acids are obtained in this reaction when diamylmercury is replaced by amyl chloride.

Possibly the amylidene disodium of Morton may orient differently from ethylsodium. A pertinent illustration is the different orientation effects of the very closely related phenyl-calcium and phenyl-lithium compounds in metalations.

(8) Gilman and Nelson, *Rec. trav. chim.*, **55**, 518 (1936).

(9) The extent of metalation varies with the R group. A 77% yield of benzoic acid was obtained from benzene and *n*-butylsodium followed by carbonation.[6]

(10) Gilman and Breuer, THIS JOURNAL, **56**, 1123 (1934).

(11) An illustration is the study by C. W. Bradley on the conversion of 1,4-dihydrodibenzofuran by phenyl-lithium to 4-dibenzofuryl-lithium and dibenzofuran.

2.5 cc. of hydrogen and 535 cc. of ethane, all volumes being corrected.

In a second experiment, using 75 cc. of benzene, reaction started slowly and four hours elapsed before an appreciable quantity of mercury separated. The yields were: 45% of benzoic acid and 17% of terephthalic acid.

From a third experiment, which differed from the second only in limiting the time of reaction to twenty hours, the yield of benzoic acid was 33% and the yield of terephthalic acid was 11%. Positive fluorescein tests were also obtained in the second and third experiments.

Metalation with Ethylsodium.—The procedure was identical with the first experiment with ethylpotassium, 1.84 g. (0.08 g. atom) of sodium being used. Reaction set in immediately. The products identified were: 41% of benzoic acid; a small quantity of terephthalic acid (mixed melting point with dimethyl ester); and phthalic acid (as indicated by a positive fluorescein test). The gas evolved contained 12 cc. of ethylene, 10 cc. of hydrogen and 420 cc. of ethane. Incidentally, the limited evolution of ethylene and hydrogen belies any considerable metalation by alkali hydride which arises from the thermal decomposition of ethylalkali compound.[12]

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(12) Carothers and Coffman, THIS JOURNAL, **51**, 588 (1929).

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED JUNE 18, 1936

Comparison of the Total Nitrogen in Wheat Seeds by the Gunning (Modified Kjeldahl) and the Dumas Combustion Methods

BY W. Z. HASSID

Smyth and Wilson[1] analyzed peas for total nitrogen before and after germination in distilled water, in salt solution media and in alkaloids. The peas showed an increase of 0.2 to 0.3% nitrogen in the dry residue after germination.

In the opinion of these authors, the increase in nitrogen was not the result of atmospheric nitrogen assimilation, but was due to the inadequacy of the Kjeldahl method to measure the total nitrogen in the ungerminated peas. By the official Kjeldahl procedure only 90% of the total nitrogen as compared with the Dumas combustion method could be obtained, and this varied with different modifications of the official procedure. On the basis of these results, Smyth and Wilson concluded that in the process of germination the nitrogen of the seeds was converted into compounds which were more easily determinable by the Kjeldahl method than those in the dry seeds.

Since Smyth and Wilson's results cast doubt on the validity of the conclusions drawn by Lipman and Taylor[2] and others who obtained similar results relative to the power of green plants to fix atmospheric nitrogen, it seemed desirable to make a study of the modified Gunning method and the Dumas combustion method as a means of determining the nitrogen in seeds and seedlings. To this end, wheat seeds of the "little club" variety were subjected to analysis for total nitrogen by both the modified Gunning and Dumas combustion methods.

TABLE I

N ANALYSIS OF 12 SAMPLES OF WHEAT SEEDS BY THE MODIFIED GUNNING METHOD

Sample no.	Sample wt.	% N	
1	1.0000	2.27	Average 2.25%
2	1.0000	2.20	
3	1.0920	2.18	
4	1.4060	2.25	
5	1.4060	2.25	
6	1.4040	2.27	
7	1.4000	2.25	
8	1.4000	2.25	
9	1.4026	2.25	
10	1.4000	2.20	
11	1.4010	2.30	
12	1.4020	2.31	

N ANALYSIS OF 6 SAMPLES OF WHEAT SEEDS BY THE DUMAS METHOD (COMBUSTION)

Sample no.	Sample wt.	% N	
1	1.0205	2.25	Average 2.28%
2	1.1100	2.27	
3	1.0000	2.28	
4	1.0344	2.31	
5	1.0000	2.30	
6	1.0000	2.29	

A study of the table makes it clear that the modified Gunning method as used in this experiment yields as much nitrogen as the Dumas method for the wheat seeds analyzed. It appears, therefore, that such results as were obtained by Lipman and Taylor and by others who claimed to have shown nitrogen fixation by wheat plants cannot be invalidated on the basis of the results and conclusions of Smyth and Wilson, cited above.

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RECEIVED AUGUST 17, 1936

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(1) E. M. Smyth and P. W. Wilson, *Biochem. Z.*, **282**, 1 (1935).

(2) C. B. Lipman and J. K. Taylor, *J. Franklin Inst.*, 475–506 (1924).

COMMUNICATION TO THE EDITOR

THE STRUCTURES OF THE ACETONE DERIVATIVES OF GALACTOSE-, GLUCOSE- AND MANNOSEDIBENZYLMERCAPTALS

Sir:

In 1929 Brigl and Schinle [*Ber.*, **62,** 1716 (1929)] found that their 2-methylglucose was capable of osazone formation with the loss of the methyl group. This striking discovery cast doubt on the structure of those partially methylated sugars whose formulas had previously been assigned on the assumption, till then unquestioned, that a 2-methyl sugar could not possibly form an osazone. Among those partially methylated sugars affected by this discovery were 4-methylglucose [Pacsu, *ibid.*, **58,** 1455 (1925)], 4-methylmannose [Pacsu and v. Kary, *ibid.*, **62,** 2811 (1929)], and 4-methylgalactose [Pacsu and Löb, *ibid.*, **62,** 3104 (1929)]. Levene and co-workers [Levene, Meyer and Raymund, *Science*, **73,** 291 (1931); *J. Biol. Chem.*, **91,** 497 (1931)] were the first to notice that the supposed 4-methylglucose was identical with 2-methylglucose. In a later publication [Pacsu, *Ber.*, **65,** 51 (1932)] this fact has been confirmed. In the same place it has also been stated that in the light of Brigl's discovery it appears certain that the supposed 4-methylmannose is likewise a 2-methyl derivative, whereas nothing definite could be said as to the structure of the supposed 4-methylgalactose until the necessary revision of the entire problem has been concluded. For the past year this reinvestigation has been in progress in this Laboratory. In a recent publication, Munro and Percival [*J. Chem. Soc.*, 640 (1936)] apparently undertook "A Revision of the Constitutions of the Supposed 4-Methyl Galactose and 4-Methyl Mannose of Pacsu. . ." and stated "The structures of the acetone compounds of the dibenzylmercaptals of glucose, galactose, and mannose, assigned by Pacsu, require revision in the light of the facts now known and this problem is under investigation." This was precisely the conclusion arrived at in my publication (*loc. cit.*), which Munro and Percival doubtless overlooked. Therefore, it is deemed advisable briefly to communicate the results so far obtained with John W. Green during the course of our reinvestigation. We have found that the formerly described crystalline "2,3-monoacetone galactosedibenzylmercaptal" with m. p. 102–103° and $[\alpha]^{18}D$ 8.8° ($C_2H_2Cl_4$), in spite of its apparent uniformity, is not a chemical individual. By repeated fractional crystallization from different solvents we have succeeded in separating this mixture into two monoacetone mercaptals, one with m. p. 112.5° and $[\alpha]^{20}D$ 17.4° ($CHCl_3$), and the other with m. p. 101.5° and $[\alpha]^{20}D$ 30.5° ($CHCl_3$). Neither compound reacts with triphenylmethyl chloride in pyridine solution. Therefore, the OH-group at carbon atom 6 must be occupied in each substance. We have tentatively assigned to them the structure of 5,6- and 4,6-monoacetone galactosedibenzylmercaptal, respectively. By removing the mercaptan residues from one of these compounds in methyl alcoholic solution according to our method which yields glycofuranosides [Pacsu and Green, THIS JOURNAL, **58,** 1723 (1936)], a crystalline, non-reducing substance has been obtained which still contains the acetone residue. The structure of this key compound is being investigated. If the formation of the diacetone mercaptal in the presence of concd. sulfuric acid will prove to have passed through the monoacetone stage, then neither the sirupy diacetone mercaptal, always used as a starting material, nor any of its sirupy derivatives could represent uniform substances. A detailed account of the revisionary work on these derivatives of galactose as well as glucose and mannose will be published as soon as it has been completed.

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EUGENE PACSU

RECEIVED SEPTEMBER 21, 1936

NEW BOOKS

Differential Equations in Applied Chemistry. By FRANK LAUREN HITCHCOCK, Ph.D., Professor of Mathematics, and CLARK SHOVE ROBINSON, S.M., Associate Professor of Chemical Engineering, Massachusetts Institute of Technology. Second edition, revised and enlarged. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, New York, 1936. viii + 120 pp. 12.5 × 19 cm. Price, $1.50.

A review of the first edition was given in THIS JOURNAL, 46, 1066 (1924). As stated there "The present volume, although frankly limited in its scope, is a splendid introduction to the application of differential equations to chemistry and chemical engineering." The book has been revised, many new examples have been added, and Chapter VI, dealing with "Numerical Solution of Differential Equations," is entirely new. The examples illustrate excellently the value of higher mathematics in the solution of the technical problems, and the reviewer is convinced that even those who have had only an elementary training in calculus will derive considerable stimulation from a study of these examples.

SAUL DUSHMAN

Annual Review of Biochemistry. Vol. V. Edited by JAMES MURRAY LUCK, Stanford University. Annual Review of Biochemistry, Ltd., Stanford University P. O., California, 1936. ix + 640 pp. Illustrated. 16 × 23 cm. Price, $5.00.

This volume contains four new sections as follows: X-ray studies on the structure of compounds of biochemical interest, by O. L. Sponsler and W. H. Dore; Clinical applications of biochemistry, by J. P. Peters, C. L. Robbins and P. H. Lavietes; The role of special elements (boron, copper, zinc, manganese, etc.) in plant nutrition, by P. Maze; and Soil microbiology, by S. A. Waksman.

A considerable number of new authors also appear, and in particular a group of eminent English biochemists, including D. E. Green and D. Keilin on oxidations and reductions; J. H. Quastel who wrote the section on enzymes; W. N. Haworth and E. L. Hirst on carbohydrates and glucosides; T. P. Hilditch on acyclic constituents of natural fats and oils; R. Robison on chemistry and metabolism of compounds of carbon; H. A. Krebs on metabolism of amino acids. In addition, other new contributors include C. Rimington on chemistry of proteins and amino acids; V. du Vigneaud and H. M. Dyer on chemistry and metabolism of compounds of sulfur; I. L. Chaikoff on carbohydrate metabolism; E. F. Terroine on fat metabolism; E. A. Doisy and D. W. MacCorquodale on the hormones; H. von Euler on the water-soluble vitamins; E. V. McCollum on the fat-soluble vitamins; A. J. Kluyver on bacterial metabolism; Hart and Elvehjem on mineral metabolism; A. C. Ivy and L. A. Crandall, Jr., on liver and bile; J. Roche on animal pigments; G. T. Nightingale on the biochemistry of the nitrogenous constituents of the green plants.

Several of the former contributors again prepared four sections. As heretofore, certain phases covered in earlier volumes are not included in volume V. On pages vii and viii appear the errata for volume I to IV, inclusive, the small number of which are a tribute to the careful work of the editorial staff.

The new sections are very appropriate and come from responsible sources. All the contributors have been carefully selected, in fact, and each is qualified to discuss the subject to which he is assigned. While the resulting reviews inevitably, and doubtless properly, reflect the individual interests of the reviewer somewhat, the changes in the staff of authors that are made from year to year militate against any overemphasis on particular aspects of the several subjects.

C. H. BAILEY

Handbuch der biologischen Arbeitsmethoden. (Handbook of Biological Procedures.) Edited by Prof. Dr. EMIL ABDERHALDEN. Abt. IV, Angewandte chemische und physikalische Methoden, Teil $^1/_2$, Heft 10 (Schluss). Fermentforschung. Urban & Schwarzenberg, Friedrichstrasse 105B, Berlin, N 24, Germany, 1936. 205 pp. 17.5 × 25.5 cm. Price, RM. 13.

This volume includes a comprehensive review on pectinases, the isolation of crystalline trypsinogen and its change to crystalline trypsin, demonstration of protective enzymes, and amylases. The treatment of pectinases by Felix Ehrlich is very thorough and complete. The author gives a good discussion of the nature, occurrence, and properties of protopectinase, pectase, pectolase, and arabanase. Methods of preparing the various enzyme infusions and the qualitative and quantitative analyses of these infusions are presented.

M. Kunitz and J. H. Northrop describe an improved method for the preparation of crystalline trypsin from crystalline trypsinogen. Complete details of the methods used are given.

The literature on amylases has been reviewed by T. Sabalitschka. This review consisting of 85 pages covers the degradation of starch by amylase, the influence of various factors such as temperature, *p*H and enzyme activity.

The various methods of determining amylase activity are discussed and methods of obtaining and purifying amylases and the properties of the various amylases are described. While the review is thorough and comprehensive in most respects, one is surprised to find that there is no reference to the literature or any discussion on the phenomenon of the action of diastase on raw starch. This is a subject of increasing importance in the malting, baking and brewing industries. Many of the analytical methods described in the review are open to serious criticism. The reviewers believe that this work would be of greater value if presented in a more critical manner.

Emil Abderhalden discusses the simplification of the methodology of demonstrating protective protease activity. The role of these enzymes in connection with the problems of immunity is discussed. He also discusses the demonstration of protective proteases without employing dialysis or using the usual ninhydrine technique. Several other improvements in methods are also given.

The volume has a complete index and table of contents.

C. N. FREY
W. R. JOHNSTON

Die Photoelemente und ihre Anwendung. 2 Teil. **Technische Anwendung.** (Photo-Cells and their Uses Part 2. Industrial Application.) By Dr. BRUNO LANGE, Berlin. Preface by Dr. Hans Thirring. Verlag Johann Ambrosius Barth, Salomonstrasse 18 B, Leipzig C 1, Germany, 1936. viii + 94 pp. 67 figs. 16 × 23.5 cm. Price, RM. 6.75.

In this second part of Dr. Lange's treatise, numerous practical applications of photo-cells are recorded. Most of the apparatus described and illustrated was designed by the author himself.

Dr. Lange is primarily interested in the cuprous oxide cell, and those of similar type. Very little space is devoted to the cesium cell. Accordingly, applications of the photo-cell to television, the talking moving pictures, etc., are not specifically included in the "technische Anwendungen."

After general discussion of cell construction, sensitivity, effect of temperature, etc., the applications are discussed under the following headings: "Determination of Light Intensity," "Photography," "The Photoelectric Cell in Photometry," "The Photoelectric Cell in Signal Devices," "Applications—in Astronomy, in Meteorology, in Medicine," and, finally, a few lines on the conversion of sun energy into electrical energy. The author closes with the statement, "Perhaps in years to come, when we know more about the inter-relation between light and electricity, this application of the photo-cell will be the most important of all."

The text is very readable and the illustrations very clear and instructive.

Dr. Bruno Lange is visiting the United States this fall.

COLIN G. FINK

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. XV. **Ni, Ru, Rh, Pd, Os, Ir.** By J. W. MELLOR, D.Sc., F.R.S. Longmans, Green and Company, 114 Fifth Avenue, New York, N. Y., 1936. viii + 816 pp. 423 figs. 15.5 × 25 cm. Price, $20.00.

The first 497 pages of this volume are given over to the chemistry of nickel; the remaining 319 pages to the chemistry of the elements of the platinum group, exclusive of platinum itself, and to an Index. The treatment follows that of the preceding volumes of the series and affords a very complete presentation of all the available information in these fields. It is enriched with an unusually large number of excellent diagrams.

This volume is the next to the last of the series. The final volume will be devoted to the chemistry of platinum and to the General Index of the Treatise. The publishers announce that it is already in the press.

ARTHUR B. LAMB

Die Interferenzen von Röntgen- und Elektronenstrahlen. (The Interference of X-Rays and Cathode Rays.) Five lectures by M. v. LAUE, Professor at the University of Berlin. Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1935. 46 pp. 15 figs. 14.5 × 22 cm. Price, RM 3.60.

The book presents a brief outline of the dynamical theory of x-ray diffraction using the author's method of derivation, and making connection with the wave mechanical method of treatment. Kossel's interference of x-rays generated within a single crystal is explained in terms of the theory, and the connection with the Kikuchi lines is discussed. The mathematical development is omitted.

B. E. WARREN

BOOKS RECEIVED

August 15, 1935–September 15, 1936

ARTHUR A. BLANCHARD, JOSEPH W. PHELAN and ARTHUR R. DAVIS. "Synthetic Inorganic Chemistry, A Course of Laboratory and Classroom Study for First Year College Students." Fifth edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 385 pp. $3.00.

HERMAN T. BRISCOE, HERSCHEL HUNT and FRANCIS M. WHITACRE. "A Laboratory Manual of General Chemistry." Houghton Mifflin Company, 2 Park St., Boston, Mass. 113 pp. + experiment record sheets. Spiral binding. $1.75.

HARRY N. HOLMES. "General Chemistry." Third edition. The Macmillan Company, 60 Fifth Ave., New York, N. Y. 700 pp. $3.50.

VLADIMIR N. IPATIEFF. "Catalytic Reactions at High Pressures and Temperatures." The Macmillan Company, 60 Fifth Ave., New York, N. Y. 876 pp. $7.50.

ALFRED WOGRINZ. "Analytische Chemie der Edelmetalle." Ferdinand Enke Verlag, Hasenbergsteige 3, Leipzig W, Germany. 141 pp. RM. 13; bound, RM. 14.80.

"Festschrift Herrn Emil Christoph Barell, Doctor Philosophiae, Doctor Medicinae H. C., Generaldirektor der F. Hoffmann–LaRoche and Co., Aktiengesellschaft, am vierzigsten Jahrestage seiner Tätigkeit im Hause 'Roche'." Überreicht von Freunden und Mitarbeitern. Hoffmann–LaRoche, Inc., Scientific Department, Nutley, N. J. 575 pp.

"Minerals Yearbook, 1936." Bureau of Mines, U. S. Department of the Interior. Superintendent of Documents, Government Printing Office, Washington, D. C. 1136 pp. $2.00.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The System Cadmium Oxalate, Potassium Oxalate and Water at 20 to 30°

BY W. C. VOSBURGH, IRA G. NEWLIN, LUCILLE A. PUETTE, ROBERT L. PECK AND ROBERT DICK

The purpose of this research was to determine what compounds can exist in equilibrium with solutions containing cadmium and potassium oxalates at 20 to 30°. Souchay and Lenssen[1] prepared the compound $K_2Cd(C_2O_4)_2 \cdot 2H_2O$, and the corresponding sodium and ammonium compounds. Schaefer[2] reported the formation of three complex salts from cadmium and ammonium oxalates in the proportions of 1:4, 1:6 and 1:8, respectively. Scholder, Gadenne and Niemann[3] prepared the salt $(NH_4)_2Cd_3(C_2O_4)_4 \cdot xH_2O$. In this investigation two complex salts were found to exist in equilibrium with saturated solutions containing an excess of potassium oxalate, namely, the compounds $K_2Cd(C_2O_4)_2 \cdot 3H_2O$ (or $K_2Cd(C_2O_4)_2 \cdot 4H_2O$) and $K_2Cd_3(C_2O_4)_4 \cdot xH_2O$ where x is uncertain.

Cadmium oxalate was prepared by slow precipitation from C. P. cadmium chloride and potassium oxalate. A complex salt was prepared by dissolving some cadmium oxalate in a hot 15 to 25% solution of potassium oxalate and allowing it to cool, when the complex salt crystallized out. The quantity of cadmium oxalate was adjusted so that the solution would contain more than 7% potassium oxalate at the end. This complex salt proved to be the compound $K_2Cd(C_2O_4)_2 \cdot 3H_2O$. Solubility experiments with this compound and with cadmium oxalate indicated the existence of a second complex salt capable of existing in equilibrium with solutions containing between 2.3 and 7.1% of potassium oxalate. By slow addition of cadmium chloride solution to a 7% potassium oxalate solution the second complex salt was precipitated. The precipitation was discontinued when the potassium oxalate content of the solution had been reduced to about 3%.

Mixtures consisting of a potassium oxalate solution and either cadmium oxalate or the appropriate complex salt were sealed in Pyrex tubes and rotated for two days or more. The solution was then separated from the wet solid phase in a manner previously described[4] and both were analyzed. Cadmium was determined electrolytically and oxalate by titration with permanganate. Many of the mixtures were made in duplicate and the analyses performed after different times of rotation. It was important that the proper solid phase be introduced at the start because otherwise the approach to equilibrium was very slow.

In most of the experiments the solutions were saturated at 25°. However, the solubilities of cadmium oxalate and the complex salts in potassium oxalate solutions is small, and the variation with temperature between 20 and 30° (and with concentration) was less than the experimental error; therefore, some of the solutions were saturated at 30° and some at temperatures between 20 and 25°.

The results are given in Table I and Fig. 1. The small values for the concentration of cadmium

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(1) Souchay and Lenssen, *Ann.*, **103**, 316 (1857).

(2) Schaefer, *Z. anorg. Chem.*, **45**, 293 (1905).

(3) Scholder, Gadenne and Niemann, *Ber.*, **60**, 1489 (1927).

(4) Tarbutton and Vosburgh, THIS JOURNAL, **54**, 4539 (1932).

oxalate in the saturated solutions are omitted from the table. They were of the order of 0.15% and subject to a large relative error. In the last column of Table I the letter A stands for cadmium oxalate, $CdC_2O_4 \cdot 3H_2O$, B for the compound $K_2Cd_3(C_2O_4)_4 \cdot xH_2O$, C for the compound $K_2Cd(C_2O_4)_2 \cdot yH_2O$ and D for hydrated potassium oxalate. The percentage of water in the dry solid in the fourth column of Table I was found by algebraic extrapolation with the assumption of the formulas $K_2Cd_3(C_2O_4)_4 \cdot xH_2O$ and $K_2Cd(C_2O_4)_2 \cdot yH_2O$.

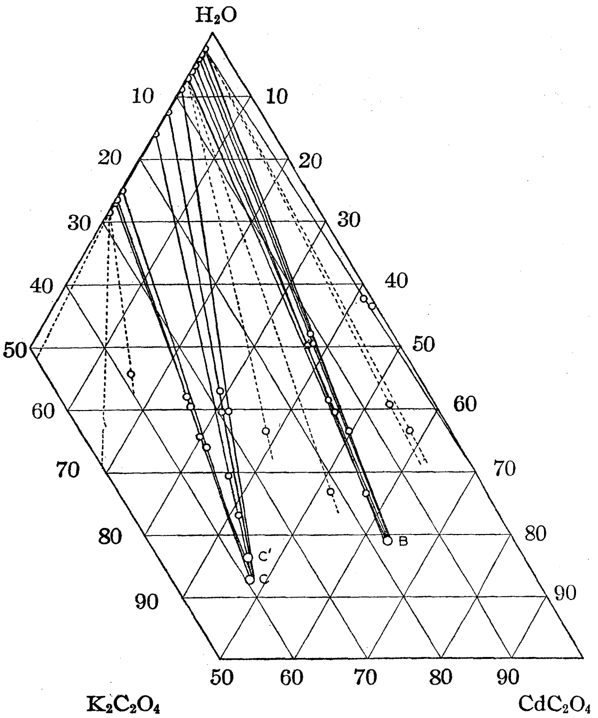

Fig. 1.—The system cadmium oxalate, potassium oxalate and water at 20 to 30°. Point B represents the composition calculated from the formula $K_2Cd_3(C_2O_4)_4 \cdot 10H_2O$ and points C and C′ the compositions calculated from the formulas $K_2Cd(C_2O_4)_2 \cdot 3H_2O$ and $K_2Cd(C_2O_4)_2 \cdot 4H_2O$.

TABLE I

COMPOSITION OF SATURATED SOLUTIONS AND SOLID PHASES

Solution	Wet solid		Dry solid	
$K_2C_2O_4$ wt. %	$K_2C_2O_4$ wt. %	CdC_2O_4 wt. %	H_2O wt. %	Solid
2.28	0.46	43.16	..	A
2.25	1.05	41.35	..	A
2.31	5.54	57.90	..	A + B
2.24	6.20	53.06	..	A + B
2.35	13.82	49.64	34	B
3.10	11.17	36.78	31	B
3.87	11.60	37.80	31	B
3.80	15.96	53.57	2	B
4.67	12.24	37.19	18	B
4.89	12.51	37.34	13	B
4.89	14.11	44.40	9	B
5.77	11.64	33.83	27	B
5.86	14.13	46.32	13	B
6.87	16.60	56.82	17	B
7.11	25.18	38.26	..	B + C
7.06	21.35	51.75	..	B + C
8.59	28.50	31.77	22.2	C
12.29	27.95	29.00	22.1	C
12.39	29.46	30.91	17.9	C
15.73	33.73	36.77	15.2	C
15.87	35.67	41.19	16.7	C
24.75	34.51	31.52	12.7	C
26.25	34.48	29.79	13.1	C
26.66	33.05	24.81	14.6	C
26.79	33.44	26.09	14.6	C
28.20	50.30	18.98	..	C + D
28.37	38.68	15.57	..	C + D
28.73	77.66	3.53	..	C + D

The percentage of water found by algebraic extrapolation for both compounds is uncertain. For compound C the first three values are subject to the largest extrapolation error, and if these three are neglected the average lies between 12.85%, which is the theoretical value for $y = 3$ and 16.43% for $y = 4$. Of the two, the value $y = 3$ is more probable because positive errors in the determination of cadmium would lead to a high value for y, and a check of the method of determining cadmium on known samples gave somewhat high results.

Summary

The compound $K_2Cd_3(C_2O_4)_4 \cdot xH_2O$ in which x is uncertain but may be as high as 10 can exist in equilibrium with solutions containing between 2.3 and 7.1% of potassium oxalate. The compound $K_2Cd(C_2O_4)_2 \cdot yH_2O$, in which y is probably 3, can exist in equilibrium with solutions from 7.1% of potassium oxalate to saturation. At temperatures of 20 to 30° the solubility of both compounds is small.

DURHAM, N. C. RECEIVED JULY 20, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE CARNEGIE INSTITUTE OF TECHNOLOGY]

Thermodynamic Properties of the Tellurides of Zinc, Cadmium, Tin and Lead

BY J. H. MCATEER[1] AND HARRY SELTZ

Introduction

The application of reversible galvanic cells to the study of the thermodynamic properties of compounds at higher temperatures has been made recently by Ölander,[2] who has studied a number of intermetallic compounds in the neighborhood of 250° using a mixture of fused acetates for an electrolyte. Seltz and DeHaven[3] have studied extensively the thermodynamic properties of cadmium antimonide (CdSb) over a rather large temperature range. The use as an electrolyte of a eutectic mixture of potassium and lithium chlorides to which was added a small amount of cadmium chloride enabled them to make observations from 390 to 440°.

Their results have shown that measurements of the electromotive force at various temperatures of cells of the type

$$\mathrm{A(s\ or\ l)}\ |\ \mathrm{A}^{\nu+}\ |\ \mathrm{A}_x\mathrm{B}_y\mathrm{(s)} + \mathrm{B(s)}$$

permit the calculation of the thermodynamic properties of the reaction.

$$x\mathrm{A(s\ or\ l)} + y\mathrm{B(s)} = A_xB_y\mathrm{(s)}$$

It is necessary, of course, that the metal electrode A have a higher electrode potential in the fused electrolyte than that of the element B. It will be noticed also that no measurements can be taken above the eutectic temperature of the compound and pure B constituent. For any system which involves an equilibrium between the solid compound and a solid solution of A in B it would be necessary to know the activity of B in the solid solution in order to determine the free energy change for the above reaction. It is obvious that a change in concentration of the metal ions in the electrolyte or the amount of the second pure constituent in equilibrium with the solid compound will have no effect upon the electromotive force of the cell.

The results of a study of the tellurides of zinc, cadmium, tin and lead by these methods are presented in this paper. Each of the four metals was substituted for the A constituent and tellurium formed the B constituent. The eutectic temperatures of the various tellurides and pure tellurium were obtained from the phase diagrams[4] of these metals with tellurium.

Experimental

Purification of Materials.—Silver-free lead was purified by electrodeposition from a fluosilicic acid bath. Baker "C. P. analyzed" cadmium, tin and lead were used without further purification. Each metal was cast into sticks under a molten mixture of lithium chloride and potassium chloride. This effectively removed any oxide from the metal.

C. P. tellurium was further purified by dissolving it in concentrated nitric acid, evaporating to dryness and then adding concentrated hydrochloric acid. After diluting this solution the insoluble material was removed and the tellurium was precipitated by the addition of sodium bisulfite. The tellurium was converted into telluric acid which, after three or four crystallizations from concentrated nitric acid, was reduced to free tellurium. The purified substance was then melted in an atmosphere of hydrogen.

Baker "C. P. analyzed" zinc chloride, cadmium chloride and lead chloride were used without further purification. These salts were fused, cast into sticks and kept in an oven at 100° until used. Stannous chloride was prepared by passing dry hydrogen chloride over molten tin and then subliming the product in a stream of carbon dioxide. The sublimed stannous chloride was kept in a desiccator. C. P. lithium chloride and potassium chloride were kept dry in an oven until used. In making the electrolyte the correct quantities of lithium chloride and potassium chloride were weighed and melted. Varying amounts of zinc, cadmium, tin or lead chloride were added to this molten mixture which was then cast into sticks and kept in an oven.

Preparation of Electrodes.—The electrodes containing the telluride were formed by melting weighed amounts of the metal and tellurium in a 6-mm. Pyrex tube under a hydrogen atmosphere. Varying amounts of tellurium in excess of that required to react with the metal were used. After the compound had dissolved completely in the molten excess tellurium, a tungsten lead, which will be described below, was inserted and the material permitted to solidify. When the electrode had cooled, the glass tubing was carefully chipped away and the electrode, now firmly attached to the tungsten tip, was removed.

Cadmium, tin and lead are liquids at the temperatures employed. The pure metal electrodes were made by melting the metals in the cells under the molten electrolyte. The tungsten leads were then immersed in the liquid

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[1] Abstracted from a thesis presented by J. H. McAteer to the Committee on Graduate Instruction of the Carnegie Institute of Technology, in partial fulfilment of the requirements for the degree of Doctor of Science, June, 1936.

[2] A. Ölander, *Z. physik. Chem.*, **A173**, 284 (1935).

[3] H. Seltz and J. C. DeHaven, *Am. Inst. Min. & Met. Engr., Tech. Pub.*, 622 (1935).

[4] (a) "I. C. T.," Vol. II, p. 441; (b) *ibid.*, p. 430; (c) Tech. Pub., International Tin Research & Development Council, Series B, No. 2; (d) "I. C. T.," Vol. II, p. 416.

metals. The pure solid zinc electrodes were made in the same manner as the telluride electrodes.

All leads consisted of tungsten wire which was welded to the copper potentiometer leads some distance from the furnace in which the measurements were made. The union at this point prevented the occurrence of thermal electromotive forces at the copper–tungsten junctions. The tungsten leads were sealed in 3-mm. Pyrex tubing in such a manner that only 2 or 3 mm. projected. This prevented contact of the leads with the electrolyte. During the process of sealing the leads in the glass a coating of oxide invariably formed on the small projecting tips. This was removed by treating with molten potassium pyrosulfate and then, after cooling, with a concentrated caustic solution. The tungsten tips were wound into the form of a small helix to ensure a tight connection with the solid electrodes.

Procedure.—The apparatus used was similar to that of Seltz and DeHaven[3] with the exception that the furnace was fitted with an iron cylinder containing a low melting mixture of lead, tin and bismuth. In this were placed the cells and thermocouple. It was impossible to detect with this arrangement any temperature gradients. The thermocouple was incased in Pyrex tubing to which a small Kipp hydrogen generator was attached. This precaution prevented oxidation and subsequent deterioration of the hot junction. The temperature lag of the thermocouple was negligible.

The necessary amount of electrolyte was melted in an H-cell by means of a Meker burner. About 2 g. of pure metal was placed in one leg. After the metal had melted, the tungsten lead was inserted and adjusted to the proper position. The gas flame was then removed, the solid telluride electrode introduced in the other leg and the cell placed in the furnace. The cell was evacuated slowly for an hour to a final pressure of 0.05 mm. of mercury. This slow evacuation prevented violent bumping caused by gas bubbles escaping from the molten electrode and electrolyte. Usually after three hours all gassing had ceased and the cell was found to have reached equilibrium. In some series of measurements pumping was continued throughout the run while in others, after complete evacuation, carbon dioxide was admitted. The results obtained with the carbon dioxide atmosphere were concordant with those obtained under vacuum except in the cells which were used for the study of tin telluride.

In the study of tin telluride the vacuum technique had to be modified since a loss of the stannous chloride occurred owing to its volatility under reduced pressures at these temperatures. For this reason an atmosphere of carbon dioxide was used exclusively. The stannous chloride was not added to the electrolyte until the initial three-hour period of pumping had been completed. Measurements were made also with cells containing pure stannous chloride as an electrolyte. These cells functioned satisfactorily even in the presence of air.

Simultaneous readings of the electromotive force and the temperature were taken from the melting point of the electrolyte to the limiting eutectic temperature except in the case of zinc telluride where readings were carried only to the melting point of zinc. The cells responded rapidly to variations in temperature, but to ensure equilibrium the temperature was never permitted to change by more than fifteen degrees an hour.

Results and Calculations

The observed values of the electromotive force are contained in Table I. The weight per cent. of the total amount of tellurium in the telluride electrode is given together with the type of atmosphere within the cell. The results appear to be correct within ±0.2 mv. at each temperature except for the measurements on zinc telluride where the limit of error is more nearly ±0.3 mv. The temperature readings can be considered accurate to within ±0.5°. These data are plotted in Fig. 1. From large scale reproductions of the

Table I

Cell	% Te and atmosphere	Temp. range, °C.	E. m. f., volts	dE/dT, volts/°C.
Zn(s)/$ZnCl_2$, LiCl, KCl(l)/Te(s) + ZnTe(s)	95.1 vac. 92.3 vac. 85.7 vac. 96.0 CO_2	355–418	0.57030 at 387°	−0.0000617
Zn(s) + ZnTe(s)/$ZnCl_2$, LiCl, KCl(l)/Te(s) + ZnTe(s)	89.6 + electrode 8.8 − electrode			
Cd(l)/$CdCl_2$, LiCl, KCl(l)/Te(s) + CdTe(s)	93.5 vac. 90.4 CO_2 87.6 CO_2 83.5 CO_2	360–440	0.50282 at 360°	− .0000879
Sn(l)/$SnCl_2$, LiCl, KCl(l)/Te(s) + SnTe(s)	76.8 CO_2 84.9 CO_2 94.7 CO_2	270–395	0.31600 at 260°	− .0000676
Sn(l)/$SnCl_2$(l)/Te(s) + SnTe(s)	84.9 air 90.9 air			
Pb(l)/$PbCl_2$, LiCl, KCl(l)/Te(s) + PbTe(s)	59.3 CO_2 75.0 CO_2 75.4 vac. 83.6 CO_2	355–408	0.34909 at 350°	− .0000669

figures the values of the electromotive force at a given temperature and dE/dT have been obtained. It will be noticed that in all cases the electromotive force–temperature curves are straight lines within the limits of experimental error.

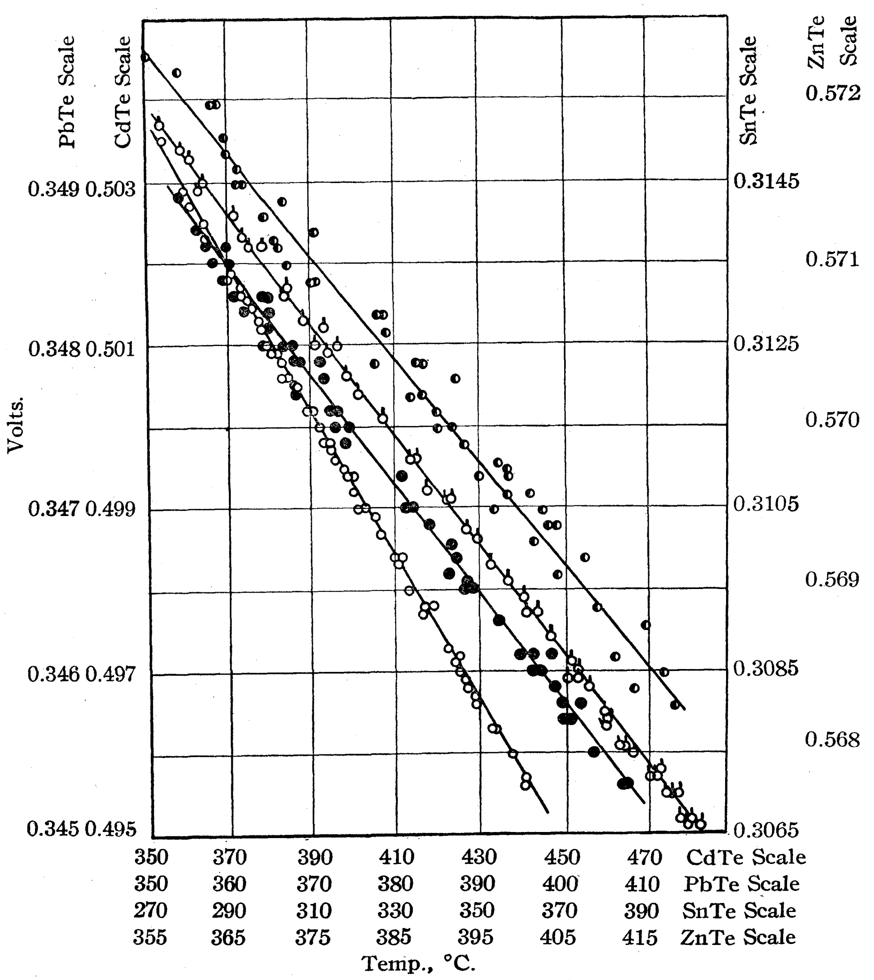

Fig. 1.—E. m. f. curves: ○, CdTe Cells; ●, PbTe Cells; ọ́, SnTe Cells; ◐, ZnTe Cells.

The free energy change, ΔF, of a cell reaction at any given temperature is related to the reversible electromotive force, E, of the cell by the equation $\Delta F = -nFE$ where n is the number of equivalents involved and F is the value of the faraday (23,074 cal. per volt equivalent). In this study all substances involved in the reactions are at their standard states (activity equal to unity) and the free energy change becomes the standard free energy change $\Delta F°$. The value of $\Delta F°$ may be expressed as a function of the temperature if the heat of reaction, ΔH, is known. This quantity may be evaluated with the aid of the Gibbs–Helmholtz equation, $\Delta H = nF \times (T\,(\mathrm{d}E/\mathrm{d}T) - E)$. If the change in heat capacity, ΔC_p, is small the value of ΔH will be nearly independent of the temperature and $\Delta F°$ at any temperature will be given by the equation $\Delta F° = \Delta H + IT$ where I is a constant of integration. The entropy change for the reaction may be calculated from the fundamental relation $\Delta F° = \Delta H - T\Delta S$.

The results of the calculations for the various tellurides are summarized in Table II. The heats of fusion used for cadmium, tin and lead were 1254, 1594 and 1228[5] cal. per gram atom, respectively.

Discussion

The cells studied in this investigation functioned reversibly and the electromotive forces were quite reproducible. Changes in composition of the electrolyte and in the amounts of tellurium in equilibrium with the solid tellurides had no effect upon the electromotive forces of the cells. The consistent data of Table I for cells in which the zinc electrode was replaced by a zinc–zinc telluride electrode also indicate the reversibility of the cell reaction.

TABLE II

THERMODYNAMIC PROPERTIES OF THE TELLURIDES AT 25°

Reaction	$\Delta F°$, cal.	ΔS, cal./°C.	ΔH, cal.	ΔH, cal. (Fabre)
$Zn(s) + Te(s) = ZnTe(s)$	−27,360	−2.9	−28,210	−33,200
$Cd(s) + Te(s) = CdTe(s)$	−23,950	−2.0	−24,530	−15,800
$Sn(\gamma) + Te(s) = SnTe(s)$	−14,660	0.0	−14,650	.....
$Pb(s) + Te(s) = PbTe(s)$	−16,590	−1.0	−16,810	− 5500

The limits of error for the values tabulated in Table II depend somewhat on the calorimetric data which have been employed. The deviations in the values of the electromotive force of the cells and of dE/dT lead to an uncertainty of

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(5) "I. C. T.," Vol. II, p. 458.

about ±50 cal. The probable errors in the heats of fusion amount to about ±40 cal. and the assumption that Kopp's law can be applied to these tellurides might introduce an error of not more than ±30 cal.

The calculations at 25° for tin telluride have been made using the γ form of the metal. Apparently this form is stable above 161° and consequently is not stable at 25°. Unfortunately no data on the heat of transition exist so that it is impossible to make calculations for the compound using the allotropic modification which is stable at 25°. The question of the existence of tellurium in two allotropic forms has been raised by S. Umino,[6] who in measuring the specific heat of tellurium up to 550° reported a transition at 348° accompanied by the absorption of 630 cal. per gram atom. However, no other investigator has mentioned this behavior and Simek and Stehlek[7] were unable to confirm his results. For this reason it has been assumed that no transition occurs. No data are available for the entropy of tellurium. Consequently the entropies of the tellurides have not been calculated.

No other measurements of the thermodynamic properties of the tellurides have been reported except those of Fabre[8] on the heats of formation. His results which were obtained by a calorimetric method are tabulated in Table VII. They are not, as will be seen, in agreement with the present values. A review of his work, however, indicates that his results may be unreliable owing to the uncertainty of some of the thermal values he used to calculate the heats of formation. Lack of data prevents recalculation of these values.

Summary

1. A potentiometric study of the tellurides of zinc, cadmium, tin and lead has been made at higher temperatures using fused salt electrolytes.

2. The method has been shown to give results which are reliable and accurate when applied to the proper substances.

3. The data thus obtained have been employed in calculating the free energies of formation, heats of formation and entropies of formation at 25°.

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[6] S. Umino, *Kinzoku no Kenyku*, [10] **3**, 498 (1928).

[7] A. Simek and B. Stehlek, *Coll. Trav. Chim. Tchechosl.*, **2**, 304 (1930).

[8] Fabre, *Ann. chim. phys.*, **14**, 110 (1888).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE CARNEGIE INSTITUTE OF TECHNOLOGY]

A Thermodynamic Study of the Lead–Bismuth System

BY H. S. STRICKLER[1] AND HARRY SELTZ

Although the properties of the alloys of lead and bismuth have been investigated extensively, the phase diagram of the system is not well established. In the "International Critical Tables"[2] diagram, two series (α and β) of solid solutions forming a eutectic at 58 weight per cent. bismuth are shown. The limits of solubility are 18 and 99% bismuth at 0° and 37 and 97.3% bismuth at 125°, the eutectic temperature. References cited for this are Guertler[3] and Herold,[4] from whose critical reviews it is evident that the limits of solubility and the solidus curves are not too well defined. Furthermore, Solomon and Jones,[5] studying alloys of this system by means of x-rays, have found recently a new solid solution phase existing from 25 to 33% bismuth.

In the present work, thermodynamic data obtained from measurements of galvanic cells of the general form Pb/Pb^{++}/Pb (in Pb–Bi solution) have been used to calculate a considerable portion of the phase diagram, making use of the methods previously proposed by Seltz.[6]

Experimental

The cells used were of the three types:

I. Pb(l)/$PbCl_2$ in LiCl–KCl(l)/Pb(in Pb–Bi liquid solution)

IIa. Pb(s)/$Pb(OAc)_2$–NaOAc(l)/Pb(in Pb–Bi liquid solution)

IIb. Pb(s)/$Pb(OAc)_2$–NaOAc(l)/Pb(in Pb–Bi equilib. liquid and solid solutions)

III. Pb(s)/$Pb(OAc)_2$–NaOAc(l)/Pb(in Pb–Bi solid solution)

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[1] Abstracted from a thesis presented by H. S. Strickler to the Committee on Graduate Instruction of the Carnegie Institute of Technology, in partial fulfilment of the requirements for the Degree of Doctor of Science, June, 1936.

[2] "International Critical Tables," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., pp. 414–417.

[3] Guertler, "Metallographie," Vol. I, Gebrüder Borntraeger, Berlin, p. 548.

[4] Herold, *Z. anorg. allgem. Chem.*, **112**, 131 (1920).

[5] Solomon and Jones, *Phil. Mag.*, **11**, 1090 (1931).

[6] Seltz, THIS JOURNAL, **56**, 307 (1934); **57**, 391 (1935).

The liquid alloys of this system have been studied by Wagner and Engelhardt,[7] who determined the electromotive forces of cells Pb(l)/KCl–$PbCl_2$(l)/Pb(in Pb–Bi liquid solution) at two temperatures, 475 and 665°. Since no reliable values of the relative partial molal heat contents could be obtained from their data, it was necessary to study cells of Type I in the present investigation.

The metals used were purified electrolytically, the lead being plated from a Betts[8] bath and the bismuth by a method described by Swift.[9] Before use, the metals were cast under oil and then *in vacuo*. The electrolytes were prepared from commercial "chemically pure" materials without further purification.

The cells of Type I were studied over the temperature range 380–470°, with variation of the composition from $N_{Bi} = 0.15$ to 0.89. The technique employed was, with modifications, that used by Seltz and DeHaven[10] in their study of the intermetallic compound CdSb. The pure metal was placed in one leg of a Pyrex H-cell containing the electrolyte and the weighed alloy constituents in the other. The electrolyte was the molten eutectic mixture of lithium and potassium chlorides, to which a small amount of lead chloride was added. Contact with the metals was made by tips of tungsten wire sealed into Pyrex tubing, the connections to the potentiometer being made by copper wire welded to the tungsten where it extended from the cell. The system was evacuated by means of a Cenco Hyvac pump. The cell was placed in an electrically heated furnace, manually controlled. Temperatures were determined by means of an iron–constantan thermocouple. A Leeds and Northrup type K potentiometer in conjunction with a Fritz Koehler galvanometer was used. The attainment of equilibrium was quite rapid and the cells were exceedingly steady and reproducible. The experimental results are given in Table I and are plotted in Fig. 1. The reaction occurring in these cells was the transfer of lead from the pure liquid state to a solution of a definite composition, Pb(l) = Pb(in Pb–Bi liquid solution). The free energy change of this reaction is given by the relation $\Delta F = -nFE$, and the activity (a_1) of lead in the alloy referred to the pure liquid as a standard state is then obtained from $-nFE = \Delta F = RT \ln a_1$. The change of heat content in the process is calculated from the Gibbs–Helmholtz equation $T\,dE/dT = E + (\Delta H/nF)$ and the electromotive force E of the cell at a given temperature T. ΔH is here the difference between the partial molal heat content of lead in the alloy and the molal heat content of liquid lead, and is designated as the relative partial molal heat content,[11] $\bar{L}$. The

TABLE I

CELLS OF TYPE Pb(l)/$PbCl_2$ IN LiCl–KCl(l)/Pb(IN Pb–Bi LIQUID SOLUTION)

Temp. range 380–470°; maximum deviations 0.05 millivolt

N_{Bi}	No. of obsns.	E. m. f. at 700°K., mv.	$dE/dT \times 10^6$ (volt/°C.)
0.152	7	5.32	7.4
.280	8	11.48	14.4
.400	8	19.29	20.8
.504	7	27.82	27.8
.586	8	35.94	37.6
.672	8	45.40	46.4
.770	9	59.76	64.4
.889	10	86.15	102.0

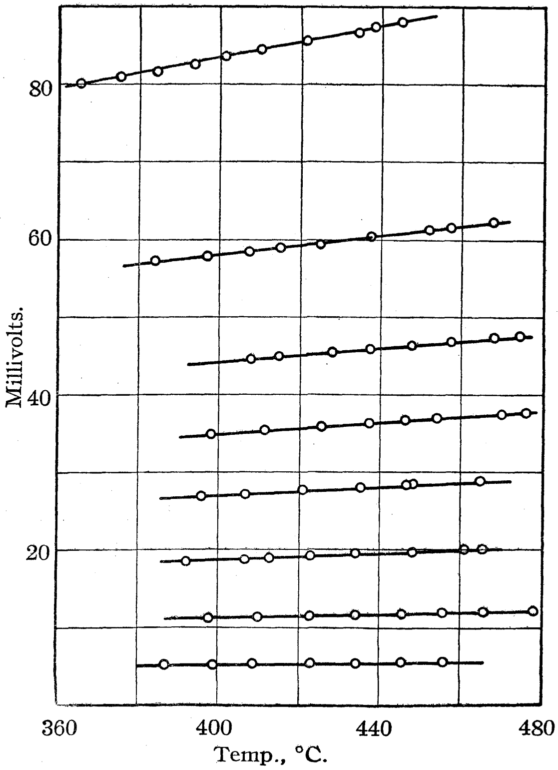

Fig. 1.—E. m. f. curves for type I cells. Starting from the bottom: $N_{Bi} = 0.152$; 0.280; 0.400; 0.504; 0.586; 0.672; 0.770; 0.889.

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(7) Wagner and Engelhardt, *Z. physik. Chem.*, **A159**, 16 (1932).

(8) Betts, "Lead Refining by Electrolysis," John Wiley and Sons, Inc., New York, N. Y., 1908.

(9) Swift, THIS JOURNAL, **45**, 371 (1923).

(10) Seltz and DeHaven, *Am. Inst. Mining Met. Engrs., Tech. Pub.*, 622 (1935).

(11) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.

quantities calculated from the measured electromotive forces and temperatures are given in Table II.

TABLE II

N_2	N_1	a_1 (700°K.)	a_1/N_1	$\bar{L}_1$
0.152	0.848	0.838	0.989	− 6
.280	.720	.684	.950	− 65
.400	.600	.528	.880	−218
.504	.496	.398	.803	−386
.586	.414	.304	.734	−444
.672	.328	.222	.677	−604
.770	.230	.139	.604	−678
.889	.111	.058	.519	−681

The corresponding quantities for the second component, bismuth, were obtained by graphical integration of the Duhem equation

$$\int_0^{\bar{L}_2} \mathrm{d}\bar{L}_2 = -\int_0^{N_1/N_2} N_1/N_2 \, \mathrm{d}\bar{L}_1$$

and

$$\int_0^{\log a_2/N_2} \mathrm{d} \log a_2/N_2 = \int_0^{N_1/N_2} N_1/N_2 \, \mathrm{d} \log a_1/N_1$$

The calculated terms, with those for lead at rounded mole fractions, are given in Table III.

TABLE III

N_2	N_1	a_1	a_1/N_1	a_2 (700°K.)	a_2/N_2	$\bar{L}_1$	$\bar{L}_2$
0.0	1.0	1.000	1.000	0.000	0.480	0	−925
.1	0.9	0.893	0.993	.052	.520	− 2	−907
.2	.8	.782	.978	.115	.577	− 20	−811
.3	.7	.657	.938	.195	.650	− 91	−606
.4	.6	.528	.880	.293	.732	−218	−376
.5	.5	.402	.804	.407	.814	−352	−213
.6	.4	.291	.728	.532	.886	−502	− 91
.7	.3	.197	.657	.655	.936	−628	− 20
.8	.2	.116	.580	.778	.973	−676	− 4
.9	.1	.052	.520	.896	.995	−692	0
1.0	.0	.000	.480	1.000	1.000	−700	0

Study of the Eutectic.—In order to determine the limits of solubility and the eutectic composition, cells of types IIa and IIb were studied from 200 to 120°, the maximum temperature range over which the mixture of lead and sodium acetates could be used safely. The composition was varied from $N_{\mathrm{Bi}} = 0.337$ to 0.995. The experimental technique differed considerably from that previously described. The lead electrode was generally lead plated on tungsten, using a bath described by Getman,[12] though in some cases bulk electrodes, cast in the same manner as the solid alloys, were used. The alloy constituents were first melted together under mineral oil or *in vacuo*, after which the alloy button was placed under the electrolyte in the cell, which was a 25-cm. test-tube blown out at the bottom to form a depression in which the molten alloy could rest. In preparing the electrolyte, the trihydrates of lead and sodium acetates were melted together in the proportions $3\mathrm{Pb(OAc)_2 \cdot NaOAc}$, the mixture then being dehydrated. Contact with the alloy was made by means of a tungsten lead as used for the higher temperature work. In these runs, the system was not evacuated, because of the increased deterioration of the electrolyte under such conditions. The type K potentiometer was used as before, with a sensitive type R Leeds and Northrup galvanometer. The cells were placed in an electrically heated oil-bath which, when desired, was thermostated by a mercury regulator and an Aminco supersensitive relay. Temperatures were measured by means of a copper–constantan thermocouple.

In the course of a run, the temperature was raised above the liquidus of the alloy, when the tungsten lead was fixed in position. Equilibrium was usually attained rapidly, after which the temperature was lowered. In only a few cases was the range of temperature above the liquidus sufficient to permit accurate measurement of the temperature coefficient for the determination of the heat content change. The first separation of solid was marked by a change in slope of the electromotive force–temperature curve, and then the temperature was decreased more slowly, at a rate of 2–4° per hour. However, the temperature was usually maintained constant for twelve hours or more at the eutectic temperature and frequently at higher temperatures. The electromotive forces then observed are designated by an asterisk. In Table IV data are given only at intervals of 5 to 10°.

In the interpretation of these data, it must be remembered that within the heterogeneous region of the system the α and β phases are in thermodynamic equilibrium, whence at a given temperature $a_{\mathrm{Pb}(\alpha)} = a_{\mathrm{Pb}(\beta)}$ and $a_{\mathrm{Bi}(\alpha)} = a_{\mathrm{Bi}(\beta)}$. Therefore, the electromotive forces of two cells $\mathrm{Pb(s)/Pb^{++}/Pb(\alpha)}$ and $\mathrm{Pb(s)/Pb^{++}/Pb(\beta)}$ should be identical if the α and β compositions correspond to the limits of the heterogeneous range. Thus every cell in which the alloy electrode contains the solid eutectic must show the same electromotive force (E_e) at the eutectic temperature, and E_e should also be the electromotive force of the cell $\mathrm{Pb(s)/Pb^{++}/Pb}$(liquid eutectic) at that temperature. A summary of the electromotive forces

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(12) Getman, THIS JOURNAL, **38**, 792 (1916).

observed for the various compositions at the eutectic temperature is given in Table V. From these data it is evident that the solubility of lead in bismuth is very small at this temperature, certainly $N_{Pb} < 0.005$. This value agrees well with that obtained by Herold[4] in his metallographical work, but is less than the values obtained by other investigators. On the lead side, the limit of solubility is seen to be very close to N_{Bi} = 0.360, and from the shape of the activity curve at this temperature, the limit is determined as N_{Bi} = 0.365, which is in fair agreement with the "Critical Tables" diagram.

TABLE IV

Temp., °C.	E. m. f., mv.
N_{Bi} = 0.337	
Alloy solid and liquid	
196.2	6.06
185.5	6.55
175.0	7.84
167.0	8.85
159.2	9.80*
148.9	10.77
138.9	11.30
Alloy solid	
130.1	11.21
N_{Bi} = 0.360	
Alloy liquid	
193.2	6.73
190.8	6.45
Alloy solid	
122.7	13.17*
124.5	13.02*
Solid and liquid	
183.0	6.80
179.8	7.27
135.9	12.46
128.5	12.78
N_{Bi} = 0.378	
Solid and liquid	
179.0	7.17
154.0	10.26
145.0	11.36
136.8	12.22*
129.6	12.92
124.8	13.36*
	(eutectic)
N_{Bi} = 0.389	
Alloy liquid	
194.5	7.98
184.5	7.32
Solid and liquid	
177.5	7.57
171.2	8.25
159.0	9.72
140.8	11.92*
131.4	12.87*
126.7	13.30
124.6	13.42*
	(eutectic)
N_{Bi} = 0.42	
Solid and liquid	
159.4	9.78
137.1	12.24
124.7	13.69
124.7	13.36*
	(eutectic)
N_{Bi} = 0.449	
Alloy liquid	
169.5	9.68
161.4	9.16
Solid and liquid	
159.3	9.70
150.5	10.76
139.5	12.16*
130.4	13.22
124.5	13.85
124.4	13.63
(note decrease with time)	
125.0	13.51*
	(eutectic)
N_{Bi} = 0.542	
Alloy liquid	
165.4	15.91
155.9	15.19
142.3	14.24
130.4	13.47
125.4	13.11
124.7	13.46
	(eutectic)
N_{Bi} = 0.564	
Alloy liquid	
176.1	18.27
166.2	17.60
157.3	16.87
141.2	15.77
133.3	15.20
126.0	14.63
125.0	13.49*
	(eutectic)
Melted, then cooled again	
127.0	14.75
124.7	14.60
	(supercooled)
125.5	13.62
	(just froze)
125.3	13.48*
	(eutectic)
N_{Bi} = 0.638	
Alloy liquid	
175.3	25.92
170.1	23.85
157.8	22.70
Solid and liquid	
151.6	20.23
145.7	18.27
129.2	14.21*
123.9	13.38
124.7	13.38
124.0	13.30
$N_{Bi}{}^{a}$ = 0.987	
Solid and liquid	
172.0	26.42
167.2	25.25
154.7	21.42
143.4	18.24
137.8	16.49
130.4	14.90
126.5	14.12
$N_{Bi}{}^{a}$ = 0.995	
Solid and liquid	
198.9	36.05
190.9	33.38
171.7	25.91
165.8	24.18*
158.9	22.06*
153.6	20.56
139.4	16.87*
128.6	14.25*
124.8	13.38*
	(eutectic)

[a] These alloys were vacuum-cast and annealed in the same manner as the solid alloys, which will be described later.

TABLE V

N_{Bi}	Temp., °C.	E_e, mv.
0.337	124.5	<11.21
.360	124.5	13.02*
.378	124.8	13.36*
.389	124.6	13.42*
.420	124.7	13.36*
.449	125.0	13.51*
.542	124.7	13.46
.564	125.0	13.49*
.564	125.3	13.48*
.638	124.0	13.30
.995	124.8	13.38*

From the chosen value for E_e, 13.40 mv., the activity of lead in the eutectic is calculated to be 0.457, referred to solid lead as the standard state. In order to find the activity referred to pure liquid lead, it is necessary to calculate the activity at this temperature of liquid lead relative to the solid. At 600°K. (327°C.), the melting point of lead, the activity is unity, for there the fugacities are identical. Therefore, the equation

$$R \ln a = \bar{L}/T + \text{const.}$$

becomes at that temperature

$$0 = L/600 + \text{const.}$$

it being assumed that the heat of fusion of lead does not change with temperature, accurate thermal data for any other treatment being lacking. Using the value 1161 cal. for the heat of fusion from the "International Critical Tables," and calculating at the eutectic temperature, one obtains the value 1.641 for the activity of liquid lead relative to the solid. On dividing 0.457 by this figure, one obtains 0.279 for the activity of lead in the eutectic (a_e) with reference to liquid lead.

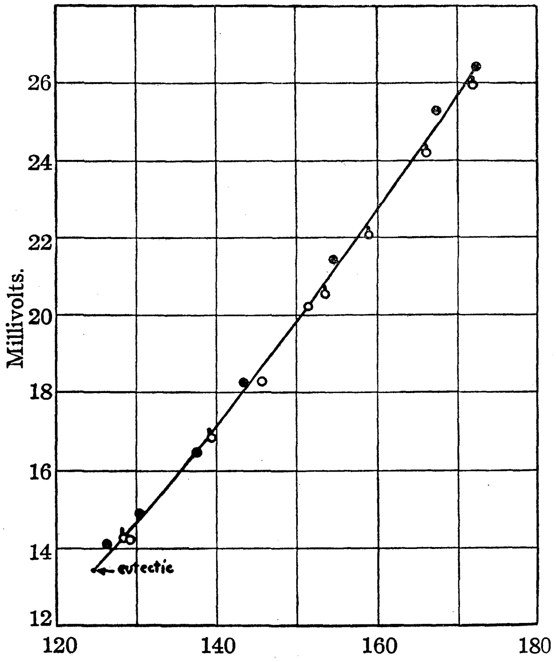

Fig. 2.—E. m. f. curve for type II-b cells: ○, N_{Bi} = 0.636; ●, N_{Bi} = 0.987; ȯ, N_{Bi} = 0.995.

The eutectic composition is now fixed within the limits of error of the computation, by comparing this a_e with values extrapolated, for different compositions, from the activity data for the liquid alloys. The necessary data are

$$N_2 = 0.510,\ a_1 = 0.320$$
$$N_2 = 0.540,\ a_1 = 0.283$$
$$N_2 = 0.563,\ a_1 = 0.257$$

Plotting activity *versus* mole fraction, one finds graphically the composition corresponding to a_e to be N_2 = 0.544. The accuracy of this calculation was checked experimentally by determining the behavior of alloys whose compositions were close to the above value. The data for these confirmatory runs are given in Table VI.

The eutectic composition is thus determined at N_{Bi} = 0.547 (54.9 wt.%), in excellent agreement with the calculated value, considering the lengthy extrapolation of the liquid data. From the intersection of the electromotive force–temperature curves for the eutectic composition in the liquid and solid states, the eutectic temperature is found to be 125°, confirming the previously accepted value. The values of the eutectic composition as determined by other investigators vary, but in general are somewhat higher, the "Critical Tables" diagram giving the value 58%, while Guertler[3] lists 55.8% (Kapp[13]) and 56.5% is the value accepted by Herold[4] from Barlow's[14] data.

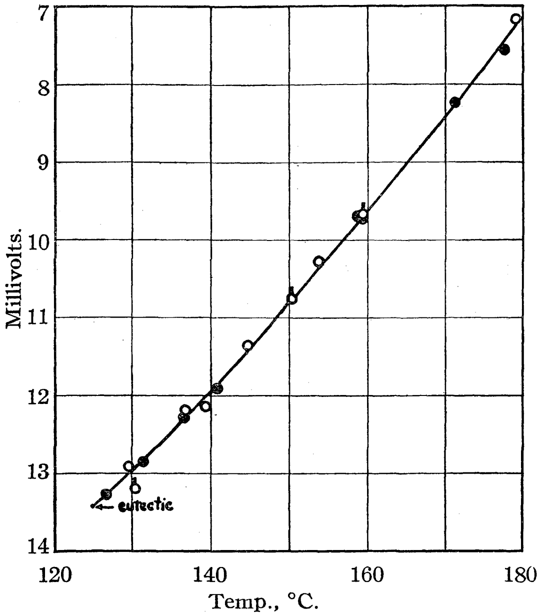

Fig. 3.—E. m. f. curve for type II-b cells: ○, N_{Bi} = 0.378; ●, N_{Bi} = 0.389; ◒, N_{Bi} = 0.420; ȯ, N_{Bi} = 0.449.

The electromotive force data obtained in the slow-cooling of the alloys inside the heterogeneous

Table VI

N_{Bi} = 0.541		N_{Bi} = 0.543		N_{Bi} = 0.547	
Temp., °C.	E. m. f., mv.	Temp., °C.	E. m. f., mv.	Temp., °C.	E. m. f., mv.
Alloy liquid		Alloy liquid			
173.2	16.30	177.7	16.80	165.4	16.27
163.0	15.61	170.5	16.30	155.6	15.64
150.2	14.66	164.2	15.83	150.1	15.12
143.0	14.18	155.0	15.25	142.3	14.59
132.3	13.42	147.7	14.66	131.4	13.84
127.4	13.11	129.5	13.47	125.8	13.46*
125.4	12.94			124.1	13.30
E at 124.5° (extrapolated) = 12.87 mv.		E at 124.5° (extrapolated) = 13.10 mv.		123.2	13.20
				122.6	13.12
				121.8	13.02
a_1 (referred to liquid) = 0.287		a_1 (referred to liquid lead) = 0.284		120.7	12.94
				119.0	12.77

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(13) Kapp, *Ann. Physik*, [4] **6**, 771 (1901).

(14) Barlow, This Journal, **32**, 1390 (1910).

region were evidently for cells of Type IIb. If the two solutions, solid and liquid, composing the alloys under these conditions were in equilibrium, then the same electromotive force should be observed in different runs (on the same side of the eutectic) at the same temperature. As the data and Figs. 2 and 3 show, this has been realized approximately. If the liquidus data obtained by thermal analysis are correct, the activity at a given temperature can be calculated from the data of the study of the liquid alloys, and some further idea as to the attainment of equilibrium in the cooling process can be obtained. A few of these calculations are tabulated in Table VII. The liquidus data of Barlow were employed, and the usual extrapolations and conversions to the same reference state (here solid) were made. The agreement is fair with the exception of the value at 63.5%. However, it is probable that Barlow's determination of the liquidus was here at fault, as will be indicated later.

TABLE VII

Composition, wt. % (Barlow)	Temp., °C.	E. m. f., mv.	a_1, obsd.	a_1, calcd.
40.0	177.3	7.50	0.679	0.670
50.0	144.4	11.47	.528	.524
63.5	150.5	20.00	.334	.300
75.0	198.9	36.05	.170	.163

Study of the Solid Phases.—In the investigation of the cells of Type III, the chief difficulty encountered was in obtaining homogeneous electrodes. Further, the probable existence of solid phases other than α complicated the interpretation of some of the data. The range of composition covered was from $N_{\text{Bi}} = 0.05$ to 0.33. The experimental arrangement was that used in the investigation of the eutectic. The electrolyte was also the same. The cells were merely Pyrex test-tubes of various sizes, depending on the number and dimensions of the electrodes placed at one time in the cell. The preparation of the alloys was, however, entirely different. It was found most convenient to cast and anneal the alloys *in vacuo* in Pyrex glass containers. These containers or electrode forms were of two types, constructed as follows. For the simpler variety, a 30-cm. piece of 5-mm. Pyrex tubing was partially constricted in the oxy-gas flame about 7 cm. from one end. Into this was slipped a length of tungsten wire, one end of which was wound into a spiral. The spiral was placed about 3 mm. from the constriction and the wire was then sealed into the glass. The short end of the tube was then bent at right angles. The other type of form was of more complex construction. A piece of Pyrex capillary was sealed at both ends to sections of 5 mm. tubing, one being about 7 cm. long and the other 20 cm. The tungsten wire was sealed into the capillary close to one end. Then the short piece of tubing was bent at right angles, and the capillary through 180°. The simpler variety was designed for use where the alloy was to be cast and annealed below the solidus, while the other was used when the alloy was to be slow-cooled. In casting the electrodes, the weighed materials were placed directly in the glass container. The open end of the electrode form was then attached to the Cenco Hyvac pump, and the metals were melted, degassed and finally sealed *in vacuo*. When the electrode was to be used, the glass was broken away cleanly from the alloy about 2 mm. below its tip. The electrode was placed immediately in the cell.

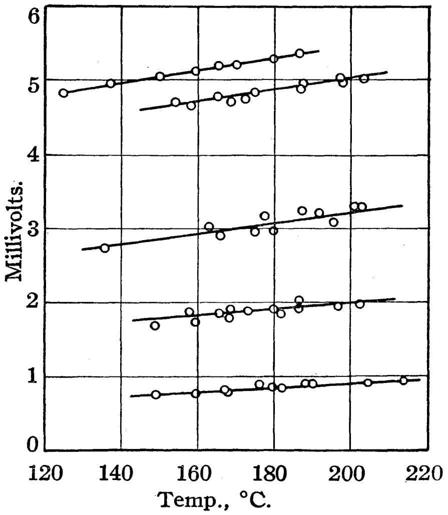

Fig. 4.—E. m. f. curves for type III cells: Starting from the bottom: $N_{\text{Bi}} = 0.050$; 0.096; 0.147; 0.200; 0.225.

For annealing, a small oil-bath and an electric furnace were used. When an alloy was to be slow-cooled, the electric furnace was connected in series with a variable electrolytic resistance, alternating current being used. The construction of the electrolytic resistance is briefly described. Two copper or brass rod electrodes were placed in a large bottle, containing a predetermined amount of calcium chloride solution. The solution was cooled by circulating water through glass tubing placed in the jar. Water was dropped in at a steady rate from a capillary connected with a constant-head device, thus lowering the conductivity of the solution and slowly decreasing the current passing through the furnace.

The data for the solid alloys are given in Table VIII and plotted in Fig. 4. The length of annealing or conditions of slow-cooling are always specified. Reproducibility of electromotive forces with different alloys of the same composition was the sole criterion of sufficient heat treatment. The data for compositions $N_{Bi} = 0.050$ to 0.200 may be considered satisfactory, but those for the region $N_{Bi} = 0.225 - 0.330$ are not accurate. The discrepancies may be attributed to non-attainment of homogeneity in the alloys or to the presence of phase changes. The difficulties in the first case might arise from the decreased velocity of diffusion in the solid state at these lower temperatures, and to the greater spread between liquidus and solidus curves. However, evidence for the existence of another solid phase has been offered by Solomon and Jones,[5] and behavior pointing to some abnormality in this region of the system has been definitely noted here. The first

TABLE VIII

CELLS OF TYPE $Pb(s)/Pb(OAc)_2$-$NaOAc(l)/Pb$(IN Pb–Bi SOLID SOLUTION)

Run no.	N_{Bi}	Heat treatment and annealing times Hours	°C.	No. of obs.	Temp. range of measurement, °C.	E. m. f., mv.	$dE/dT \times 10^6$ volts/°C.	Deviation from mean curve, mv.
1	0.050	140	200	3	149–213	0.83 at 160°	2.0	±0.05
2	.050	320	200	4				
3	.050	500	200	4				
4	.097	274	200	4	149–202	1.82 at 160°	4.8	± .08
5	.096	461	200	6				
6	.096	309	200	3				
7	.147	298	200	4	135–200	2.73 at 124.5°	6.7	± .1
8	.147	Slow-cooled 2°/hr., then annealed 140 hrs. at 190°		5				
9	.147	460	200	2				
10	.200	309	200	6	157–200	4.69 at 160°	8.33	± .05
11	.201	88	200	5				
12	.225	Slow-cooled 2°/hr., then annealed 40 hrs. at 155°		8	....124.5–185	4.83 at 124.5°	9.0	± .05

The behavior of alloys from $N_{Bi} = 0.25$ to $N_{Bi} = 0.33$ is shown by the following data.

$N_{Bi} = 0.250$

Run 13

Quick-cooled, then annealed. No significant change of electromotive force after 71 hours at 175°. For temperature coefficient:

Temp., °C.	E. m. f., mv.
156.0	5.97
167.2	6.18
175.0	6.32
183.6	6.49

$dE/dT = 19.0 \times 10^{-6}$ v./°C.

$N_{Bi} = 0.330$

Run 18

Slow cooled as above

Temperature 131.2°

Time, hrs.	E. m. f., mv.
0.0	12.02
20.6	10.44
68.9	9.91
91.7	9.82
123.5	9.67

$E_\infty = 9.32$ millivolts (extrapolated)

$dE/dT = 20.8 \times 10^{-6}$ v./°C.

$N_{Bi} = 0.248$

Run 14

Slow-cooled, then annealed 50 hours at 155°. Steady decrease of electromotive force at various temperatures with time observed.

Time, hrs.	
	at 174°
0	7.31
12	7.02
	at 163°
0	6.95
17	6.66

When decrease with time appeared to stop, the data below were obtained for the temperature coefficient.

Temp., °C.	E. m. f., mv.
139.4	6.26
152.9	6.45
155.9	6.47
160.4	6.52
171.3	6.67

$dE/dT = 13.3 \times 10^{-6}$ v./°C.

$N_{Bi} = 0.298$–0.299

Run 15

Annealed 290 hours

Temp., °C.	E. m. f., mv.
144.0	5.54
150.0	5.64
156.0	5.77
161.5	5.88

Run 16

Temp., °C.	E. m. f., mv.
149.8	5.91
156.0	6.05
160.6	6.09
163.8	6.18
168.6	6.22
172.0	6.29

$dE/dT = 18.3 \times 10^{-6}$ v./°C.

$N_{Bi} = 0.298$

Run 17

Slow-cooled, then placed in cell and decrease of electromotive force with time noted.

Temperature 147.7°

Time, hrs.	E. m. f., mv.
0.0	9.30
47.0	7.95
115.0	7.43
163.0	7.27

$E_\infty = 6.82$ mv., extrapolated

From a temperature coefficient determination.

$dE/dT = 17.6 \times 10^{-6}$ v./°C.

effect is a marked increase in electromotive force–temperature slope observed with alloys of composition $N_{Bi} = 0.225$ in passing through the narrow temperature range 185–190°. The fact that the activities for $N_{Bi} = 0.250$ and 0.300 are considerably above the values read from a smooth curve drawn from the limit of solubility to $N_{Bi} = 0.200$ constitutes the second definite indication. Other less marked irregularities also have been observed.

In Table IX, the activity and $\bar{L}_1$ data for the compositions $N_{Bi} = 0.050$ to 0.200 at 124.5° are given, together with data representative of the region $N_{Bi} = 0.225 - 0.330$. The activities are plotted *versus* mole fraction of bismuth in Fig. 5, where the dotted line indicates the possible appearance if the unusual results noted are due to the presence of two solid phases. It should be noted that in the first range practically perfect solution behavior prevails.

TABLE IX

N_{Bi}	a_1 (124.5°)	a_1/N_1	$\bar{L}_1$
0.050	0.956	1.00	0
.096	.908	1.00	0
.147	.853	1.00	0
.200	.774	0.97	−50
		Mode of treatment	
0.225	0.754	Slow-cooled	
.250	.730	Quick-cooled and annealed	
.248	.700	Slow-cooled	
.298	.733	Quick-cooled and annealed	
.298	.688	Slow-cooled	
.330	.590	Slow-cooled	

Determination of the Phase Diagram of the System.—In the previous section, the limits of solubility have been found to be $N_{Bi} = 0.365$ and $N_{Bi} = 0.995$, and the eutectic composition has been determined as $N_{Bi} = 0.547$. It is possible to check the liquidus curve on the bismuth side of the eutectic since, from the above, the solid phase there is practically pure bismuth. On the lead side, accepting the liquidus data of Barlow,[14] the solidus may be calculated up to about 20% bismuth. The methods of calculation are briefly as follows. The activity of solid relative to liquid bismuth is calculated at several temperatures between the eutectic and the melting point. In the equation for the dependence of this activity on temperature, the heat of fusion is assumed independent of the temperature, since no reliable heat capacity data for bismuth are available. The value of the heat of fusion used here is 2518 calories, the mean of the results of several investigators listed by Awbery and Griffiths.[15] The activity curves of bismuth in the liquid alloys are now extrapolated to these temperatures. The intersection of one of these curves with a calculated activity of solid bismuth fixes the liquidus composition for that particular temperature. The results, tabulated in Table X, are in fair agreement with Barlow's data, but those of Kapp are found to be far too low. In a similar manner, the solidus on the lead side of the eutectic is calculated. From the smoothed curve through Barlow's liquidus data, the temperatures corresponding to various concentrations are read. The activities of lead in the liquid alloys are now extrapolated to those temperatures by the usual procedure. The standard state is changed by multiplying these values by the activity of liquid lead relative to solid lead, whence the activities are referred to solid lead. Since at a given temperature the activity in the equilibrium solidus and liquidus must be the same, the activity curves for the solid solutions may be extrapolated to the chosen temperatures, where by interpolation the solidus composition is fixed. These results also are listed in Table X. A survey of the literature on the sys-

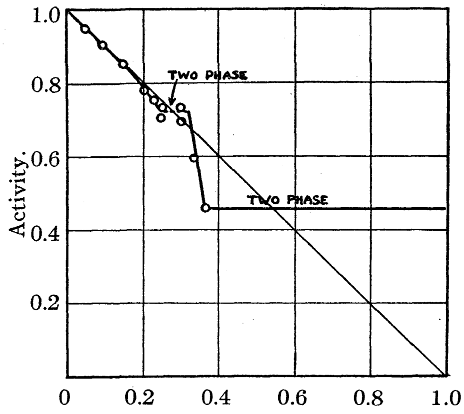

Fig. 5.—Activity of lead in solid lead-bismuth alloys at 124.5°.

TABLE X

Liquidus temp., °C.	N_{Bi}, calcd.	N_{Bi} (from curve through Barlow's data)	Solidus temp., °C.	N_{Bi}, calcd.
140	0.581	0.598	312	0.026
180	.685	.698	295	.056
213	.789	.793	279	.087
250	.915	.920	250	.141
			220	.197

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(15) Awbery and Griffiths, *Proc. Phys. Soc.* (London), **38**, 378 (1926).

tem has failed to reveal any other accurate solidus data.

The results of the above determinations and calculations are summarized graphically in Fig. 6 where data from other studies of the system are plotted also. The possible change of the solubility of bismuth in lead with temperature is indicated by the dotted line drawn from Solomon and Jones' limit of 33% at room temperature to our value at 125°. In drawing a smooth curve through all of Barlow's liquidus data on the lead side, the shape of the curve indicates the possibility of a peritectic. This, with the behavior of the solid alloys previously mentioned, and the report of Solomon and Jones, led us to postulate such a transition at about 180°. This was subsequently verified by thermal analysis, the temperature being fixed at 184°. In the thermal work, large amounts of the metals, 150 to 300 g., were taken and a differential copper–constantan thermocouple was used. The effect was observed with a 26 and a 30% alloy, but not with a 37% alloy, whose liquidus was about two degrees under the peritectic temperature. It should be noted that Hansen[16] has postulated the existence of the peritectic change for this system in his recent treatise, based entirely on the x-ray study of Solomon and Jones and on superconductivity measurements of Meisner.[17]

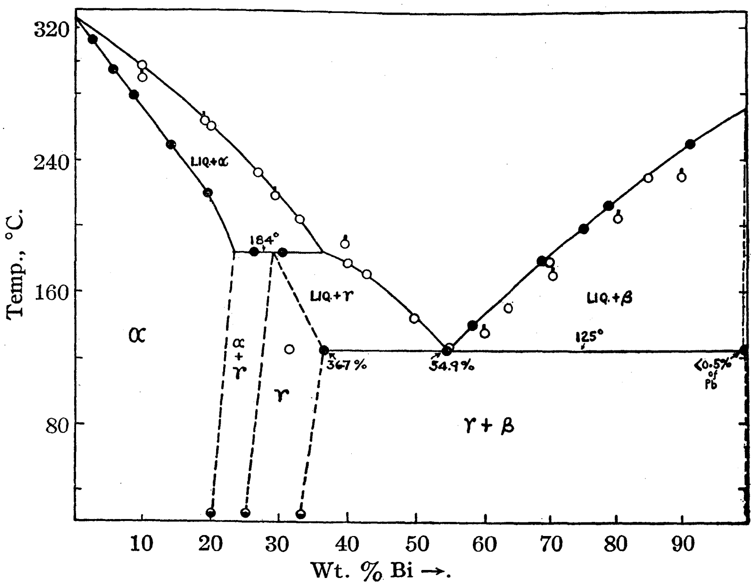

Fig. 6.—Phase diagram for the Pb–Bi system: ●, this study; ○, Barlow; ȯ, Kapp; ◒, Solomon and Jones.

Regular Solution Behavior of the Liquid Alloys

Hildebrand,[18] in the study of deviations from perfect solution behavior, introduced the term "regular solutions" to apply to those in which, due to the absence of particular orientations, the partial molal entropies of the constituents may be assumed the same as in an ideal solution of the same composition. Where the atomic volumes are the same, which is true for lead and bismuth, his most recent treatment yields the result

$$\overline{U}_1 - U_1^0 = [(\Delta U_1^0)^{1/2} - (\Delta U_2^0)^{1/2}]^2 N_2^2$$

where $\overline{U}_1$ and U_1^0 are the partial molal and molal total energies, respectively, of the first constituent and where the ΔU terms represent the energies of vaporization. As may easily be shown, the equation may be converted by a simple assumption into the form

$$RT \ln a_1/N_1 = bN_2^2$$

where a_1/N_1 is the activity coefficient of the first component and "b" represents the square of the quantity in brackets above. In this case, because of the extreme variation of reported values for the heat

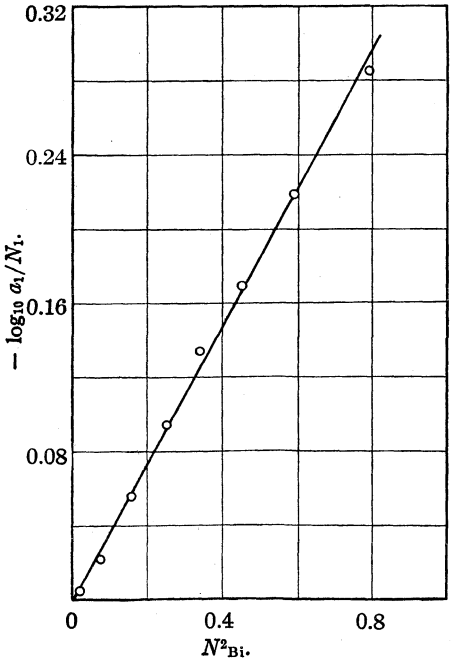

Fig. 7.—Regular solution behavior of liquid alloys.

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[16] M. Hansen, "Der Aufbau der Zweistofflegierungen," Julius Springer, Berlin, 1936.

[17] Meisner, *et al.*, *Ann. Phys.*, **13**, 979 (1932).

[18] Hildebrand, "Solubility," A. C. S. Monograph, No. 17, 2nd edition, 1936.

of vaporization of bismuth, it was impossible to evaluate the term $[(\Delta U_1^0)^{1/2} - (\Delta U_2^0)^{1/2}]^2$. However, as a test for regular solution behavior, the quantity "b" was calculated from the experimental data and its approximate constancy with variation of composition demonstrated. The results of these calculations are given in Table XI and plotted in Fig. 7. Also, it may be shown that from the above $dE_1/dT = -R/nF \ln N_1$ for regular solutions; that is, the slope of the electromotive force–temperature curve should be a function of composition only. This is true for the lead–bismuth liquid alloys, as shown by the values in Table XII.

TABLE XI

N_2	N_2^2	a_1/N_1	$\log_{10} a_1/N_1$	"b"
0.152	0.023	0.989	−0.0048	− 666
.280	.079	.950	− .0223	− 911
.400	.160	.880	− .0555	−1112
.504	.254	.803	− .0953	−1202
.586	.343	.734	− .1345	−1255
.672	.452	.677	− .1694	−1202
.770	.594	.604	− .2190	−1182
.889	.792	.519	− .2848	−1153

TABLE XII

N_2	$\log_{10} N_1$	dE/dT, calcd. volts/°C. $\times 10^6$	dE/dT, obsd. volts/°C. $\times 10^6$
0.152	−0.0716	7.2	7.4
.280	− .1427	14.2	14.4
.400	− .2218	22.0	20.8
.504	− .3045	30.2	27.8
.586	− .3830	38.0	37.6
.672	− .4841	48.0	46.4
.770	− .6383	63.3	64.4
.889	− .9547	94.7	102.0

Summary

1. Methods of calculation have been presented whereby thermodynamic data can be used to establish accurately the conditions of phase equilibria in binary systems.

2. The activities and relative partial molal heat contents of lead and bismuth in their liquid alloys have been determined, and it is shown that the alloys may be classified as regular solutions.

3. The activities and relative partial molal heat contents of lead in solid solutions of lead and bismuth have been determined accurately up to 20% bismuth, and the approximate activities have been established from 22.5 to 33% bismuth.

4. The eutectic composition and temperature are fixed at 54.7 atomic per cent. bismuth and 125°. The compositions of the two solid phases comprising the eutectic solid have been found to be 36.5 atomic per cent. bismuth and practically pure bismuth.

5. The liquidus curve on the bismuth side of the eutectic and the solidus on the lead side up to 20% bismuth have been calculated.

6. The indicated existence of a peritectic at 184° on the lead side of the system has been verified by thermal analysis.

7. A revised phase diagram of the system is presented.

PITTSBURGH, PENNA. RECEIVED JUNE 22, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Zinc and Zinc Amalgam Electrodes

BY WILLIAM J. CLAYTON AND WARREN C. VOSBURGH

The difference of potential between zinc and saturated zinc amalgam electrodes in a solution containing zinc ion was considered by Cohen in 1900 to be practically zero.[1] This conclusion was based partly on the results of earlier workers and partly on some measurements of his own. The results of the latter measurements, given in a footnote in the same article[1] (pp. 618–619), are 0.570 mv. at 25° and 0.488 mv. at 0° for the cell

$$\text{Zn(s)/Zn}^{++}\text{/Zn (satd. amalgam)} \qquad (1)$$

On the basis of these results Scatchard and Tefft[2] and Shrawder, Cowperthwaite and La Mer[3] used the value 0.6 mv. at 25° in the calculation of the normal electrode potential of zinc. Puschin[4] found a value of about −2 mv. for cell 1. Garner, Green and Yost[5] have assumed that the electromotive force of cell 1 is zero.

In this investigation the electromotive force of cell 1 has been found to be zero. A similar cell in which a superficially amalgamated zinc electrode was substituted for the pure zinc electrode was found to have zero electromotive force also. The

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[1] Cohen, *Z. physik. Chem.*, **34**, 612 (1900).

[2] Scatchard and Tefft, THIS JOURNAL, **52**, 2280 (1930).

[3] Shrawder, Cowperthwaite and La Mer, *ibid.*, **56**, 2348 (1934).

[4] Puschin, *Z. anorg. Chem.*, **63**, 230 (1903).

[5] Garner, Green and Yost, THIS JOURNAL, **57**, 2056 (1935).

latter would be expected because Clark cells made with superficially amalgamated zinc electrodes agree in electromotive force with those made with saturated amalgam electrodes, as pointed out by Cohen[1] (p. 613).

Materials and Apparatus.—Mercury was purified by washing with a solution of nitric acid and mercurous nitrate and distilling in a current of air. Zinc sulfate was recrystallized. The zinc chloride used was of the best commercial grade. Most of the zinc used was the best grade of commercial stick zinc, but a few measurements were made with some spectroscopically pure zinc which the Research Division of the New Jersey Zinc Company kindly furnished, and a few with strips of sheet zinc intended for standardizing. The treatment of the stick zinc in making the electrodes was found to be of considerable importance, and is described below. Zinc amalgam containing 5% of zinc was prepared electrolytically with stick zinc as the anode and zinc chloride as the electrolyte.

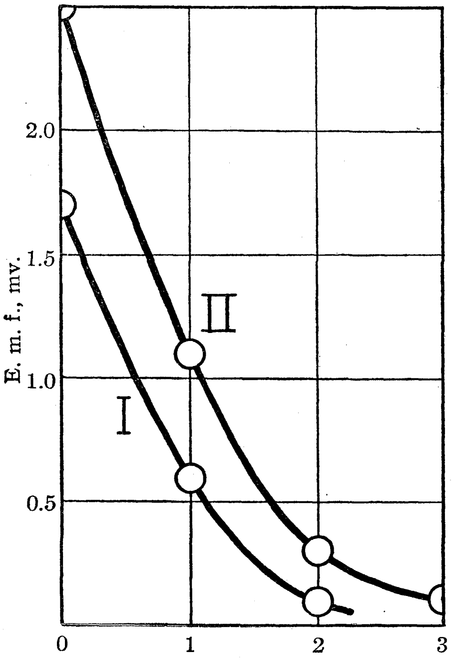

Fig. 1.—Electromotive force of the cell Zn(stick)/Zn^{++}/Zn (Hg) when the stick zinc electrode has been immersed in acidified zinc chloride solution from one to three days.

Zinc sulfate solution for use in the cells was made by dividing a solution containing 20 g. per liter of hydrated zinc sulfate in two equal parts, digesting one part with precipitated zinc hydroxide, filtering off the excess and reuniting the two parts. Zinc chloride solution for use in the cells was prepared by dissolving 20 g. of anhydrous zinc chloride per liter with the addition of enough hydrochloric acid to prevent precipitation of basic material and digesting with zinc oxide. Zinc acetate solution was prepared in the same manner as the zinc chloride solution, using 20 g. of hydrated zinc acetate per liter.

Nitrogen was prepared by passing air through four bottles of ammoniacal cuprous chloride solution.[6] The solution in the last bottle remained colorless.

Preparation of Zinc Stick Electrodes.—Most of the zinc sticks used as pure zinc electrodes were annealed, and all were treated as described below with an acidified solution of zinc chloride. Annealing was accomplished by sealing the zinc inside a glass tube and heating it in a muffle furnace to a temperature near or in some cases above the melting point, and cooling very slowly. The treatment with an acidified zinc chloride solution was best carried out in the following manner. The zinc sticks were immersed in a concentrated zinc chloride solution (200 g. of anhydrous zinc chloride to 100 ml. of water) and concentrated hydrochloric acid was added until hydrogen was generated uniformly over the surface of the zinc. Additional small portions of acid were added from time to time (about six or seven times a day) to keep the reaction going slowly.

To show the changes taking place during the treatment with acidified zinc chloride solution, the treatment of eight zinc sticks was interrupted at one-day intervals and the difference of potential between the sticks and zinc amalgam electrodes was determined by the procedure described below. The results are shown in Fig. 1. Curve I shows the change in the average electromotive force as the treatment progressed for four annealed electrodes and curve II for four unannealed electrodes. In two days for the annealed electrodes and three days for the unannealed the electromotive force had fallen to about 0.1 mv. Experience with other electrodes showed that a further slow decrease goes on for two to three weeks, after which no further change takes place, and the electrodes are in very good agreement with each other.

It is shown in Fig. 1 that for commercial stick zinc the annealing process is of less importance than the treatment with the acidified zinc chloride solution. Occasionally unannealed electrodes had to be rejected for disagreement with the others, but annealed electrodes could always be brought to excellent agreement. The annealing was essential for electrodes cast in the laboratory in Pyrex tubes.

Some of the spectroscopically pure zinc was treated with acidified zinc chloride solution, and some was not treated, but used for electrodes as received. No attempt was made to anneal it.

Superficially amalgamated zinc electrodes were prepared by immersing zinc sticks about 0.5 cm. in diameter to a depth of 4 cm. in 0.1 *M* hydrochloric acid solution at 40° and touching them to three or four small droplets of mercury about 1 mm. in diameter. By rubbing two sticks together the spreading of the mercury over the surface was hastened. No annealing or other treatment was necessary.

Preparation of the Cells.—Figure 2 is a diagram of the cell vessel used, with the electrodes in place. Stick electrodes, either of pure or superficially amalgamated zinc, were soldered to brass rods of small diameter which were passed through one-holed rubber stoppers. The strips of sheet zinc were treated similarly. A clean, dry cell vessel was connected by means of the tube projecting downward from the cross-arm to the three-way stopcock of the

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[6] Van Brunt, This Journal, **36**, 1448 (1914).

apparatus shown in Fig. 3, using a rubber tube for a connector. The cell vessel was stoppered and evacuated and filled with nitrogen. Some amalgam was washed with dilute acid and water, then dried and heated to a temperature near its boiling point. It was then passed through a small hole in a filter paper into the two legs of the cell vessel, with a stream of nitrogen flowing to protect from oxidation. The stick electrodes which had been treated as described above were next washed with dilute hydrochloric acid, water and alcohol and then quickly placed in an empty cell vessel, the rubber stoppers fitting tightly in the tops of the vertical tubes. The vessel was immediately evacuated and the alcohol all evaporated. The electrodes were then transferred to the cell vessel containing the amalgam electrodes. The cell vessel was evacuated for at least forty-five minutes by means of an efficient vacuum pump.[7] Then some zinc sulfate solution was allowed to flow into the flask of the apparatus of Fig. 3. The low pressure caused it to boil, expelling dissolved gases. By allowing air to enter the flask, part of the solution was forced into the cell vessel. The vessel was filled to the lower part of the stick electrodes, then the three-way stopcock was turned to allow the entrance of nitrogen. Care was taken that no nitrogen bubbles stuck to the electrodes, as these seemed to cause disagreement. The cell was removed from the apparatus of Fig. 3 by closing the rubber tube connection by means of a screw clamp and disconnecting from tube A. Some of the cells were placed in a constant-temperature air-bath for measurement, and some were measured at room temperature.

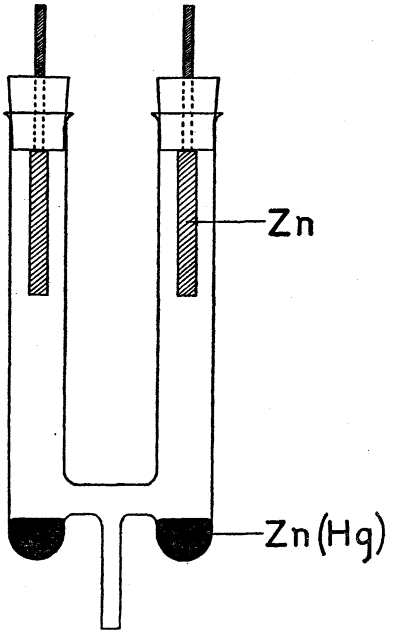

Fig. 2.—Diagram of cell vessel with electrodes in place.

The spectroscopically pure zinc was used in the form of irregular chunks as received. Chunks of the proper size were soldered to platinum wires which at the opposite ends were sealed into glass tubes. The level of the electrolyte was adjusted so that only part of the zinc electrode was immersed and the platinum wire did not touch the electrolyte.

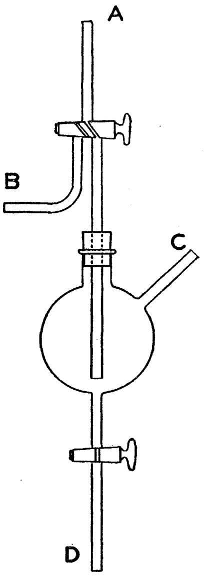

Fig. 3.—Apparatus used in evacuating the cell vessels and introducing the electrolyte without contact with air. The cell vessel was connected at A. Tube B was connected with a source of nitrogen, and tube C with either a vacuum pump or the atmosphere by means of a three-way stopcock. The electrolyte was introduced through D.

Electromotive Force Measurements.—In the best cells, as soon as temperature equilibrium was attained, the electromotive force became constant at a value very near zero for all combinations of the electrodes and remained so indefinitely. As an example of the agreement obtainable between similar electrodes, the potential difference between pure zinc stick electrodes averaged 0.01 mv. for eight pairs, between amalgamated stick electrodes 0.006 mv. for five pairs, and between amalgam electrodes 0.006 mv. for eight pairs. Average potential differences between zinc and amalgam electrodes in cells in which the electrolyte was zinc sulfate are given in Table I. A positive value indicates that the zinc electrode was negative. In giving the number of cells, each cell as described above is counted as two, since it contained two of each kind of electrode. For cells with pure zinc electrodes the average deviation from the mean value in the table was 0.01 mv. and for the amalgamated stick electrodes the average deviation was 0.003 mv.

It was found that a zinc chloride solution or a zinc acetate solution if prepared as described above could be used in the cells in place of the zinc sulfate solution. The results so obtained were practically the same as those shown in Table I, and need not be given in detail.

The strips of sheet zinc as purchased were covered with grease. Washing with alcohol (without further treatment) gave electrodes that were positive toward amalgam to the extent of 3.5 to 4.5 mv. Washing the same strips with ether left a surface that still seemed to be greasy but

TABLE I

ELECTROMOTIVE FORCE OF THE CELL $Zn(s)/Zn^{++}/Zn$ (SATD. AMALGAM)

Zinc electrode	No. of cells	Average, e. m. f. 20°	25°	30°
Amalgamated stick	18	−0.002	0.002	0.001
Annealed stick	12	.000	.005	.002
Unannealed stick	4	.02	.01	.01
Spectroscopic (treated)	4	...	.005	.001
Spectroscopic (untreated)	4	...	− .002	− .005

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(7) The evacuation is an important part of the process. When properly carried out equilibrium was reached in the cells as soon as the temperature became uniform. When a water pump was used for the evacuation more time was required for equilibrium, but about 80% of the cells came to excellent agreement within three or four days.

lowered the potential difference to about 0.5 mv. Immersion of the ether-washed electrodes in very dilute hydrochloric acid solution resulted in potential differences within 0.1 mv. of zero against amalgam electrodes. On greasing these electrodes with petrolatum the performance could be repeated.

The zinc strip electrodes could not be treated successfully with an acidified zinc chloride solution because the dissolution of some of the zinc left the strip so fragile that it was difficult to avoid bending it in subsequent operations. Bending caused an electrode potential considerably more negative than that of the amalgam, as might be expected.

The Normal Electrode Potential of Zinc.—The electromotive force of cell 1 is shown to be zero within the rather narrow limits of experimental error. A correction of −0.6 mv. is therefore necessary to the values for the electrode potential of zinc given by Scatchard and Tefft and Shrawder, Cowperthwaite and La Mer. Application of this correction makes better agreement between these two values and the value of Getman[8] which was obtained from cells with pure zinc electrodes. The three values are as follows:

Scatchard and Tefft (corr.)	0.7610 v.
Getman	.7613
Shrawder, Cowperthwaite and La Mer (corr.)	.7614

Additional Observations.—Of the three kinds of zinc electrode, namely, pure zinc, amalgamated zinc stick and zinc amalgam, the first is the most troublesome to prepare in a highly reproducible condition. The amalgamated stick electrode is easy to prepare and handle, and gives the same potential difference against a zinc salt solution as a pure zinc electrode when measured as described above. For some purposes this electrode might be preferable to amalgam electrodes. Amalgamated electrodes rubbed with filter paper for the purpose of spreading the mercury over the zinc surface were found to be about 0.2 more negative than zinc amalgam when first put in contact with an electrolyte in the presence of air. This value persisted for some time when the electrolyte contained a small amount of free acid, but when the electrolyte had been treated with zinc oxide or hydroxide the electromotive force soon dropped to zero.

Sticks of pure zinc prepared as described above when partially immersed in a 60% slightly acidified zinc chloride solution in contact with air agreed within 0.02 mv. However, when such a solution was used as a cell electrolyte, with exclusion of oxygen, the agreement of the zinc electrodes was poor.

Zinc salt solutions containing added acid, or even the quantity of acid resulting from hydrolysis, gave erratic results in the cells. The treatment of the solutions with zinc oxide as described above was necessary for the best results. The disturbing effect of acid was less in the presence of air than in its absence.

Twelve cells with amalgamated stick electrodes prepared with slightly acid electrolytes and with fairly good protection from air differed rather widely for some time, but after four months the electromotive forces were between −0.01 and +0.05 mv.

The introduction of hydrogen into a cell in place of nitrogen caused the pure zinc electrodes to be more positive than the amalgams by 0.2 to 0.3 mv. When bubbles stuck to the electrode the values were a little higher. Air when introduced caused a large temporary effect and a more or less permanent effect of the same order of magnitude as that of hydrogen. A few cells were allowed to come to thermal equilibrium and measured before the introduction of the nitrogen. These gave the same values as after the introduction of nitrogen, showing that nitrogen has no effect on the electrodes. This seems to disagree somewhat with Getman's[9] conclusion on the effect of nitrogen.

Finely divided zinc samples prepared both by electrolysis and by reduction by magnesium and also zinc deposited by electrolysis on platinum wires were tried. A few samples of the finely divided zinc came to good agreement with the stick electrodes. Most of the difficulty was probably in washing this zinc properly. The zinc deposited on platinum wires was always positive with relation to the other electrodes.

Summary

The electromotive force of the cell Zn(s)/Zn^{++}/Zn (satd. amalgam) is zero. The symbol Zn(s) may be understood to stand for either a pure zinc electrode or a superficially amalgamated zinc electrode, these two having the same electrode potential.

Durham, N. C.

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[8] Getman, *J. Phys. Chem.*, **35**, 2755 (1931).

[9] Getman, *ibid.*, **36**, 2662 (1932).

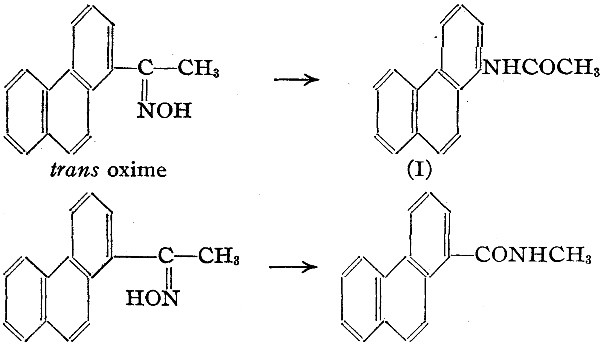
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Phenanthrene Derivatives. V. The Beckmann Rearrangement of the Oximes of Acetylphenanthrenes and Benzoylphenanthrenes

BY W. E. BACHMANN AND CHARLOTTE H. BOATNER[1]

We have investigated the Beckmann rearrangement of the oximes of acetylphenanthrenes and benzoylphenanthrenes for two reasons. First, we wished to know how various phenanthryl groups were oriented with respect to the hydroxyl group in the two series of oximes. Secondly, the rearrangement appeared to offer a method for the practical preparation of certain phenanthrene derivatives. Accordingly we have prepared the oximes of 1-, 2-, 3- and 9-acetylphenanthrene and of 1-, 2-, 3- and 9-benzoylphenanthrene, and have submitted them to rearrangement by the action of phosphorus pentachloride. A preliminary communication was reported a year ago and one more recently.[2]

All eight ketones containing the phenanthryl group give mixtures of stereoisomeric oximes, *cis* and *trans*.[3] Although it would be difficult or even impossible to separate these mixtures quantitatively into the two components in order to determine the relative proportions of the two forms, this is not the case with the products obtained on rearrangement of the oximes. Thus, an acetylphenanthrene oxime would rearrange to give either an acetylaminophenanthrene (as I) or a N-methyl-phenanthroic acid amide (as II). Hydrolysis of these products would yield an aminophenanthrene and a phenanthroic acid, respectively, and these can be separated easily and quantitatively through their water-soluble salts. If we assume that each oxime gives rise to a single rearrangement product—and the work of most investigators indicates that this is the case—then the proportions of aminophenanthrene and phenanthroic acid would be a measure of the relative amounts of the *cis* and *trans* oximes in the original mixture. We have therefore rearranged the *mixture* of stereoisomeric oximes which was obtained in each case, and have determined the relative proportions of the two isomers by this procedure. The results obtained from the oximes of 1-, 2-, 3- and 9-acetylphenanthrene are presented in Table I.



trans oxime (I)

cis oxime (II)

The yields of the products do not total 100% because a certain amount of decomposition occurred during the rearrangement. On the basis of Meisenheimer's proof of the interchange of the hydroxyl group and the *trans* group[4] our results show that in the acetylphenanthrene oximes the 1-, 2-, 3- and 9-phenanthryl groups orient themselves for the most part *trans* with respect to the hydroxyl group.

TABLE I

REARRANGEMENT OF ACETYLPHENANTHRENE OXIMES

	Rearrangement products	
Isomer	$C_{14}H_9NHCOCH_3$, %	$C_{14}H_9CONHCH_3$, %
1-	71	1
2-	81	1
3-	87	2
9-	50	6

Inasmuch as the 1-, 2-, 3- and 9-aminophenanthrenes can be obtained in yields of 50–87% from the ketones, the Beckmann rearrangement constitutes the most practical method of preparing these aminophenanthrenes, and by this procedure we have prepared several hundred grams of the amines. Although the 1-acetylphenanthrene is not obtained as easily as its isomers, nevertheless this method is the only one available for preparing the new 1-aminophenanthrene. Of interest in this connection is the work of Adelson and Bogert[5] who recently obtained 6-aminoretene by hydrolysis of the rearrangement product from 6-acetylretene oxime.

The mixtures of the stereoisomeric oximes ob-

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(1) From part of the Ph.D. dissertation of Charlotte H. Boatner.

(2) Bachmann, THIS JOURNAL, **57**, 1381 (1935); Bachmann and Boatner, *ibid.*, **58**, 857 (1936); see also Mosettig and Krueger, *ibid.*, **58**, 1311 (1936).

(3) We have used these terms to designate the relative positions of the phenanthryl and hydroxyl groups with respect to each other.

(4) Meisenheimer, *Ber.*, **54**, 3206 (1921); Meisenheimer, Theilacker and Beisswenger, *Ann.*, **495**, 249 (1932).

(5) Adelson and Bogert, THIS JOURNAL, **58**, 653 (1936).

tained from 1-, 2-, 3- and 9-benzoylphenanthrene are rearranged quantitatively without decomposition to mixtures of benzoylaminophenanthrene $C_{14}H_9NHCOC_6H_5$ and phenanthroic acid anilide $C_{14}H_9CONHC_6H_5$. The proportions of these products obtained from the various isomeric ketones are shown in Table II. From these results it is apparent that in the benzoylphenanthrene oximes the phenanthryl group is oriented chiefly *cis* with respect to the hydroxyl group. Apparently the size of the groups has little effect on the orientation of the groups in the oximes. From the results obtained with the two classes of oximes the various groups may be arranged in the following order of decreasing tendency toward *trans* orientation with respect to the hydroxyl group: phenyl, 2-phenanthryl, 3-phenanthryl, 1-phenanthryl, 9-phenanthryl, methyl.

Table II

Rearrangement of Benzoylphenanthrene Oximes

	Rearrangement products	
	$C_{14}H_9NHCOC_6H_5$, %	$C_{14}H_9CONHC_6H_5$, %
1-	18	82
2-	44	56
3-	37	63
9-	4	96

The products obtained by rearrangement of the stereoisomeric oximes of 1-benzoylphenanthrene proved particularly valuable, for on hydrolysis there are produced 1-phenanthroic acid (hitherto rare) and the new 1-aminophenanthrene. Moreover, by reduction of the 1-phenanthroic acid anilide the new 1-phenanthraldehyde can be prepared in excellent yield. As a result the way is now open for the preparation of 1-phenanthrene derivatives.

Experimental Part

1-Acetylphenanthrene was prepared in two ways: (A) by oxidation of 1-phenanthrylmethylcarbinol and (B) by interaction of 1-cyanophenanthrene and methylmagnesium iodide.

(A) **1-Phenanthrylmethylcarbinol.**—To the Grignard reagent which had been prepared from 1.5 cc. of methyl iodide in 10 cc. of ether was added 10 cc. of benzene, followed by 2.6 g. of 1-phenanthraldehyde (preparation described later). After being refluxed for fifteen minutes the solution was hydrolyzed by ice-cold ammonium chloride solution; evaporation of the solvents gave the carbinol in crystalline form. By recrystallization from benzene 1-phenanthrylmethylcarbinol was obtained in the form of colorless plates: yield 2.5 g. (90%); m. p. 108–110°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.5; H, 6.3. Found: C, 86.3; H, 6.6.

1-Acetylphenanthrene.—A solution of 1.5 g. of 1-phenanthrylmethylcarbinol in 25 cc. of glacial acetic acid was treated with a solution of 0.5 g. of chromic acid anhydride in 0.5 cc. of water and 10 cc. of acetic acid; throughout the reaction the temperature was kept at 20°. After standing for twelve hours the solution was poured into water and the ketone was extracted with benzene. The benzene solution, after being heated with charcoal and filtered, was evaporated and the residue was recrystallized from alcohol, yielding 1-acetylphenanthrene as large colorless diamond-shaped plates; weight 0.80 g. (53%); m. p. 112–113°.

Anal. Calcd. for $C_{16}H_{12}O$: C, 87.2; H, 5.5. Found: C, 87.0; H, 5.7.

(B) 1-Cyanophenanthrene was prepared from 1-phenanthroic acid amide which was obtained from the acid through the acid chloride.[6] A mixture of 5 g. of 1-phenanthroic acid amide and 5 g. of phosphorus pentoxide was heated at 140° for fifteen minutes; throughout the reaction the mixture was stirred and pressed with a glass rod. Most of the nitrile was obtained by decantation; the remainder was secured after extracting the phosphoric acid by water. The 1-cyanophenanthrene was then recrystallized from benzene–methyl alcohol; yield 4.3 g. (96%).

To the Grignard reagent prepared from 3 cc. of methyl iodide in 15 cc. of ether was added 25 cc. of benzene and then 4.3 g. of 1-cyanophenanthrene. After being refluxed for five hours the clear solution was cooled, whereupon the addition product crystallized; this solid was filtered off, washed with benzene and hydrolyzed to 1-acetylphenanthrene by refluxing it with dilute hydrochloric acid for four hours. The ketone which crystallized on cooling was obtained pure by distillation under reduced pressure, followed by recrystallization from alcohol; yield 4.0 g. (85%). The product was identical with the ketone prepared by method (A).

9-Acetylphenanthrene.—We prepared this ketone by the Grignard reaction from 9-cyanophenanthrene. The latter compound was made by heating 9-bromo-phenanthrene and cuprous cyanide[7] in a Claisen flask; when the reaction was at an end the nitrile was distilled from the flask under reduced pressure, b. p. 190–200° (3 mm.). This procedure avoids the long extraction otherwise required to separate the nitrile and cuprous salts.

To the Grignard reagent prepared from 7 cc. of methyl iodide in 30 cc. of ether was added 25 cc. of benzene and then 15 g. of 9-cyanophenanthrene. After being refluxed for three hours, the mixture was cooled and hydrolyzed with ice-cold ammonium chloride solution. The ether–benzene layer was shaken with ice-cold dilute hydrochloric acid and the aqueous solution which now contained the ketone-imine hydrochloride was heated for an hour in order to hydrolyze the product to the ketone. The latter, which precipitated as an insoluble oil, was purified by distillation under reduced pressure, followed by recrystallization from alcohol; yield 9.5 g. (57%); m. p. 73–74°. Mosettig and van de Kamp,[8] who prepared the ketone by a different method, reported a melting point of 74.5°.

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(6) Bachmann, This Journal, **57**, 555 (1935).

(7) Mosettig and van de Kamp, *ibid.*, **54**, 3328 (1932).

(8) Mosettig and van de Kamp, *ibid.*, **55**, 3442 (1933).

2- and 3-acetylphenanthrene were prepared according to the procedure of Mosettig and van de Kamp[9] with the modification that the mixture of crude ketones was distilled under reduced pressure, b. p. 180–214° (4 mm.). By digestion of the distillate with ether most of the 3-isomer was dissolved; the residue of the 2-isomer was obtained pure by two recrystallizations from benzene, the 3-isomer by recrystallization from methyl alcohol.

Oximation of Acetylphenanthrenes.—The preparation of oximes of ketones with large hydrocarbon radicals has often been found difficult and sometimes impossible. The use of pyridine by Bryant and Smith[10] in the hydroxylamine method for the titration of ketones and aldehydes suggested its use for the preparation of the oximes whose rearrangement we wished to study. With the modification of leaving out the water entirely we found that quantitative oximation of 1-, 2-, 3- and 9-acetylphenanthrene could be accomplished by heating a mixture of the ketone and hydroxylamine hydrochloride in a solution of absolute alcohol and pyridine for three hours on a steam-bath. The advantages of this procedure have been pointed out by one of us;[11] by this method it is possible to prepare oximes which do not form readily under the usual conditions.[12]

A mixture of 20 g. of 3-acetylphenanthrene (similarly for the 1- or 9-isomer) and 16 g. of hydroxylamine hydrochloride in 75 cc. of absolute alcohol and 28 cc. of pyridine was refluxed for three hours. A practically quantitative yield of the oxime was obtained by removing most of the solvent and pouring the residue into water. For the preparation of the 2-acetylphenanthrene oxime we refluxed a mixture of 2 g. of the ketone with 1.6 g. of hydroxylamine hydrochloride in 4 cc. of absolute alcohol and 12 cc. of pyridine on a steam-bath for three hours; a 97% yield of oximes (m. p. 187–190°) was obtained. By recrystallization from methyl alcohol the pure *trans*-2-acetylphenanthrene oxime was obtained as colorless needles; m. p. 196–197°.

Anal. Calcd. for $C_{16}H_{13}ON$: N, 6.0. Found: N, 6.2.

The properties of the 3- and 9-acetylphenanthrene oximes were similar to those prepared by the usual method.[9] Mosettig and Krueger[2] reported a melting point of 196–198° for the 2-acetylphenanthrene oxime which they prepared recently by the pyridine method.

1-Acetylphenanthrene Oxime.—The *trans* form of this oxime crystallizes from methyl alcohol in colorless plates; m. p. 174–176°.

Anal. Calcd. for $C_{16}H_{13}ON$: N, 6.0. Found: N, 6.0.

Rearrangement of the Acetylphenanthrene Oximes.—Anhydrous ether is generally employed as the solvent in the Beckmann rearrangement and at first we employed this solvent. We found, however, that the cheaper solvent benzene could be substituted and, indeed, in several cases we obtained better results; moreover, smaller volumes of this solvent suffice. The mixture of *cis* and *trans* oximes prepared from 5 g. of 3-acetylphenanthrene (or 1- or 9-isomer) was suspended in 80 cc. of dry benzene and treated with 5 g. of powdered phosphorus pentachloride. After the mixture had been refluxed for fifteen minutes, the mixture was cooled and hydrolyzed. In the rearrangement of the 2-acetylphenanthrene oximes 20 cc. of benzene was used for each gram of oxime and the solution was refluxed for a period of three hours. Using these procedures we have rearranged quantities of 50–100 g. of oxime at one time.

The mixture of acetylaminophenanthrene and N-methylphenanthroic acid amide obtained on rearrangement of the oximes from 5 g. of ketone was refluxed with 200 cc. of alcohol and 7 cc. of concentrated hydrochloric acid for twenty-four hours. After the alcohol had been removed by distillation the residue was digested with 300 cc. of boiling water and filtered. Addition of ammonium hydroxide to the aqueous filtrate precipitated the free aminophenanthrene (3.12 g. of 1-, 3.58 g. of 2-, 3.83 g. of 3- and 2.21 g. of 9-amine). The residue was then heated with a solution of 7 cc. of hydrochloric acid in 200 cc. of alcohol in order to hydrolyze the acid amide, and the phenanthroic acid was isolated through its water-soluble sodium salt (after hydrolysis by potassium hydroxide of any ester formed in the previous reaction). The acid amide was also hydrolyzed by a mixture of acetic acid and hydrochloric acid in a sealed tube at 200° for six hours.

The amines as obtained were usually practically colorless and pure. Further purification can be best accomplished by distillation under reduced pressure. The melting points of the 2- and 3-amines and their acetyl derivatives were in agreement with the values reported by Werner[13] for the products obtained from the corresponding phenanthrene sulfonic acids. Although Werner obtained 2-aminophenanthrene as yellow crystals we were able to isolate it in a colorless state.

1-Aminophenanthrene.—This amine, obtained in 72% yield (based on the ketone) in the manner described, crystallizes from a mixture of benzene and petroleum ether in broad, colorless glistening needles; m. p. 145–146°. The amine is insoluble in water, slightly soluble in cold petroleum ether and benzene and soluble in hot benzene.

Anal. Calcd. for $C_{14}H_{11}N$: N, 7.2. Found: N, 7.0.

The hydrochloride of this amine crystallizes from alcohol in the form of fine colorless needles; m. p. 253–255° with previous decomposition. The salt is soluble in water but not very soluble in cold alcohol.

1-Acetylaminophenanthrene.—This substance is the principal product of the rearrangement of 1-acetylphenanthrene oxime. A 90% yield of this compound was obtained by refluxing a mixture of 0.1 g. of 1-aminophenanthrene and 2 cc. of acetic anhydride for ten minutes, adding 3 cc. of water and cooling the solution. 1-Acetylaminophenanthrene crystallizes from acetic acid in broad colorless needles or plates; m. p. 219–220.5°.

Anal. Calcd. for $C_{16}H_{13}ON$: N, 6.0. Found: N, 6.2.

1-Benzoylaminophenanthrene.—A 99% yield of this derivative was obtained by treating a solution of 0.1 g. of 1-aminophenanthrene in 1 cc. of pyridine with 0.2 cc. of

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(9) Mosettig and van de Kamp, THIS JOURNAL, **52**, 3704 (1930).

(10) Bryant and Smith, *ibid.*, **57**, 57 (1935).

(11) "Annual Survey of American Chemistry," Reinhold Publishing Co., New York, Vol. X, 1935, p. 188.

(12) See for example Cook, Hewett and Lawrence, *J. Chem. Soc.*, 79 (1936).

(13) Werner, *Ann.*, **321**, 312 (1902).

benzoyl chloride and heating the mixture for five minutes. 1-Benzoylaminophenanthrene crystallizes from acetic acid in broad colorless needles; m. p. 224–226°.

Anal. Calcd. for $C_{21}H_{15}ON$: N, 4.7. Found: N, 4.9.

1-Aminophenanthrene Picrate.—The picrate, prepared by mixing hot benzene solutions of the amine and picric acid, crystallizes from *n*-propyl alcohol in fine pale-yellow needles; m. p. 203–204° with decomposition. The picrate is nearly insoluble in cold benzene, chloroform and alcohol.

Anal. Calcd. for $C_{14}H_{11}N \cdot C_6H_3O_7N_3$: N, 13.3. Found: N, 13.7.

1-Phenanthrylurethan.—A solution of 0.1 g. of 1-aminophenanthrene in 5 cc. of benzene was treated with 0.1 cc. of ethyl chlorocarbonate and 0.1 cc. of pyridine. After being warmed for a few minutes the mixture was allowed to stand at room temperature for three hours. 1-Phenanthrylurethan crystallizes from alcohol in colorless transparent plates; yield, quantitative; m. p. 153.5–154°.

Anal. Calcd. for $C_{17}H_{15}O_2N$: N, 5.3. Found: N, 5.3.

N-Phenyl-N′-(1-phenanthryl)-urea.—A solution of 0.2 g. of 1-aminophenanthrene and 0.15 g. of phenyl isocyanate in 5 cc. of benzene was warmed on a steam-bath for fifteen minutes and then allowed to stand at room temperature twelve hours. N-Phenyl-N′-(1-phenanthryl)-urea crystallizes from a mixture of chloroform and alcohol in fine colorless needles; m. p. 323–325° with decomposition; yield, quantitative. The compound is nearly insoluble in alcohol and in benzene but is soluble in hot chloroform.

Anal. Calcd. for $C_{21}H_{16}ON_2$: N, 9.0. Found: N, 8.8.

Synthesis of N-Methylphenanthroic Acid Amides.—These compounds, formed to a slight extent in the rearrangement of the acetylphenanthrene oximes, were synthesized from the acids. The acid chloride[6] from 1 g. of phenanthroic acid (1-, 2-, 3- or 9-isomer) was dissolved in 10 cc. of acetone and the resulting solution was poured into an ice-cold 33% aqueous solution of methylamine. The amide which precipitated immediately was filtered off, washed with water, dried and recrystallized from a mixture of benzene and methyl alcohol; yields 90–95%.

The properties of the N-methylphenanthroic acid amide (calcd. for $C_{16}H_{13}ON$: N, 6.0) are: 1-isomer, plates, m. p. 204–205.5° (N, 5.7); 2-isomer, needles, m. p. 201–202° (N, 6.2); 3-isomer, needles, m. p. 207–207.5° (N, 5.9); 9-isomer, needles, m. p. 191–192° (N, 6.3).

Benzoylphenanthrene Oximes.—1-Benzoylphenanthrene was prepared by the Perrier modification of the Friedel and Crafts reaction and the other ketones were prepared from the corresponding cyanophenanthrenes by means of the Grignard reaction.[6] Oximation was carried out according to the procedure described for the acetylphenanthrenes though usually twelve to twenty-four hours were allowed for heating. The yields of oximes were nearly quantitative. Thus, by heating a mixture of 70 g. of 1-benzoylphenanthrene and 68 g. of hydroxylamine hydrochloride in 500 cc. of absolute alcohol and 100 cc. of pyridine for twelve hours 67 g. of the oximes was obtained.

All of the oximes crystallized from methyl alcohol as colorless needles. The properties of the benzoylphenanthrene oximes (Calcd. for $C_{21}H_{15}ON$: N, 4.7) are: 1-isomer, m. p. 185–186° (N, 4.4); 2-isomer, m. p. 182–183° (N, 4.5); 3-isomer, m. p. 201–203° (N, 4.9); 9-isomer, m. p. 218–220 (N, 4.9).

The benzoylphenanthrene oximes were rearranged in the same manner as the acetylphenanthrene oximes. Thus, a mixture of 20 g. of the oximes in 100 cc. of ether (or benzene) was treated with 15 g. of phosphorus pentachloride. After being warmed for fifteen minutes the solution was carefully hydrolyzed; 19 g. of rearrangement products was obtained. When the mixture was heated with alcoholic hydrochloric acid for three weeks on a steam-bath, the benzoylaminophenanthrene was hydrolyzed to aminophenanthrene while the phenanthroic acid anilide was only slightly affected. The weight of aminophenanthrene (2.45 g. 1-aminophenanthrene from 20 g. of 1-benzoylphenanthrene, for example) indicated the proportion of *trans*-benzoylphenanthrene oxime in the original mixture.

1-Phenanthroic Acid Anilide.—This compound was obtained in a pure state by recrystallization of the rearrangement products obtained from the 1-benzoylphenanthrene oximes. For identification it was synthesized from 1-phenanthroic acid. The acid chloride, prepared from 0.15 g. of 1-phenanthroic acid by means of phosphorus pentachloride, was dissolved in warm acetone and treated with 1 cc. of aniline. After five minutes the mixture was digested with dilute hydrochloric acid and the precipitate of the anilide was filtered off. 1-Phenanthroic acid anilide crystallizes from acetone in colorless plates; m. p. 248–249°; yield, quantitative.

Anal. Calcd. for $C_{21}H_{15}ON$: N, 4.7. Found: N, 4.4.

1-Phenanthraldehyde.—This new aldehyde was prepared from the rearrangement product of 1-benzoylphenanthrene oximes which contained 82% of 1-phenanthroic acid anilide. An intimate mixture of 36 g. of the rearrangement product and 25 g. of phosphorus pentachloride in 40 cc. of anhydrous ether was heated on a steam-bath for fifteen minutes. The ether and phosphorus oxychloride were removed under reduced pressure at 140° (temperature of oil-bath), the imide chloride was dissolved in 50 cc. of ethylene dibromide and added to a solution of 94 g. of anhydrous stannous chloride in 340 cc. of anhydrous ether saturated with dry hydrogen chloride. After the mixture had stood at 0° for twenty hours, the precipitate was filtered off, washed with benzene and hydrolyzed by hot dilute hydrochloric acid. The crude aldehyde was digested with carbon tetrachloride and the filtered solution was evaporated to dryness. The residue was dissolved in a mixture of chloroform and ether and the solution was shaken with a saturated aqueous solution of sodium bisulfite for thirty-six hours; the addition product was filtered off and the filtrate was shaken with a fresh solution of sodium bisulfite for four days. The aldehyde obtained by hydrolysis of the addition compound with dilute hydrochloric acid was purified by distillation under reduced pressure and recrystallization; yield 16 g. (75%). 1-Phenanthraldehyde crystallizes from benzene and petroleum ether in colorless needles; m. p. 110.5–111.5°.

Anal. Calcd. for $C_{15}H_{10}O$: C, 87.3; H, 4.9. Found: C, 87.2; H, 5.1.

1-Phenanthraldehyde oxime crystallizes from benzene in colorless needles; m. p. 187–189°.

Anal. Calcd. for $C_{15}H_{11}ON$: N, 6.3. Found: N, 6.0.

1-Phenanthroic Acid.—1-Phenanthroic-acid-anilide hydrolyzes with difficulty; it is practically unaffected by a boiling alcoholic solution of hydrochloric acid or potassium hydroxide. Small amounts can be hydrolyzed readily in a sealed tube. A mixture of 2.0 g. of the product which was obtained by rearrangement of the oximes (containing 82% of 1-phenanthroic-acid-anilide), 10 cc. of concentrated hydrochloric acid and 50 cc. of glacial acetic acid was heated in a sealed tube at 200° for eight hours. The liquids were evaporated and the residue was digested with hot water in order to remove the 1-aminophenanthrene (0.17 g.). The 1-phenanthroic acid which remained was purified through its ammonium salt; yield 0.95 g. (77%).

For making larger amounts of 1-phenanthroic acid it was found more practical to carry out the following reactions: $C_{14}H_9CONHC_6H_5 \longrightarrow C_{14}H_9C(Cl){=}NC_6H_5 \longrightarrow C_{14}H_9COOH$. The imide chloride prepared from 20 g. of the rearrangement products as described above was added to a solution of sodium methylate which had been prepared from 5 g. of metallic sodium, 20 cc. of methyl alcohol and 20 cc. of ether. After the mixture had been refluxed for an hour, the solvents were distilled off, and the inorganic material was removed by extraction with water. The methoxyl derivatives of the imides were then hydrolyzed by heating them with a mixture of 50 cc. of concentrated hydrochloric acid and 200 cc. of methyl alcohol for two days. After removal of the solvents, the residue was heated with 100 cc. of a 25% solution of potassium hydroxide in methyl alcohol for twelve hours in order to hydrolyze the methyl ester of 1-phenanthroic acid which had formed in the preceding treatment. The solvent was removed, and the potassium salt of 1-phenanthroic acid was extracted from the residue by 1 liter of boiling water; yield of 1-phenanthroic acid, 7.2 g. From the undissolved residue 2.45 g. of 1-aminophenanthrene was extracted by hot dilute hydrochloric acid. The remainder of the product was unchanged 1-phenanthroic-acid-anilide which could be used over again.

Summary

The orientation of the 1-, 2-, 3- and 9-phenanthryl groups with respect to the methyl and the phenyl group in the oximes of the acetylphenanthrenes and benzoylphenanthrenes has been determined.

The Beckmann rearrangement has been developed as a practical method for the preparation of 1-, 2-, 3- and 9-aminophenanthrene.

A number of new 1-phenanthrene derivatives have been synthesized.

ANN ARBOR, MICHIGAN RECEIVED AUGUST 17, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND SWARTHMORE COLLEGE]

The Effect of Various Catalysts on the Phenanthrene–Bromine Reaction

BY CHARLES C. PRICE

The reasons for undertaking an investigation of the influence of catalysts on the reaction of phenanthrene with bromine have been presented in a previous paper.[1]

Since dioxane, one of the few available non-polar solvents unattacked by bromine at room temperature, has been found useless as a solvent for the rate determinations due to its phenanthrene-induced bromination,[1] carbon tetrachloride was used, although it was by no means ideal for the purpose. The slight solubility of hydrogen bromide in this solvent makes it difficult to determine accurately the rate of formation of this product, even when ground-glass-stoppered reaction flasks are used. In a blank test at the maximum concentration of hydrogen bromide of the experiments, the sodium hydroxide titer decreased about 25% in ten hours. The bromine, carbon tetrachloride and phenanthrene were purified as described in the previous paper. The iodine was resublimed.

All the rate measurements were made at 25°. Samples of the reaction mixture were pipetted into dilute potassium iodide, the liberated iodine then being titrated with sodium thiosulfate and the acid with carbonate-free sodium hydroxide. The disappearance of the iodine color was taken as the end-point of the first titration while phenolphthalein was the indicator in the second. The thiosulfate titer is a measure of the course of both addition and substitution, while the acid is produced by substitution alone.

The bromination catalysts investigated included aluminum chloride, antimony pentachloride, iodine, phosphorus trichloride, phosphorus pentachloride and stannic chloride. When one-tenth equivalent of catalyst was added to an equimolecular solution of bromine and phenanthrene, all of these compounds, especially iodine, catalyzed the formation of hydrogen bromide in appreciable quantities within an hour or two, although without the catalyst there was none formed after several days. Since iodine gave the

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(1) Price, THIS JOURNAL, **58**, 1834 (1936).

best catalysis, as well as more conveniently and accurately measurable rates, it was employed in a majority of the experiments.

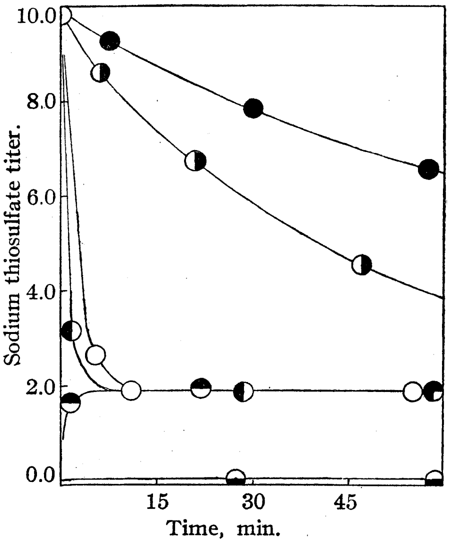


Fig. 1.—Rate of phenanthrene–bromine addition reaction: ○, phenanthrene and pure bromine; ◑, phenanthrene and commercial bromine; ◐, phenanthrene, commercial bromine and antimony pentachloride (10:10:1); ●, phenanthrene, pure bromine and iodine (20:20:1); ◒, phenanthrene dibromide; ◓, phenanthrene dibromide and antimony pentachloride (10:1).

In addition to their effect on the substitution reaction, two of the catalysts had a pronounced effect on the addition, iodine retarding the rate while antimony pentachloride greatly accelerated it. As little as one-twentieth equivalent of iodine in 0.05 *M* phenanthrene and bromine increased the time required to reach the equilibrium of the addition reaction from less than ten minutes to at least three or four hours. With twice as much iodine the rate was practically identical, while with five times as much, or one-fourth the equivalent amount, the rate was slightly greater. The reason for this retardation of the bromination being so little dependent on the iodine concentration may be because, although the rate of the addition reaction is diminished in some fashion proportional to the iodine concentration, the rate of bromine substitution increases so as to become appreciable.

This inhibitory effect of iodine is most probably due to interruption of the chain mechanism for the reaction suggested in the previous paper.[1]

$$C_{14}H_{10} + Br \rightleftharpoons C_{14}H_{10}Br \overset{Br_2}{\rightleftharpoons} C_{14}H_{10}Br_2 + Br$$

The iodine probably reacts with the chain-propagating bromine atoms.

The results of the experiments showing the catalytic effect of antimony pentachloride on the addition reaction are given graphically in **Fig. 1.** Since the rate of addition of pure bromine to phenanthrene was so rapid as to make it difficult to detect a catalytic effect, commercial "pure" bromine was employed. That the effect of the antimony pentachloride is true catalysis of the addition reaction and not neutralization of the effect of some negative catalyst present was clearly demonstrated by its catalytic effect on the reverse reaction, the attainment of equilibrium by the dissociation of the dibromide. Since antimony pentachloride has frequently been employed as a chlorinating agent, it appears capable of donating a molecule of halogen, perhaps stepwise as atoms, which would initiate the chain reaction for the bromine addition or its reversal.

The results of three measurements of iodine-catalyzed substitution are shown in Fig. 2. In one experiment one-fifteenth equivalent of iodine was added to equimolecular quantities of phenanthrene and bromine (*ca.* 0.10 *M*), while in a second the same amount of iodine was added to 0.10 *M* phenanthrene dibromide. A third experiment was identical with the second with the exception of the addition of bromine equivalent to the iodine.

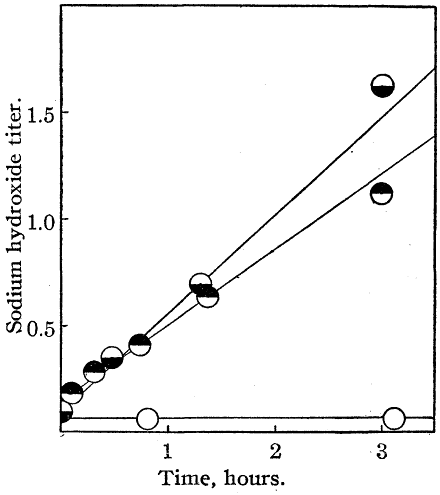
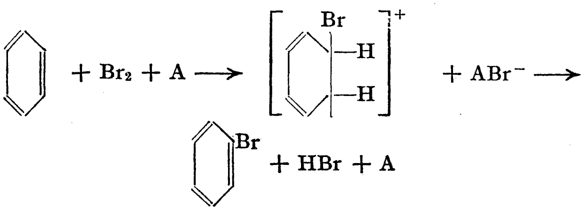


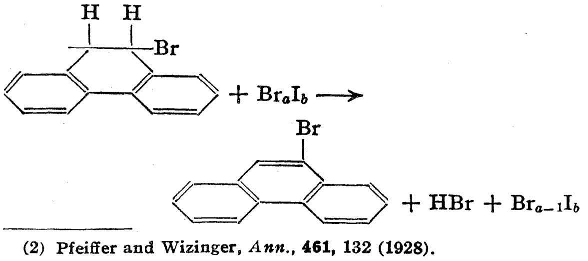
Fig. 2.—Rate of formation of 9-bromophenanthrene: ◓, phenanthrene, bromine and iodine (15:15:1); ○, phenanthrene dibromide and iodine (15:1); ◒, phenanthrene dibromide, bromine and iodine (15:1:1).

The only way to reconcile the experimental data with the addition–elimination theory is to suppose that iodine strongly catalyzes the elimination reaction, thus counteracting its inhibitory effect on the addition reaction. The fact that no hydrogen bromide was formed in the second experiment above might then be explained by supposing that the presence of bromine is essential. The identity of the rates in the first and third experiments, however, eliminates the possibility of direct action on phenanthrene dibromide (or phenanthrene) as the mechanism of the production of the hydrogen bromide since in either case the initial rate in one of the two experiments would have been zero. Thus an addition–elimination definitely does not seem to be involved.

Since solutions of phenanthrene dibromide are quite stable and only proceed to equilibrium on the addition of a small amount of bromine, and from the results of the second and third experiments above, it appears that the progress of the addition reaction is necessary to the catalytic effect. These facts, as well as the identity of the rate of hydrogen bromide formation starting with phenanthrene or the dibromide, seem to point to an intermediate radical, perhaps that of the addition reaction, as the molecular species influenced by the catalyst, since this would be present in approximately equal amounts in both experiments. The course of the reaction would then be quite similar to that proposed by Pfeiffer and Wizinger[2] for aromatic substitution. Taking the bromination of benzene as an example, they propose the mechanism



A being a catalyst for the reaction, perhaps a molecule of bromine itself. It seems more likely, at least in the case under investigation, that the intermediate is not a carbonium ion type but a free radical.



Due to lack of completely quantitative accuracy in the experimental method the exact values of the quantities *a* and *b* could not be determined. An indication of their probable value, however, can be obtained by a recalculation of experimental work of Bruner,[3] who has presented a detailed account of extensive kinetic measurements of the bromination of benzene with iodine as catalyst. Since excess benzene was used as the solvent, the rates were dependent only on the bromine and iodine concentrations. Bruner calculated rate constants of the second order with respect to bromine but was unable to derive any relation for their dependence on the iodine concentration. However, rate constants of the three-halves order with respect to bromine have been calculated from Bruner's data and found to be equally as good as his second order constants with the additional argument in their favor that the dependence on the iodine concentration now can be determined readily by assuming proportionality to the five-halves power, giving the following expression for the rate of bromination of benzene in benzene as solvent with iodine as catalyst

$$dx/dt = k[Br_2]^{3/2}[I_2]^{5/2}$$

Table I summarizes the results of these calculations with Bruner's second order constants included for comparison. If the substitution is considered to take place in two steps, it would then appear that, either according to the mechanism proposed by Pfeiffer and Wizinger with charged intermediates or with radicals as intermediates, the catalyst molecule is BrI_5. Further experimental work is contemplated to determine the exact kinetics of the reaction with phenanthrene in order to verify the identity of the kinetics for the bromination of benzene and phenanthrene.

TABLE I

RATE CONSTANTS FOR THE IODINE-CATALYZED BROMINATION OF BENZENE FROM BRUNER'S DATA

Table[a]	k_2	$[I_2]$, (M)	$k_{3/2}$, exptl.	$k_{3/2}$, calcd.[b]
1A	9.35	0.214	6.70	(6.70)
1B	2.70	.143	2.41	2.43
1C	1.15	.107	1.19	1.19
1D	0.54	.0856	0.65	0.67
2A	3.10	.144	2.54	2.50
2B	0.67	.0898	0.78	0.77
3A	.25	.0717	.38	.42
4D	1.35	.1002	.97	1.00

[a] Numbered as in Bruner's paper.[3] [b] Calculated from the relation $k_{3/2} = 6.70(0.214/[I_2])^{5/2}$.

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(2) Pfeiffer and Wizinger, *Ann.*, **461**, 132 (1928).

(3) Bruner, *Z. physik. Chem.*, **41**, 514 (1902).

Grateful acknowledgment is due Professor Louis F. Fieser for proposing the problem and for advice and criticism.

Summary

The effects of iodine on the phenanthrene-bromine reaction have been determined, and from an analysis of the results it is shown that the observations cannot be reconciled with the addition-elimination theory for aromatic substitutions.

SWARTHMORE, PA. RECEIVED AUGUST 14, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

High Vacuum Distillation of N-Acyl Amino Acid and Polypeptide Esters

BY SAMUEL GURIN[1]

An observation that certain N-benzenesulfonyl polypeptide esters suffer no apparent decomposition at temperatures appreciably above their melting points, suggested that such substances might be distilled satisfactorily under suitable conditions. Since Fischer's work upon the vacuum distillation of amino acid esters, very little further extension of this technique to N-acyl amino acid esters has been made; apparently no successful distillation of polypeptide derivatives of this type has been reported.

Acetylglycine ethyl ester,[2] as well as carbethoxyglycine and alanine ethyl esters[3] may be distilled easily. Muhlemann[4] attempted to apply this technique to several benzoylated amino acid esters, but observed considerable decomposition at a pressure of 2 mm. Cherbuliez[5] prepared a number of N-acetyl amino acid esters, and successfully distilled them, although considerable racemization accompanied the distillation of optically active compounds of this type.

It was found that butyl esters of benzenesulfonylated amino acids could be distilled without decomposition or racemization at pressures of 10^{-6}–10^{-7} mm. with the aid of a mercury vapor pump of the type described by Copley, Simpson, Tenney and Phipps.[6] In Table I are described the results obtained with a number of such compounds which were prepared in most cases by the method previously described by Gurin and Clarke.[7] Although butyl esters were first prepared in order to obtain greater stability (in contrast to methyl and ethyl esters),[8] this precaution was later found to be unnecessary since corresponding ethyl esters could be equally well distilled. Under these conditions distillation begins, in most cases, at temperatures ranging from 10 to 35° above the melting point. No racemization was observed to take place when optically active derivatives of this type were distilled. Thus, benzenesulfonyl-*l*-leucine butyl ester as well as di-benzenesulfonyl-*l*-tyrosine butyl ester showed no change in rotation after distillation. In Table I are listed the approximate distillation temperature ranges, as well as mixed melting points which were made with original and distilled material. Di-benzenesulfonyl-*d*-lysine butyl ester[9] distils extremely slowly, and at a temperature consid-

TABLE I

Substance	M. p., °C.[a]	Dist. temp.	Mixed m. p., °C.
$PhSO_2$-Glycine butyl ester[b]	26	50–55	25–26
$PhSO_2$-Alanine butyl ester[b]	114	120–125	113.5–114
$PhSO_2$-*l*-Leucine butyl ester[b,c]	51	68–73	50.5–51
$PhSO_2$-Phenylalanine butyl ester	107	120–125	106–107
N-$PhSO_2$-Serine butyl ester	55	70–75	55
$PhSO_2$-Methionine ethyl ester	45	75–80	45
Di-$PhSO_2$-*l*-tyrosine butyl ester	98	150–155	98
Di-$PhSO_2$-*d*-Lysine butyl ester	62	155–160	62
Dibutyl-$PhSO_2$-*d*-glutamate[b]	58–59	80–85	58
Dibutyl-$PhSO_2$-*i*-β-hydroxyglutamate[b]	74	95–100	73–74

[a] All temperatures are corrected. [b] Prepared according to method previously described.[7] [c] After distillation $[\alpha]^{25}_D$ −15.9° (1% in ethyl alcohol).

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(1) National Research Fellow in Biochemistry.

(2) T. Curtius, *Ber.*, **17**, 1672 (1884).

(3) E. Fischer and E. Otto, *ibid.*, **36**, 2106 (1903); E. Fischer and W. Axhausen, *Ann.*, **340**, 123 (1905).

(4) G. W. Muhlemann, *C. A.*, **22**, 1756 (1928).

(5) E. Cherbuliez and Pl. Plattner, *Helv. Chim. Acta*, **12**, 317 (1929).

(6) Copley, Simpson, Tenney and Phipps, *Rev. Sci. Instruments*, **6**, 265 (1935).

(7) S. Gurin and H. T. Clarke, *J. Biol. Chem.*, **107**, 395 (1934).

(8) E. Abderhalden and S. Suzuki, *Z. physiol. Chem.*, **176**, 101 (1928).

(9) The author wishes to acknowledge his indebtedness to Dr. Hans T. Clarke for furnishing a supply of this material.

erably higher than its melting point, while dibenzenesulfonyl-*l*-cystine diethyl ester does not distil but slowly decomposes at 185–200° yielding a colorless oily distillate.

In Table II are shown the results obtained with similar peptide derivatives. Again, ready distillation took place, although very little decomposition was observed. Successful distillation of N-benzenesulfonyl peptide ethyl esters indicates that it is unnecessary to prepare butyl esters for this purpose. Furthermore, carbethoxy peptide esters were found to be still more readily and rapidly distilled than their N-benzenesulfonyl analogs. For example, 0.2–0.3 g. of carbethoxyglycylglycine ethyl ester was distilled in approximately fifteen minutes at 95–100°.

Table II

Substance	M. p., °C.	Dist. temp., °C.	Mixed m. p., °C.
$PhSO_2$-Glycylalanine butyl ester[a]	101	120–125	100.5–101
$PhSO_2$-Glycylalanine ethyl ester	74	90–95	74
$PhSO_2$-Alanylglycine butyl ester[a]	76.5	100–105	75.5–76
$PhSO_2$-Glycyl-*l*-leucine butyl ester[a]	107	125–130	106.5
$PhSO_2$-Alanylalanine butyl ester	102	115–120	101
Carbethoxyglycylglycine ethyl ester	86	95–100	86
Carbethoxy-diglycylglycine ethyl ester	159	170–175	158–159
$PhSO_2$-Leucylglycylglycine ethyl ester	171	190–195	171

[a] Prepared by method previously described.[7]

Several artificial mixtures were fractionated by this method. Benzenesulfonyl-methionine ethyl ester was almost quantitatively separated from dibenzenesulfonyl-cystine diethyl ester by distillation at 75–95°, while the cystine component was left behind unchanged and undecomposed. Similarly, benzenesulfonyl-glycine butyl ester and benzenesulfonylalanine butyl ester were separated in pure form from a mixture of the two. From a mixture of carbethoxyglycylglycine ethyl ester and carbethoxydiglycylglycine ethyl ester, both components were separated easily in pure form as were the N-benzenesulfonyl butyl ester derivatives of glycylalanine and alanylglycine from a mixture of the two. Finally, benzenesulfonylleucylglycylglycine ethyl ester and benzenesulfonylglycylalanine ethyl ester were similarly separated. Recoveries of 90% or better were obtained in every case.

The application of this method to problems of protein structure is at present in progress.

Experimental

Benzenesulfonyl - *d,l* - alanylalanine Butyl Ester.—*d,l*-Alanylalanine was prepared according to Fischer and Kautzsch[10] (amino-N, 8.60; calcd. amino-N, 8.75). To 0.6 g. of the dipeptide dissolved in 10 cc. of water plus 1 cc. of 5 *N* sodium hydroxide were added with good stirring 1.4 g. of benzenesulfonyl chloride and 2 cc. of 5 *N* sodium hydroxide. The reaction mixture was kept just alkaline to thymolphthalein, and, after stirring for four hours, was acidified to Congo red with concentrated hydrochloric acid. The solution was extracted repeatedly with butyl alcohol and esterification carried out as previously described.[7] The ester crystallized as needles from ether and petroleum ether and weighed 0.569 g. (40%); m. p. 102°.

Anal. Calcd. for $C_{16}H_{24}O_5N_2S$: N, 7.86. Found: N, 8.02.

Benzenesulfonyl - glycyl - *d,l* - alanine Ethyl Ester.—Glycyl-*d,l*-alanine, prepared according to Fischer and Schulze,[11] was benzenesulfonylated as previously described.[7] The precipitate which separated out of the aqueous acid reaction mixture was filtered, dried and esterified by boiling for a few minutes with absolute ethyl alcohol previously saturated with dry hydrogen chloride gas. On evaporation of the alcoholic solution, followed by recrystallization from chloroform and petroleum ether, needles were obtained melting at 74°.

Anal. Calcd. for $C_{13}H_{18}O_5N_2S$: N, 8.90. Found: N, 8.93.

Benzenesulfonyl - *d,l* - leucylglycylglycine Ethyl Ester.—Two and forty-five hundredths grams of *d,l*-leucylglycylglycine prepared according to Fischer[12] (N, 17.30; calcd. 17.12) was dissolved in 10 cc. of *N* sodium hydroxide and treated with 3.5 g. of benzenesulfonyl chloride and 20 cc. of *N* sodium hydroxide; the reaction mixture was kept just alkaline to thymolphthalein. After stirring for three hours, a small amount of insoluble material was removed by filtration, and the filtrate acidified to Congo red with 5 *N* hydrochloric acid. The solution was concentrated *in vacuo* to dryness, and the residue extracted with 3–15 cc. portions of the hot methyl alcohol. After evaporating the methyl alcohol solution to dryness, the residue was suspended in 75 cc. of cold absolute ethyl alcohol previously saturated with dry hydrogen chloride gas, and boiled for a few minutes until a clear solution was obtained. The solution was concentrated *in vacuo* to approximately 10 cc. and, after chilling, the ester was obtained in the form of small bars. A further crop was obtained by addition of petroleum ether to the mother liquor. After recrystallization from hot absolute alcohol, the product weighed 2.51 g. (61% yield); m. p. 171°. *Anal.* Calcd. for $C_{18}H_{27}O_6N_3S$: N, 10.16. Found: N, 10.27.

Carbethoxyglycylglycine Ethyl Ester.—Prepared according to Fischer and Fourneau;[13] m. p. 86°; N, 12.20; calcd. for $C_9H_{16}O_5N_2$: N, 12.07.

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(10) E. Fischer and K. Kautzsch, *Ber.*, **38**, 2375 (1905).

(11) E. Fischer and A. Schulze, *ibid.*, **40**, 946 (1907).

(12) E. Fischer, *ibid.*, **38**, 605 (1905).

(13) E. Fischer and E. Fourneau, *ibid.*, **34**, 2868 (1901).

Carbethoxydiglycylglycine Ethyl Ester.—Carbethoxydiglycylglycine was prepared according to the method described by Fischer;[14] m. p. 208–209°; N, 16.02; calcd. for $C_9H_{15}O_6N_3$: N, 16.08. The ester was obtained by treatment with absolute ethyl alcohol and dry hydrogen chloride; the solution obtained after boiling for a few minutes, was concentrated *in vacuo* to a small volume and the ester precipitated by addition of ether. On recrystallization from hot absolute alcohol, needles were obtained melting at 159°: N, 14.44; calcd. for $C_{11}H_{19}O_6N_3$, N, 14.53. This ester was prepared by Fischer[15] using a different method of synthesis.

Dibenzenesulfonylcystine Diethyl Ester.—Dibenzenesulfonylcystine was prepared according to the method described by Fruton and Clarke;[16] m. p. 208°. The diethyl ester was obtained by suspending in absolute ethyl alcohol and saturating with dry hydrogen chloride. After refluxing for ten minutes, the clear solution was concentrated *in vacuo* to dryness, and the residue recrystallized from hot ethyl acetate. The ester (tufts of needles) melted at 121°: N, 4.96; S, 22.40; calcd. for $C_{22}H_{28}O_8N_2S_4$, N, 4.86; S, 22.22.

Benzenesulfonyl-*d,l*-phenylalanine Butyl Ester.—This was prepared from benzenesulfonyl-*d,l*-phenylalanine by vacuum distillation in the presence of excess butyl alcohol by the general method described by Gurin and Clarke.[7] The product is obtained in the form of needles after recrystallization from ether and petroleum ether: m. p. 107°; N, 3.95; calcd. for $C_{19}H_{23}O_4NS$, N, 3.88.

***N*-Benzenesulfonyl-*d,l*-serine Butyl Ester.**—After esterifying in the same manner with butyl alcohol, needles are obtained from ether and petroleum ether, m. p. 55°; N, 4.78; calcd. for $C_{13}H_{19}O_5NS$, N, 4.65.

Dibenzenesulfonyl-*l*-tyrosine Butyl Ester.—Obtained as needles from ethyl acetate and petroleum ether or from amyl ether; m. p. 98°; N, 2.74; calcd. for $C_{25}H_{27}O_7NS_2$, N, 2.72. $[\alpha]^{26}_D$ +20.1° (1% in ethyl alcohol). After distillation $[\alpha]^{26}_D$ +20.2°.

Benzenesulfonyl-*d,l*-methionine Ethyl Ester.—Prepared from benzene-sulfonyl-*d,l*-methionine by treatment with absolute ethyl alcohol and dry hydrogen chloride gas. The product crystallizes from ether and petroleum ether as tufts of fine needles; m. p. 45°; N, 4.60; calcd. for $C_{13}H_{19}O_4NS_2$, N, 4.41.

Separation of Dibenzenesulfonylcystine Diethyl Ester and Benzenesulfonyl-*d,l*-methionine Ethyl Ester.—From a mixture containing 50 mg. of dibenzenesulfonylcystine diethyl ester and 50 mg. of benzenesulfonyl-*d,l*-methionine ethyl ester, 49 mg. of the methionine derivative was recovered by high vacuum distillation at a temperature range of 75–95°. The benzenesulfonyl-*d,l*-methionine ethyl ester so recovered, melted at 45°; N, 4.50; calcd. for $C_{13}H_{19}O_4NS_2$, N, 4.41. The dibenzenesulfonylcystine diethyl ester remained in the distillation bulb unchanged; m. p. 120–121°.

Benzenesulfonylglycine Butyl Ester and Benzenesulfonyl-*d,l*-alanine Butyl Ester.—A mixture containing 100 mg. of benzenesulfonylglycine butyl ester and 85 mg. of benzenesulfonyl-*d,l*-alanine butyl ester was similarly subjected to high vacuum distillation. On heating to 50–75°, 98 mg. of a colorless oil was recovered, which crystallized on chilling and proved to be benzenesulfonylglycine butyl ester; m. p. 26°; N, 5.01; calcd. for $C_{12}H_{17}O_4NS$, N, 5.16. Upon raising the temperature to 125–135°, 81 mg. of benzenesulfonyl-*d,l*-alanine butyl ester was recovered; m. p. 113.5–114°; N, 4.78; calcd. for $C_{13}H_{19}O_4NS$, N, 4.91.

Carbethoxydiglycylglycine Ethyl Ester and Carbethoxyglycylglycine Ethyl Ester.—A mixture was made up consisting of 35.0 mg. of carbethoxyglycylglycine ethyl ester and 27.0 mg. of carbethoxydiglycylglycine ethyl ester. After distilling at 95–115° for one hour, a first fraction was recovered weighing 34.8 mg. and melting at 86°; N, 12.02; calcd. for $C_9H_{16}O_5N_2$, N, 12.07. The product obviously was pure carbethoxyglycylglycine ethyl ester.

A second fraction weighing 24.1 mg. was obtained at 175–185°, and appeared to be pure carbethoxydiglycylglycine ethyl ester; m. p. 158–159°; N, 14.35; calcd. for $C_{11}H_{19}O_6N_3$, N, 14.53. The remaining few mg. was accounted for by a small amount of decomposed material in the distilling bulb.

Benzenesulfonyl-*d,l*-leucylglycylglycine Ethyl Ester and Benzenesulfonyl-glycyl-*d,l*-alanine Ethyl Ester.—In a similar manner, a mixture consisting of 75.4 mg. of benzenesulfonyl-glycyl-*d,l*-alanine ethyl ester and 54.1 mg. of benzenesulfonyl-*d,l*-leucylglycylglycine ethyl ester was fractionated. At 90–110° a colorless oil was obtained weighing 70.3 mg.; after chilling, crystals were obtained melting at 74°, thereby indicating the product to be benzenesulfonyl-glycylalanine ethyl ester; N, 9.08; calcd. for $C_{13}H_{18}O_5N_2S$, N, 8.90.

The second fraction, obtained at 190–200°, weighed 48.5 mg. and appeared to consist of pure benzenesulfonylleucylglycylglycine ethyl ester; m. p. 171°; N, 10.25; calcd. for $C_{18}H_{27}O_6N_3S$; N, 10.16.

Summary

N-Benzenesulfonyl amino acid esters have been distilled at pressures of 10^{-6}–10^{-7} mm. No racemization and very little decomposition were observed under the conditions described.

A number of N-benzenesulfonyl di- and tripeptide esters were prepared and similarly distilled without decomposition. Carbethoxy peptide esters may likewise be distilled.

Several artificial mixtures containing N-acyl amino acid, dipeptide and tripeptide esters were fractionated by this method. In every case reported, the individual components were isolated in pure form, and in yields corresponding to 90% or more.

URBANA, ILLINOIS RECEIVED AUGUST 10, 1936

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(14) E. Fischer, *Ber.*, **36**, 2982 (1903).

(15) E. Fischer, *ibid.*, **36**, 2094 (1903).

(16) J. Fruton and H. T. Clarke, *J. Biol. Chem.*, **106**, 667 (1934).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Helianthates of Amino Acid and Polypeptide Esters

BY SAMUEL GURIN[1] AND C. F. SEGAL

Sulfonic acid salts of amino acid and polypeptide esters have been infrequently described, or prepared for the characterization of such substances. Colombano[2] reported the preparation of the *d*-camphor-10-sulfonates and *d*-bromocamphorsulfonates of glycine and alanine ethyl esters. In addition to their mineral acid salts, the tartrates and picrates of amino acid esters have been described.[3] The preparation of helianthates of a number of bases by Dehn,[4] as well as the use of helianthin by Williams[5] for the removal of bases from aqueous solution, suggested the possible application of this method to the characterization of amino acid and polypeptide esters.

It was found that such salts could be prepared by the addition of methyl orange to amino acid ester hydrochlorides in aqueous solution (Table I). Orange colored crystalline precipitates of low solubility in water were obtained in yields ranging from 65–95%. These substances were generally recrystallized from hot water, alcohol or aqueous acetone; they are sparingly soluble in ether, chloroform and other organic solvents.

$$\mathrm{RCH(NH_2)COOR{\cdot}HCl + (CH_3)_2NC_6H_4N_2C_6H_4SO_3Na \longrightarrow RCH(NH_2)COOR{\cdot}(CH_3)_2NC_6H_4N_2C_6H_4SO_3H + NaCl}$$

Similar salts likewise may be prepared by the addition of helianthin to the free esters in appropriate solvents. This method has been employed only with butyl esters since they show considerably less tendency to form piperazines than do their corresponding methyl and ethyl esters.[6] For this purpose, several amino acids and peptides were esterified successfully at temperatures below 55° by prolonged vacuum distillation in the presence of a continuous excess of butyl alcohol containing just enough mineral acid for neutralization of the amino groups. The free esters were liberated with sodium hydroxide and sodium carbonate, followed by extraction with ether; after drying, and evaporating *in vacuo*, the residual sirup was usually dissolved in aqueous acetone and converted to the helianthate by the addition of an equivalent amount of helianthin.

Similar well crystallized salts are obtained with peptide esters (Table II). In these cases, hot aqueous solutions of methyl orange were added in equivalent proportion to cold and well-stirred aqueous solutions of peptide ester hydrochlorides.

In general, all of the helianthates are orange in color, and decompose over a narrow temperature range upon heating; in most cases darkening and gas formation were observed before the salts melted.

Colorimetric helianthin estimations were carried out in 50% aqueous acetic acid against helianthin standards dissolved in the same solvent. Concentrations of approximately 10^{-5} molar were used, since readings can be taken quite easily at this strength. The analytical figures given in the tables were obtained with a "Step" photometer equipped with an appropriate light filter, or with a K. and E. color analyzer using monochromatic light at 5100 Å.

In Table III are listed helianthates prepared from esters having one or more functional basic groups. It will be observed that lysine, histidine, arginine and cystine esters, as well as α-glycyllysine methyl ester,[7] form di-helianthates whereas ϵ-carbobenzoxylysine ester[7] yields a mono-helianthate. Within limits, therefore, colorimetric estimation of helianthin in such compounds affords another method for the titration of combining basic groups.

Guanidine salts are rapidly and almost completely precipitated from aqueous solution by methyl orange. It is interesting to note that free amino acids and polypeptides as well as their N-acyl derivatives do not yield similar products; cystine hydantoic acid and 5-methylhydantoin likewise failed to react.

Although helianthates of volatile bases have been decomposed by heating at temperatures sufficiently high to produce appreciable dissociation,[8] this method of recovering the base appar-

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[1] National Research Fellow in Biochemistry.

[2] (a) A. Colombano and G. Lama, *Atti accad. Lincei*, **22**, 234 (1914); A. Colombano, G. Sanna and I. Delitala, *Gazz. chim. ital.*, **44**, 97 (1914).

[3] E. Fischer, *Ber.*, **34**, 433 (1901).

[4] Dehn, THIS JOURNAL, **39**, 1348, 1377 (1917); **40**, 1573 (1918).

[5] R. R. Williams, R. E. Waterman and J. C. Keresztesy, *ibid.*, **56**, 1187 (1934).

[6] E. Abderhalden and S. Suzuki, *Z. physiol. Chem.*, **176**, 101 (1928).

[7] The authors wish to acknowledge their indebtedness to Dr Max Bergmann and Dr. W. F. Ross for kindly supplying samples of these compounds.

[8] Hantzsch, *Ber.*, **41**, 1187 (1908).

TABLE I

Helianthates	Formula	M. p., dec., °C.	Crystal shape	Helianthin, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found
Glycine ethyl ester	$C_4H_9O_2N\cdot(C_{14}H_{15}O_3N_3S)$	203.0	Blocks	74.7	78.0	13.72	13.55
Alanine ethyl ester	$C_5H_{11}O_2N\cdot(C_{14}H_{15}O_3N_3S)$	211.5	Needles	72.3	73.5	13.27	13.38
l-Leucine ethyl ester	$C_8H_{17}O_2N\cdot(C_{14}H_{15}O_3N_3S)$	210.5	Needles	65.7	65.5	12.07	11.86
Phenylalanine ethyl ester	$C_{11}H_{15}O_2N\cdot(C_{14}H_{15}O_3N_3S)$	210.0	Bars	61.5	62.7	11.24	11.44
l-Tyrosine ethyl ester	$C_{11}H_{15}O_3N\cdot(C_{14}H_{15}O_3N_3S)$	209.0	Blocks	59.3	62.5	10.89	10.72
Methionine ethyl ester	$C_7H_{15}O_2NS\cdot(C_{14}H_{15}O_3N_3S)$	210.5	Needles	63.3	68.1	11.62	11.53
Alanine butyl ester	$C_7H_{15}O_2N\cdot(C_{14}H_{15}O_3N_3S)$	201.5	Needles	67.8	68.1	12.44	12.64
d-Glutamic dibutyl ester	$C_{13}H_{25}O_4N\cdot(C_{14}H_{15}O_3N_3S)$	199.0	Bars	54.1	56.1	9.93	9.95

TABLE II

Helianthates	Formula	M. p., dec., °C.	Crystal shape	Helianthin, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found
Glycylglycine ethyl ester	$C_6H_{12}O_3N_2\cdot(C_{14}H_{15}O_3N_3S)$	210	Plates	65.6	66.0	15.05	15.09
Glycyl-*l*-leucine ethyl ester	$C_{10}H_{20}O_3N_2\cdot(C_{14}H_{15}O_3N_3S)$	216	Prisms	58.5	59.7	13.43	13.60
Alanylalanine butyl ester	$C_{10}H_{20}O_3N_2\cdot(C_{14}H_{15}O_3N_3S)$	210	Needles	58.5	59.1	13.43	13.32
Glycylalanine butyl ester	$C_9H_{18}O_3N_2\cdot(C_{14}H_{15}O_3N_3S)$	...	Blocks	60.2	59.6	13.80	13.71
Alanylglycine butyl ester	$C_9H_{18}O_3N_2\cdot(C_{14}H_{15}O_3N_3S)$	210	Plates	60.2	63.0	13.80	13.93
Diglycylglycine ethyl ester	$C_8H_{15}O_4N_3\cdot(C_{14}H_{15}O_3N_3S)$	215	Plates	58.4	58.1	16.09	15.85
Leucylglycylglycine ethyl ester	$C_{12}H_{23}O_4N_3\cdot(C_{14}H_{15}O_3N_3S)$	187	Blocks	52.8	54.6	14.53	14.35

TABLE III

Substance	Formula	M. p., °C.	Crystal shape	Helianthin, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found
d-Lysine methyl ester di-helianthate	$C_7H_{16}O_2N_2\cdot2(C_{14}H_{15}O_3N_3S)$	242.5	Needles	79.2	78.3	14.54	14.43
ε-Carbobenzoxy-*d*-lysine methyl ester helianthate	$C_{15}H_{22}O_4N_2\cdot(C_{14}H_{15}O_3N_3S)$	183.0	Plates	50.9	50.6	11.68	11.70
α-Glycyl-*d*-lysine methyl ester di-helianthate	$C_9H_{19}O_3N_3\cdot2(C_{14}H_{15}O_3N_3S)$	232.5	Plates	73.8	75.5	15.23	15.16
l-Cystine diethyl ester di-helianthate	$C_{10}H_{20}O_4N_2S_2\cdot2(C_{14}H_{15}O_3N_3S)$	212.0	Bars	67.3	70.1	12.36	12.20
l-Histidine methyl ester di-helianthate	$C_7H_{11}O_2N_3\cdot2(C_{14}H_{15}O_3N_3S)$	221.0	Bars	78.3	76.3	16.17	16.05
d-Arginine methyl ester di-helianthate	$C_7H_{16}O_2N_4\cdot2(C_{14}H_{15}O_3N_3S)$	229.5	Blocks	76.4	77.0	17.54	17.65
Guanidine helianthate	$CH_5N_3\cdot(C_{14}H_{15}O_3N_3S)$	270.0	Needles	83.8	84.9	23.07	23.08

ently cannot be applied to the more heat stable amino acid ester helianthates; alanine butyl ester could not be recovered by dry distillation of the helianthate. A satisfactory method of recovery involves acidification of an alcoholic solution of the salt with dry hydrogen chloride. A very small amount of acid is generally sufficient to precipitate the greater part of the helianthin, leaving the ester hydrochloride in solution. Glycine ethyl ester hydrochloride was recovered in this manner from its helianthate in a yield of 79%. Attempts to decompose helianthates with alkali, followed by extraction with ether, have in several cases resulted in poor recovery of the amino acid esters.

Preliminary experiments indicate that salts of similar sparing solubility in water are apparently formed by Congo red, although this reagent appears to offer no advantage over methyl orange. Furthermore, ethane sulfonic, *n*-butane-sulfonic, benzyl-sulfonic, *m*-nitrobenzenesulfonic and *d*-camphor-10-sulfonic acids were found to yield hygroscopic and extremely water soluble sulfonates of amino acid and polypeptide esters. These substances were not investigated further.

Experimental

Glycine Ethyl Ester Helianthate.—To 10 cc. of a chilled aqueous solution of 1.39 g. of glycine ethyl ester hydrochloride was added with good stirring and cooling, 75 cc. of a hot water solution containing 3.27 g. of methyl orange. After stirring for twenty minutes, a heavy orange precipitate was filtered and washed several times with cold water. The product after recrystallization from hot methyl alcohol weighed 3.2 g. (78%). It may also be recrystallized from hot water.

Dibutyl-*d*-glutamate Helianthate.—To a solution of 5 g. of *d*-glutamic acid in 20 cc. of water containing 2 cc. of concentrated sulfuric acid, 100 cc. of butyl alcohol was added, and the material subjected to prolonged vacuum distillation at a temperature not higher than 55°. Butyl alcohol was added from time to time as required, and distillation continued for eight to ten hours, although esterification is practically complete in four to five hours. After removal of excess butyl alcohol by vacuum distillation, the residual yellow oil was dissolved in 20 cc. of cold water, made alkaline, and the butyl ester extracted into ether by the usual Fischer method. From the ether solution, 7.445 g. (84%) of the ester was obtained as a yellow oil. It was then dissolved in 50 cc. of 50% aqueous acetone, and a solution of 8.7 g. of helianthin in 100 cc. of the same solvent added. On evaporation to approximately 75 cc., a heavy precipitate of orange needles was filtered, and washed with 50 cc. of cold water. After recrystallization from hot methyl alcohol (1 g. requires 40 cc. boiling alcohol), 11.83 g. of helianthate was obtained (75% from ester). The product is sparingly soluble in cold water, ether or petroleum ether, but somewhat more so in acetone, aqueous acetone, and hot methyl alcohol, dioxane or water.

***d,l*-Alanine Butyl Ester Helianthate.**—Alanine (5 g. in 50 cc. of water containing 3.5 cc. concentrated sulfuric acid) was converted to its butyl ester sulfate by vacuum distillation in the presence of excess butyl alcohol as described above. From this material, 4.37 g. of free ester was obtained and converted to the helianthate by the addition of 9.2 g. of helianthin in aqueous acetone solution. After recrystallization from hot alcohol, the salt weighed 10.45 g. (77% from ester).

Methionine Ethyl Ester Helianthate.—Methionine ethyl ester hydrochloride was prepared from synthetic methionine with absolute ethyl alcohol and dry hydrogen chloride gas; it was recrystallized from alcohol and ether; m. p. 212° dec., N, 6.61; calcd. for $C_7H_{16}O_2NSCl$, N, 6.55. To a solution of 1 g. of methionine ethyl ester hydrochloride in 10 cc. of cold water, was added 1.5 g. of methyl orange in 25 cc. of hot water. After stirring and cooling for thirty minutes, the precipitate was filtered, washed with cold water and recrystallized from boiling methyl alcohol (1 g. requires 150 cc. of methyl alcohol). The product weighed 1.8 g. (81%).

Glycylglycine Ethyl Ester Helianthate.—Ninety-eight hundredths gram of glycylglycine ethyl ester hydrochloride prepared according to Fischer and Fourneau[9] (m. p. 181–182°), was dissolved in 5 cc. of cold water, and a solution of 1.63 g. of methyl orange in 25 cc. of hot water added with good stirring and chilling. The precipitate was filtered, washed with cold water and, after recrystallization from boiling alcohol, weighed 1.97 g. (85%).

Glycyl-*l*-leucine Ethyl Ester Helianthate.—Glycyl-*l*-leucine ethyl ester hydrochloride was prepared in the usual way from glycyl-*l*-leucine.[10] The product is appreciably soluble in alcohol from which it may be precipitated by 2–3 volumes of ether in the form of glistening plates; m. p. 163–164°; N, 11.20; calcd. for $C_{10}H_{21}O_3N_2Cl$, N, 11.09. The helianthate was obtained as described above in 92% yield after recrystallization from hot ethyl alcohol.

Guanidine Helianthate.—To a solution of 2 g. of guanidine sulfate in 50 cc. of water was added with stirring a hot solution of 6.1 g. of methyl orange in 150 cc. of water. After filtering and washing with water, the precipitate was recrystallized from 800 cc. of boiling water. The product weighed 6.35 g. (95%).

Glycine Ethyl Ester Hydrochloride from Glycine Ethyl Ester Helianthate.—Two-tenths gram of glycine ethyl ester helianthate was dissolved in 100 cc. of hot absolute ethyl alcohol and acidified with a small amount of dry hydrogen chloride gas producing an almost immediate precipitate of helianthin. After cooling, the helianthin was removed by filtration, and the alcoholic solution concentrated *in vacuo* to a volume of 10 cc. On chilling, glycine ethyl ester hydrochloride was obtained, and, after recrystallization from 10–15 cc. of hot absolute alcohol, weighed 0.0539 g. (78.9%); m. p. 142°. A mixed m. p. with synthetic glycine ethyl ester hydrochloride showed no depression.

Summary

By the addition of methyl orange to amino acid and polypeptide ester hydrochlorides, crystalline helianthates have been prepared. These salts are non-hygroscopic and sufficiently insoluble in water to serve as a convenient means for isolating or characterizing amino acid and polypeptide esters. Similar salts may likewise be prepared by the addition of helianthin to the free esters.

Butyl esters of amino acids and polypeptides may be prepared conveniently by vacuum distillation with excess butyl alcohol containing small amounts of mineral acid.

Amino acids and polypeptides do not yield similar products; guanidine forms a characteristic helianthate having a low solubility in water.

Colorimetric estimations of helianthin in these salts have been carried out in 50% aqueous acetic acid, thereby furnishing a simple method for the titration of combining basic groups as well as analysis of the substances. Lysine, histidine, arginine and cystine esters have been found to form di-helianthates.

A method is described for the recovery of ester hydrochlorides from their helianthates.

URBANA, ILLINOIS RECEIVED AUGUST 10, 1936

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[9] Fischer and Fourneau, *Ber.*, **34**, 2868 (1901).

[10] Fischer and Steingroever, *Ann.*, **365**, 167 (1909).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Action of Alkalies on Mixtures of Aromatic Aldehydes

BY JOHN C. BAILAR, JR., ALLAN J. BARNEY AND R. F. MILLER

It has been shown[1] that a crossed Cannizzaro reaction may take place between two aliphatic aldehydes or an aromatic and an aliphatic aldehyde. This paper reports some experiments which demonstrate that a crossed Cannizzaro reaction may also take place between two aromatic aldehydes.

The first experiments undertaken were directed toward carrying out such a reaction between benzaldehyde (which undergoes the Cannizzaro reaction readily) and *p*-dimethylaminobenzaldehyde (which does not react under the conditions of our experiments). That the reaction might take place seemed logical in view of Staudinger's discovery[2] that both benzaldehyde and *p*-chlorobenzaldehyde form mixed benzoins with *p*-dimethylaminobenzaldehyde although *p*-dimethylaminobenzaldehyde alone does not undergo the benzoin condensation. It was found, however, that the *p*-dimethylaminobenzaldehyde could be recovered unchanged, the benzaldehyde reacting in the normal manner. Likewise, when a mixture of benzaldehyde and *m*-nitrobenzaldehyde was stirred with 14% potassium hydroxide, only the *m*-nitrobenzaldehyde seemed to react. Benzaldehyde undergoes the Cannizzaro reaction readily with concentrated alkali but will not react in a solution of this concentration.

When a mixture of *p*-chlorobenzaldehyde and anisaldehyde was allowed to react with alkali, a definite disproportionation took place. This discovery led to a study of several mixtures containing halogen substituted benzaldehydes, the results of which are summarized in Table I. In every case a crossed Cannizzaro reaction took place. In two cases (numbers 7 and 14) the individual acids were separated from their mixtures, but in most cases the mixtures were simply analyzed for halogen and the composition of the mixture calculated. Experiments 1, 2 and 8 were carried out under different conditions than the rest.

The analysis of the alcohol mixtures containing benzyl alcohol did not give consistent results. This evidently is due to the volatility of benzyl alcohol, which makes it difficult to free the alcohol mixture from ether and water without losing benzyl alcohol, and so altering the composition of the mixture. On this account, the analyses for the alcohol mixtures obtained from meta- and para-bromobenzaldehyde with benzaldehyde are not reported, and the results in these cases must be considered as tentative.

While the data are insufficient to allow any theoretical deductions, they indicate plainly that crossed Cannizzaro reactions can take place with mixtures of aromatic aldehydes. It is interesting to note that in every case the halogen substituted aldehyde is preferentially oxidized at the expense of the other aldehyde.

Experimental

Benzaldehyde and *p*-Dimethylaminobenzaldehyde.—A mixture of five grams of each of the aldehydes was shaken vigorously with 20 g. of a 50% solution of potassium hydroxide for two hours and allowed to stand for twenty-four hours. The mixture was diluted with 300 cc. of water, and extracted with three 40-cc. portions of ether. The ether extract was shaken with a saturated solution of sodium bisulfite (which precipitated part of the dimethylaminobenzaldehyde as the bisulfite addition product) and was then distilled. The fraction boiling between 200–206° was taken as benzyl alcohol. The yield was 2.2 g. (88% of the theoretical). The residue from the distillation solidified on cooling. After recrystallization, this solid melted at 73°. *p*-Dimethylaminobenzaldehyde melts at 74°. The recovery of the substituted aldehyde from the bisulfite compound and from the distillation was almost quantitative.

The aqueous residue from the ether extraction was acidified, and the precipitated benzoic acid was filtered off. It melted at 121° and weighed 2.1 g. (84% yield). The filtrate was neutralized carefully, but no *p*-dimethylaminobenzoic acid could be obtained.

Benzaldehyde and *m*-Nitrobenzaldehyde.—A mixture of 18.1 g. of *m*-nitrobenzaldehyde and 13.7 g. benzaldehyde was allowed to drip into 280 g. of a 14% solution of potassium hydroxide with vigorous stirring. After standing for twenty-four hours, the solution was diluted and extracted with ether as before. Treatment with sodium bisulfite resulted in the recovery of 11.9 g. of unchanged aldehydes, practically all of which was benzaldehyde. The aqueous residue from the ether extractions was acidified, and the copious precipitate of acid steam distilled. No benzoic acid was present in the distillate, as was shown by extracting it with ether and evaporating the extract.

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[1] Nord, *Biochem. Z.*, **106**, 275 (1920); *Beitrage Physiol.*, **2**, 301 (1924); Nakai, *Biochem. Z.*, **152**, 258 (1924); Endoh, *Rec. trav. chim.*, **44**, 866 (1925); Orloff, *Bull. soc. chim.*, [4] **35**, 360 (1924); Nenitzescu and Gavat, *Bull. soc. chim. Romania*, **16A**, 42 (1934) (*British Chemical Abstracts*, 74 (1936)); Davidson and Bogert, THIS JOURNAL, **57**, 905 (1935).

[2] Staudinger, *Ber.*, **46**, 3535 (1913).

TABLE I

Substituted benzaldehydes	Expt.	Ratios: Halo acid to other acid				Ratios: Halo alcohol to other alcohol			
p-Chloro- and *p*-methoxy-	1, 2, 3, 4	2.3:1	2.3:1	1.6:1	1.6:1	1:2.7	1:2.5	1:2.0	....
p-Chloro- and benz-	5, 6, 7, 8	1.45:1	1.3:1	1.7:1	2.5:1	1:1.3	1:1.3	....	1:2.8
p-Chloro- and (*m*,*p*-methylenedioxy)-	9			1.8:1					1:1.95
p-Bromo- and *p*-methoxy-	10, 11			2.3:1	2.8:1			1:1.8	1:2.1
p-Bromo- and benz-	12, 13, 14		1.4:1	1.3:1	1.2:1				
m-Bromo- and *p*-methoxy-	15, 16			1.9:1	1.7:1			1:1.8	1:2.0
m-Bromo- and benz-	17, 18, 19		2.4:1	2.1:1	2.2:1				

Procedure for Experiments Recorded in Table I (Except Numbers 1, 2 and 8).—A mixture of the two aldehydes (0.05 mole of each) was allowed to drop slowly into a solution of 27.5 g. of potassium hydroxide in 25 cc. of water with vigorous stirring. When the addition was complete, the temperature was raised slowly to 100° and held at that point for two hours. The solution was diluted to 400 cc. and extracted with four portions of ether. The ether extracts were combined, treated with bisulfite (which in no case gave more than 0.1 g. of precipitate), washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was analyzed for halogen by decomposition in the Parr bomb and titration by the Volhard method. The aqueous residue from the ether extractions was acidified with hydrochloric acid, and extracted with four portions of ether. The ether solutions were dried and evaporated and the residue analyzed as described for the alcohols.

Procedure for Experiments 1, 2 and 8 of Table I.—A mixture of five grams of each aldehyde, 10 g. of potassium hydroxide, and 10 cc. of water was shaken vigorously for two hours and allowed to stand a day. The remainder of the procedure was the same as that described above.

In Experiments 7 and 14 the acids were separated by steam distillation. This does not give a sharp separation of *p*-chlorobenzoic acid and benzoic acid, so the ratio given in Experiment 7 is only approximate. The separation of *p*-bromobenzoic acid and benzoic acid is very good, however, the recovered acids melting at 249 and 120° (reported, 251–253 and 122°).

Summary

It has been shown that 50% potassium hydroxide solution, acting on a mixture of benzaldehyde and *p*-dimethylaminobenzaldehyde induces the Cannizzaro reaction for the benzaldehyde only. The other aldehyde is not affected. A mixture of *m*-nitrobenzaldehyde and benzaldehyde, under the action of 14% potassium hydroxide, gives nitrobenzoic acid and nitrobenzyl alcohol, without attacking the benzaldehyde.

Seven reactions have been studied in which a crossed Cannizzaro reaction takes place between aromatic aldehydes. One member of the aldehyde pair in each of these was halogen substituted, and in every case, the halogen substituted molecule showed a tendency to be oxidized to the acid at the expense of the other aldehyde.

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Dipole Moment and Structure of Organic Compounds. XVI.[1] The Electric Moments of Some Chlorinated Diphenyls

BY G. C. HAMPSON AND A. WEISSBERGER

It has been suggested[2] that the electric moments of mono- and dichloronaphthalenes indicate a polarization of the naphthalene system by the polar C–Cl link, this polarization causing the observed moments to deviate considerably from those calculated when this effect is neglected, and a similar behavior has been found with the chlorodiphenyls. In the case of the dichlorodiphenyls with substituents in *both* rings, in either the ortho or meta position, a further complication is introduced, for there the moment will depend primarily on the configuration of the two rings about the diphenyl link. In view of the forces which govern the probability of the various configurations, special attention has been drawn to the case of *o*,*o*′-dichlorodiphenyl. The moment of this compound is larger than that of the *m*,*m*′-isomeride, and this is even more surprising in view of the fact that in the *o*,*o*′-compound the *cis*-configuration and a wide range of positions in the neighborhood of the *cis*-position which would contribute to a large moment are precluded for steric reasons. To account for the facts we suggested that *London forces* play an important role in determining the inner configuration of the molecule.

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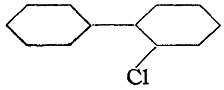
(1) Hampson and Weissberger, Paper XV, *J. Chem. Soc.*, 393 (1935).

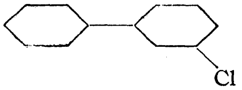
(2) Weissberger, Sängewald and Hampson, *Trans. Faraday Soc.*, **30**, 884 (1934).

In the preceding paper[1] the polarization effect in the case of the chloronaphthalenes has been treated quantitatively. The present paper deals in a similar way with the three monochlorodiphenyls, and also attempts to give a quantitative treatment of the factors governing rotation about the diphenyl link in the case of the *o,o'*- and *m,m'*-dichlorodiphenyls.

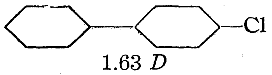
The moments of the compounds under consideration have been redetermined to obtain consistent data of sufficient accuracy. They are



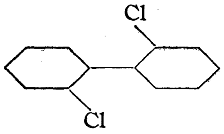
1.45 *D*



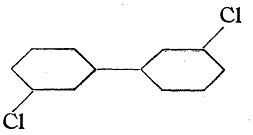
1.64 *D*



1.63 *D*



1.91 *D*



1.80 *D*

In calculating the polarizing influence of the C–Cl bond, each of the monochlorodiphenyls has been regarded as a chlorobenzene molecule to which a polarizable benzene ring has been attached, the method of calculation following precisely as in the case of the monochloronaphthalenes.[1] Each of the rings has been assumed to be a regular hexagon of side 1.4 Å.,[3] the length of the internuclear C–C bond being taken as 1.48 Å.[4] The substituted chlorine atom has been assumed to be directed as from the center of the ring and μ_{C-Cl} has been taken as 1.55 *D*.[5] Since a benzene molecule is more polarizable in the plane of the ring than perpendicular to the ring, the magnitude of the polarization in the case of the chlorodiphenyls will vary with the relative configurations of the two rings.

Table I gives the calculated moments for *o*-, *m*- and *p*-monochlorodiphenyl (a) when the rings are co-planar, (b) when they are mutually perpendicular, (c) when there is free rotation, the polarizability of a benzene ring in the plane of the ring being taken as 12.5×10^{-24} and perpendicular to the ring 6.2×10^{-24}.[6]

TABLE I

	Rings co-planar	Rings perpendicular	Free rotation
o-Chlorodiphenyl	1.31	1.40	1.355
m-Chlorodiphenyl	1.601	1.604	1.603
p-Chlorodiphenyl	1.64	1.64	1.64

The results are in quite good agreement with the experimentally determined values, especially as one would expect that in *o*-chlorodiphenyl there would be a tendency for the rings to be perpendicular for steric reasons. An obvious cause of the small discrepancies is the fact that the moment 1.55 of chlorobenzene has been assumed to be located solely in the C–Cl bond, whereas part of it is certainly spread over the rest of the molecule.

In dealing with the *o,o'*- and *m,m'*-dichlorodiphenyls the most important factor in deciding the resultant moment of the molecules is the disposition of the two rings about the diphenyl link. The forces which regulate the probabilities of the various configurations are (a) electrostatic repulsions and attractions, (b) quantum mechanical attractions (London forces), (c) quantum mechanical repulsions (impenetrability of colliding atoms).

In the calculation of these forces the authors have enjoyed the help of Dr. F. London and they acknowledge with sincere thanks his valuable assistance.

Suppose that in any molecule the two rings are oriented about the diphenyl link so that the angle between their planes is ϕ; if now the component moment of each of the two C–Cl bonds perpendicular to the axis of rotation is μ'

$$\text{the resulting moment of the molecule} = 2\mu' \cos \phi/2 \quad (1)$$

In calculating the electric moment of an assemblage of such molecules the problem is to determine the mean angle ϕ. Now the measured polarization is a function of the square of the dipole moment, which in turn is a function of $\cos \phi/2$, hence the measured polarization is made up of a series of terms characteristic of the various orientations, each term being a function of $\cos^2 \phi/2$. Having performed the summation and deduced the mean square of $\cos \phi/2$, the dipole moment is calculated from the root mean square according to equation (1).

The potential as a function of the disposition of the rotating groups has been calculated and discussed for ethane by Eyring[7] and by Teller and

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[3] J. M. Robertson, *Proc. Roy. Soc.* (London), **A142**, 659 (1933); Pauling and Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[4] Pickett, *Proc. Roy. Soc.* (London), **A142**, 333 (1933).

[5] Table of Dipole Moments, *Trans. Faraday Soc.*, Appendix, **30** (1934).

[6] Debye, "Handbuch der Radiologie," Vol. VI, Leipzig, 1925, p. 786, and Landolt-Börnstein-Roth, "Tabellen," 5th ed.

[7] Eyring, THIS JOURNAL, **54**, 3191 (1932).

Weigert.[8] A general quantum mechanical treatment which involves all forces between the hydrogen atoms results in showing minima for the positions in which the hydrogen atoms of one CH_3 group are not eclipsing those of the other CH_3 group when viewed along the C–C axis. The potential differences however are so small in comparison with kT, that at ordinary temperatures free rotation is developed; *i. e.*, all positions from 0 to 2 π have practically the same probability. Calculations for 1,2-dichloroethane have been made by Meyer[9] and by Smyth, Dornte and Wilson.[10] Meyer treats the problem classically and considers only the electrostatic effect of the C–Cl moments on each other. These are assumed to be located on the C–Cl axis in a point one-eighth of the C–Cl distance from the center of the chlorine atom.

The calculation gives a minimum of the potential for the *trans*-position, and the potential difference between the *cis*- and *trans*-positions is sufficiently large in comparison with kT to establish a distinct preference for the *trans*-position at ordinary temperatures. This result has been confirmed by Smyth, Dornte and Wilson[10] with a different location of the C–Cl moment and also taking into consideration the effect of the C–H dipoles. These authors further undertake a wave-mechanical treatment and show that the classical treatment of the problem is adequate.

More recently a complete mathematical treatment of the interaction between rotating polar groups in a molecule has been given by Lennard-Jones and Pike[11] and by Altar.[12] Altar introduces a factor neglected hitherto by considering the effect of the variation of the moment of inertia of the molecule with rotation of the polar groups. In a molecule such as 1,2-dichloroethane, for example, where the polar groups are heavy in comparison with the rest of the molecule and unsymmetrically distributed about the molecular axis, the three moments of inertia of the molecule do not remain constant, but vary with the internal configuration of the molecule. Also since the probability of a molecule existing in a given configuration depends on the moment of inertia of the molecule in that configuration, the probability being greater the greater the moment of inertia, one cannot apply simply a Boltzmann formula in order to deduce the mean angle ϕ, but one has to consider the statistics of all degrees of freedom involved, *i. e.*, one must weigh each individual configuration according to its moment of inertia, by multiplying by an appropriate weight factor. The weight factors calculated[12] in the case of 1,2-dichloroethane for several configurations are as follows:

	ϕ	W
cis config.	0°	0.68
	45°	.96
	90°	1.20
	135°	1.02
trans config.	180°	0.96

the effect of the moment of inertia being to favor the 90° configuration.

In the case which we are considering, namely, *o,o'*-dichlorodiphenyl, the variation of the moment of inertia with rotation will be smaller since the molecule is a comparatively large and heavy one and the only dissymmetry is caused by the two chlorine atoms. Also since configurations with small values of ϕ are precluded for steric reasons, the variations in the weight factor will certainly not be more than 10%, which, in view of the other uncertainties involved in these calculations, justifies the neglect of this effect.

Stuart,[13] in discussing the equilibrium between *cis* and *trans* dichloroethylene, also considers the London forces and the induction effect which in this case is high, due to the great polarizability of the double bond. These calculations, owing to the rigidity of the double bond, deal only with the two "plane" configurations of the geometrical isomers. They show, in agreement with the experimental facts, that the potential for the *cis*-position is lower than that for the *trans*-position.

With dichlorodiphenyl, as with dichloroethane, rotation about a single bond is involved, and one needs to know the potential over the whole range of a revolution.

The general method of procedure was to calculate the sum of the potentials Σv due to the electrostatic and quantum mechanical forces for various values of ϕ and construct Boltzmann terms $e^{-\Sigma v/kT}$ giving the probabilities of the molecules existing in the different configurations. The dipole moment μ was then calculated from the formula

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[8] Teller and Weigert, *Nachr. Ges. Wiss. Göttingen*, **2**, 218 (1933).

[9] Meyer, *Z. physik. Chem.*, **B8**, 27 (1930).

[10] Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4242 (1931).

[11] Lennard-Jones and Pike, *Trans. Faraday Soc.*, **30**, 830 (1934).

[12] Altar, *J. Chem. Phys.*, **3**, 460 (1935).

[13] Stuart, *Physik. Z.*, **32**, 793 (1931).

$$\mu = 2\,\mu' \sqrt{\frac{\int_0^\pi e^{-\Sigma v/kT} \cos^2 \frac{\phi}{2}\, d\phi}{\int_0^\pi e^{-\Sigma v/kT}\, d\phi}} \qquad (2)$$

In computing the *electrostatic* potentials we have adopted a method which is different from that of either Meyer or of Smyth, Dornte and Wilson. We consider the dipole as being formed by positive and negative charges of magnitude ϵ at the centers of the constituting atoms, ϵ being equal to μ/d where μ is the moment and d the distance between the atomic centers. The electrostatic potential is then given by $\Sigma(\epsilon_i\epsilon_j/r_{ij})$; r is the distance between the point charges ϵ_i and ϵ_j and varies with the angle of rotation ϕ.

The variable distances are calculated from the formulas

$$\begin{aligned} r &= \sqrt{b^2 + 4a^2 \sin^2 \phi/2} \\ r' &= \sqrt{b'^2 + (a - a')^2 + 4aa' \sin^2 \phi/2} \qquad (3) \\ r'' &= \sqrt{b''^2 + 4a'^2 \sin^2 \phi/2} \end{aligned}$$

where r, r' and r'' are the distances Cl_1 to Cl_2, Cl_1 to C_2, and C_1 to C_2, respectively; the significance of the symbols is evident from Fig. 1.

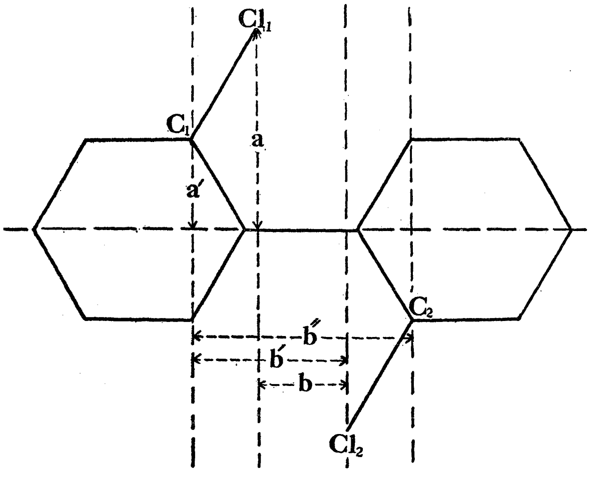

Fig 1.

The numerical data used are those given on page 2112; the distance C–Cl has been taken as 1.69 Å.;[14] $\phi = 0$ indicates the co-planar *cis* configuration. The total electrostatic potential for each angle is $\epsilon^2(1/r + 1/r'' - 2/r')$.

As was shown by Smyth, Dornte and Wilson,[10] the nature of the potential energy curve varies somewhat with the arbitrary location of the dipoles. We have no reason to believe that our convention, just described, is any more exact than that of other authors, and so for the purpose of comparison we have also calculated the electrostatic potential energies by Smyth's method. The results obtained by the two methods are shown in Fig. 2, U_1 being the electrostatic potential energy curve calculated by the charge-separation method, and U_2 the electrostatic potential energy curve calculated by Smyth's method. They have the same general shape and give approximately the same potential energy difference between the *cis*- and *trans*-positions. The most important factor, however, in governing the orientation of the molecule is the *London dispersion force.*

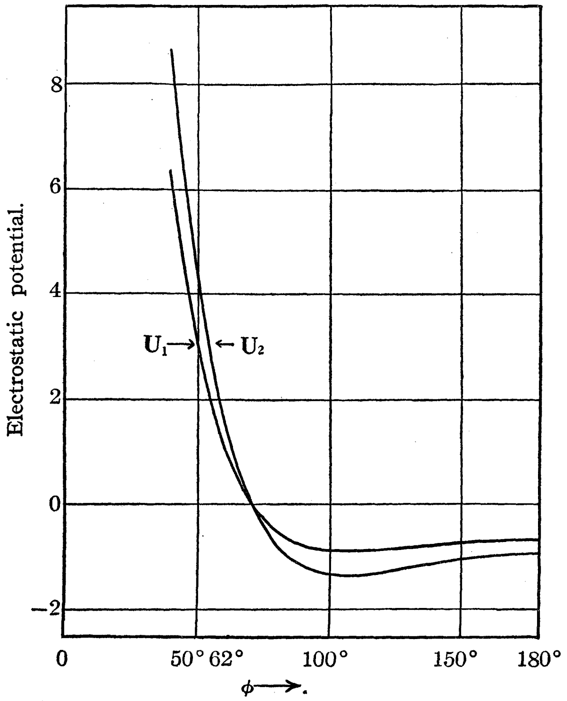

Fig. 2.

The *London forces* are of interest only for the chlorine atoms in *o,o′*-dichlorodiphenyl since for the other atoms they are negligible in their absolute magnitudes and furthermore do not vary much with ϕ. This applies also to the chlorine atoms in *m,m′*-dichlorodiphenyl but in this case they have been evaluated for comparison with the *o,o′*-compound. The London potential for the chlorine atoms has been taken as $115 \times 10^{-60}/r^6$, terms involving higher powers of r, which become important only when the atoms approach very close to each other, being neglected.

The numerical results for *o,o′*- and *m,m′*-dichlorodiphenyl are given in Tables II and III under the appropriate symbols.

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[14] De Laszlo, *Proc. Roy. Soc.* (London), **A146**, 698 (1934).

TABLE II

o,o'-DICHLORODIPHENYL

ϕ	r	r'	r''	$U_1 = \epsilon^2 (1/r + 1/r'' - 2/r')$ (ergs × 10^{14})	U_2 (ergs × 10^{14})	$L = (115 \times 10^{-60})/r^6$ (ergs × 10^{14})	$U_1 + L$ (ergs × 10^{14})	$U_2 + L$ (ergs × 10^{14})	$e^{-(U_1+L)/kT}$	$e^{-(U_2+L)/kT}$	$e^{-(U_1+L)/kT}$ $\cos^2 \phi/2$	$e^{-(U_2+L)/kT}$ $\cos^2 \phi/2$
40°	2.184	2.793	2.997	6.34	8.70	−105.9	−99.56	−97.2	3.897×10^{10}		3.44×10^{10}	
45°	2.369	2.861	3.025	4.52	6.35	−65.05	−60.53	−58.7	2.748×10^{6}	1.753×10^{6}	2.346×10^{6}	1.496×10^{6}
50°	2.555	2.933	3.056	3.08	4.42	−41.32	−38.24	−36.9	1.169×10^{4}	8.416×10^{3}	9.60×10^{3}	6.913×10^{3}
55°	2.743	3.008	3.089	1.98	2.88	−26.97	−24.99	−24.09	4.554×10^{2}	3.653×10^{2}	3.58×10^{2}	2.874×10^{2}
60°	2.929	3.087	3.125	1.14	1.67	−18.22	−17.08	−16.55	65.63	57.62	49.22	43.22
65°	3.112	3.167	3.161	0.52	0.75	−12.65	−12.13	−11.90	19.53	18.45	13.89	13.12
70°	3.293	3.248	3.199	.03	.07	−9.01	−8.98	−8.94	9.025	8.944	5.98	6.00
75°	3.467	3.331	3.237	−.25	−.43	−6.62	−6.87	−7.05	5.381	5.629	3.387	3.543
80°	3.641	3.414	3.275	−.50	−.78	−4.94	−5.44	−5.72	3.788	4.063	2.223	2.384
85°	3.807	3.493	3.313	−.67	−1.02	−3.78	−4.45	−4.80	2.975	3.245	1.617	1.764
90°	3.967	3.575	3.352	−.77	−1.18	−2.95	−3.72	−4.13	2.490	2.751	1.245	1.375
100°	4.269	3.728	3.427	−.87	−1.31	−1.90	−2.77	−3.21	1.970	2.197	0.814	0.908
120°	4.785	4.001	3.564	−.86	−1.26	−0.96	−1.82	−2.22	1.563	1.721	.391	.430
140°	5.168	4.212	3.672	−.75	−1.09	−.60	−1.35	−1.69	1.392	1.513	.163	.177
160°	5.403	4.344	3.741	−.67	−0.96	−.46	−1.13	−1.42	1.319	1.418	.040	.043
180°	5.482	4.388	3.764	−.65	−.92	−.42	−1.07	−1.34	1.299	1.388	.0	.0

TABLE III

m,m'-DICHLORODIPHENYL

ϕ	r	r'	r''	$U = \epsilon^2(1/r + 1/r'' - 2/r')$ (ergs × 10^{14})	$L = (115 \times 10^{-60})/r^6$ (ergs × 10^{14})	$U + L$ (ergs × 10^{14})	$e^{-(U+L)/kT}$	$e^{-(U+L)kT}$ $\cos^2 \phi/2$
0°	7.370	6.687	5.680	1.064	−0.072	+0.992	0.784	0.784
10°	7.385	6.694	5.684	1.057	−.071	+.986	.785	.779
20°	7.428	6.716	5.696	1.042	−.068	+.974	.788	.764
30°	7.499	6.752	5.715	1.020	−.065	+.955	.791	.738
40°	7.594	6.800	5.740	0.991	−.060	+.931	.796	.703
50°	7.709	6.858	5.771	.957	−.055	+.902	.802	.659
60°	7.841	6.926	5.808	.921	−.049	+.872	.808	.606
70°	7.984	6.999	5.848	.884	−.044	+.840	.814	.546
80°	8.134	7.077	5.890	.850	−.040	+.810	.820	.481
90°	8.285	7.156	5.933	.821	−.036	+.785	.825	.413
100°	8.434	7.234	5.976	.793	−.032	+.761	.830	.343
110°	8.576	7.309	6.017	.770	−.029	+.741	.834	.275
120°	8.706	7.379	6.055	.756	−.026	+.730	.836	.209
130°	8.824	7.442	6.090	.739	−.024	+.715	.840	.150
140°	8.923	7.495	6.120	.726	−.023	+.703	.842	.099
150°	9.003	7.539	6.143	.720	−.022	+.698	.843	.057
160°	9.061	7.570	6.161	.712	−.021	+.691	.844	.026
170°	9.097	7.589	6.172	.708	−.020	+.688	.845	.006
180°	9.108	7.595	6.176	.705	−.020	+.685	.846	.0

The case of *m,m'*-dichlorodiphenyl, where the centers of the chlorine atoms even in the *cis*-position do not come nearer to each other than to a distance of 7.37 Å., is not of any special interest except for comparison with the *o,o'*-compound. Figure 3 shows the probability $e^{-(U+L)/kT}$ for the *m,m'*-isomeride. It indicates a slight preference for the *trans*-position, but the potential energy $(U + L)$ difference between the *cis*- and *trans*-positions (*ca.* 0.3×10^{-14} ergs) is so small in comparison with kT (*ca.* 4×10^{-14} ergs) that free rotation is virtually established. The moment for free rotation ($\sqrt{2} \times 1.55 \cos 30°$) would be 1.90 *D*, that calculated from eq. (2) is 1.89 *D*,[15] the measured moment is 1.80 D. The difference is probably due to induced effects by the two dipoles, similar to those calculated in the case of the monochlorodiphenyls on page 2112.

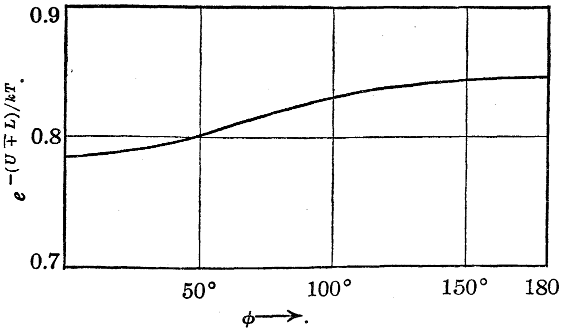

Fig. 3.—Probability distribution curve for *m,m'*-dichlorodiphenyl.

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[15] The integrals were evaluated graphically.

For *o,o'*-dichlorodiphenyl the data reveal the striking fact that the electrostatic potentials (U_1 or U_2 according to the mode of calculation), which favor the *trans*-position, are largely overcompensated by the London potentials, and that the internal configuration of the molecule depends almost entirely on the latter. As these decrease with the sixth power of r, they produce a considerable preference for positions with small angles ϕ. The probability of the various configurations as a function of ϕ is given by the numerical values of $e^{-(U_1 + L)/kT}$ and by the full line in Fig. 4.[16] This proves our suggestion of the influence of the London forces as previously stated.[2] The curve indicates that the smaller the angle ϕ the greater is the probability. A limit, of course, must be set by a steric factor. In agreement with the resolvability of *o*-substituted diphenyl compounds, the table of values of r shows that no chance of a co-planar *cis*-configuration exists. Already at an angle $\phi = 35°$, the Cl–Cl distance is that of two chlorine atoms in a chlorine molecule. At a value $\phi = 60°$ they are at the distance 2.93 Å. which has been measured for the two chlorine atoms in methylene chloride,[17] where there still seems to be a slight repulsion between the chlorine atoms as is indicated by a deflection (2–3°) of the carbon valences. Configurations with a smaller angle ϕ can have only a small probability, and so the probability function must be characterized by a maximum where the repulsion forces (electrostatic and steric) are in equilibrium with the London attraction forces.

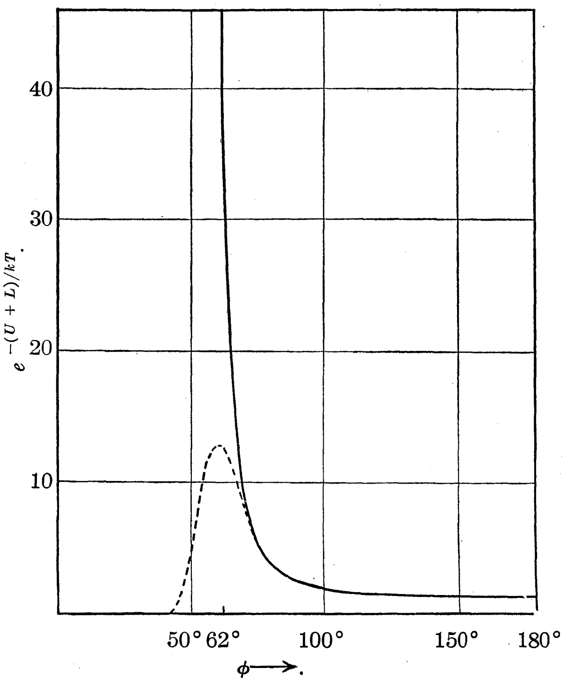

Fig. 4.—Probability distribution curve for *o,o'*-dichlorodiphenyl.

Little is known about the law of steric repulsion in question. For ions Born and Mayer[18] use a repulsion law of the form $be^{-r/\rho}$ (4) where b is a constant characteristic of the ions in question and they found that for the alkali halides ρ has a mean value of 0.345×10^{-8} cm. It seems reasonable to assume that such a law holds also in the case of covalently bound atoms but there is, of course, no reason for assuming that ρ especially equals 0.345.

In order to get an idea of the equilibrium distance the value for 60°, whose significance has been pointed out above, will be taken as a lower limit. The close packing distance between two chlorine atoms not belonging to the same molecule, and found to be 3.74 Å. for hexachlorobenzene,[19] gives the upper limit. The distance of equilibrium for *o,o'*-dichlorodiphenyl should be smaller than that owing to the smaller freedom of motion. Sidgwick's suggestion to add 0.5 Å. to the radius of the bound atom[20] gives a value of about 2.98 Å. for the distance of equilibrium. No other data appear to be available. In these circumstances the least hypothetical treatment will be to consider the repulsion potential as a rigid barrier, and to try at what angle we must cut the probability curve by a straight line parallel to the ordinate to obtain the experimental value for the moment from equation (2). This angle is 62° and it corresponds to a distance of 3.0 Å. between the chlorine atoms. If instead of this vertical barrier we multiply the probability function by an exponentially increasing repulsion term of the form $e^{-be^{-r/\rho}/kT}$ we get a probability curve shown by the dotted line in Fig. 4. Owing to the uncertainty in the law of repulsion, however, a calculation of the moment from this probability curve hardly seems justified.

Another effect which should be considered is the induction effect of the two C–Cl dipoles. This will tend to make the resultant moment of the compound low, especially in the case of the

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[16] $e^{-(U_2+L)/kT}$ gives essentially the same type of curve.

[17] Sutton and Brockway, This Journal, **57**, 473 (1935).

[18] Born and Mayer, *Z. Physik*, **75**, 1 (1932).

[19] Hendricks and Blicke, This Journal, **48**, 3007 (1926).

[20] "Annual Reports," 1933, p. 119.

o,o'-compound where the two dipoles come close to one another. On the other hand, this induction will contribute to the forces which favor molecules with smaller angles ϕ, and since both effects will be small and of inverse influence on the measured moment, their evaluation *in extenso* has not been undertaken.

The main results of our investigation may be summarized thus. The moments of the monochlorodiphenyls are explained if one takes into account the inducing effects of the polar group on the unsubstituted nucleus, as in the case of the chloronaphthalenes. The configuration of *o,o'*-dichlorodiphenyl is governed predominantly by the London forces.

Experimental

Polarization Results.—The measurements were carried out in benzene solution at 25.0°. The symbols have their usual significance.

o-Chlorodiphenyl

f_2	d	e	n^2	P_2	eP_2
0.012289	0.8801	2.3167	2.26559	101.1	57.4
.008942	.8784	2.3039	2.26321	99.9	57.0
.006342	.8771	2.2951	2.26166	100.4	56.8
.003451	.8756	2.2846	2.25978	99.4	56.1
.0	.87385	2.2727	2.25797	...	..

$P_{A+O} = 100.2 - 56.8 = 43.4$ cc. $\mu = 1.45$ *D*.

m-Chlorodiphenyl

0.022820	0.8858	2.3722	2.27285	112.3	58.0
.017568	.8833	2.3503	2.26952	113.0	57.8
.011424	.8801	2.3231	2.26542	113.2	57.9
.010396	.8796	2.3180	2.26480	112.4	57.9
.0	.8743	2.2727	2.25797	...	..

$P_{A+O} = 113.5 - 57.9 = 55.6$ cc. $\mu = 1.64$ *D*.

p-Chlorodiphenyl

0.017357	0.8833	2.3501	2.27008	112.9	57.7
.013914	.8815	2.3333	2.26754	111.4	57.5
.008394	.8785	2.3096	2.26384	112.2	57.8
.006196	.8774	2.2998	2.26228	111.6	57.4
.0	.8740	2.2727	2.25797	...	..

$P_{A+O} = 112.6 - 57.6 = 55.0$ cc. $\mu = 1.63$ *D*.

o,o'-Dichlorodiphenyl

0.011263	0.8825	2.3367	2.26505	135.0	60.9
.009917	.88145	2.3299	2.26398	136.3	60.6
.008776	.88055	2.3228	2.26304	135.6	60.2
.007935	.8799	2.3173	2.26256	134.3	60.2
.0	.8737	2.2727	2.25797	...	..

$P_{A+O} = 136 - 60.5 = 75.5$ cc. $\mu = 1.91$ *D*.

Remeasurement of *o,o'*-dichlorodiphenyl. (This was made on an independent sample of material.)

0.017073	0.88675	2.3703	.....	135.4	..
.010177	.8814	2.3313	2.26412	136.4	60.7
.0	.8735	2.2727	2.25797	...	..

m,m'-Dichlorodiphenyl

0.014915	0.8854	2.3514	2.26893	128.7	62.1
.011293	.8826	2.3320	2.26568	128.3	61.3
.008686	.8805	2.3187	2.26423	129.2	61.9
.0	.8736	2.2727	2.25797	...	..

$P_{A+O} = 129.2 - 61.8 = 67.4$ cc. $\mu = 1.80$ *D*.

The substances were either identical with, or prepared by, the same methods as those described by Weissberger and Sängewald.[21] A slight alteration has been made in the preparation of *o,o'*-dichlorodiphenyl. The Ullmann reaction was carried out for twelve hours at 260° with an *o*-chloroiodobenzene obtained from *o*-chloroaniline (purified according to Orton and King),[22] and worked up by vacuum distillation; b. p. (16 mm.) 145–165°; m. p. 52–55°; yield 40%; m. p. after repeated recrystallization from alcohol and finally from hexane 60.7–62°.

We wish to thank Professor R. Robinson, F.R.S. for his hospitality to A. W., and Imperial Chemical Industries Ltd. for a grant.

Summary

The electric moments of the monochlorodiphenyls and the dichlorodiphenyls with the substituents in identical position in both rings have been determined.

The moments of the monochlorodiphenyls are explained by taking into account the inducing effects of the polar group on the unsubstituted nucleus, as in the case of the chloronaphthalenes.

The forces which determine the configuration of *m,m'*- and *o,o'*-dichlorodiphenyl have been evaluated. Since the electrostatic attraction and repulsion forces largely compensate each other, the configuration of the latter substance is predominantly determined by the London dispersion forces between the chlorine atoms. This explains the high moment of *o,o'*-dichlorodiphenyl.

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(21) Weissberger and Sängewald, *Z. physik. Chem.*, **B20**, 145 (1933).

(22) Orton and King, *J. Chem. Soc.*, **99**, 1380 (1911).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A Differential Method Employing Variable Heaters for the Determination of the Specific Heats of Solutions, with Results for Ammonium Nitrate at 25°

BY FRANK T. GUCKER, JR., FRED D. AYRES AND T. RICHARD RUBIN

Introduction

The adiabatic twin-calorimeter method is admirably suited to the precise measurement of the specific heats of solutions. A "thermal balance" employing this method has been in use for some time in this Laboratory.[1] In preparation for a new series of experiments, several modifications and improvements were introduced and a method was worked out whereby the electrical energy input in the calorimeters could be changed by means of variable resistance heating coils. This made the new apparatus much more flexible and convenient; and also increased its accuracy somewhat, as the new experimental results indicate. After a brief summary of the experimental method the significant new features of the present apparatus will be considered in more detail. For experimental details which were not appreciably changed, the reader is referred to the earlier articles mentioned above.

The apparatus consists of two similar calorimeters, one containing a solution, the other a fixed tare weight of water, enclosed side by side in a submarine jacket contained in an adiabatic water-bath. Starting at the same initial temperature, the calorimeters are heated one degree by means of a pair of variable resistance coils connected in series. The resistance ratio of these coils is adjusted until the two calorimeters are heated at the same rate, as determined by a multiple thermel connected to a high sensitivity galvanometer. The heat capacity of the solution is then calculated from the measured resistance ratio and the known heat capacity of the calorimeter.

Apparatus

General Description.—A general idea of the apparatus may be obtained from the simplified drawing, Fig. 1. The two calorimeters, C, C, of 280-ml. capacity, are enclosed in a water-tight submarine jacket, J, which is completely immersed in the water-bath, B. The stirrers, S, S, are rotated at 215 r. p. m. by a sprocket chain driven from a synchronous motor. The Bakelite thermal insulators (indicated by cross-hatching) in the stirrer shafts prevent leakage of heat into the calorimeters from the bearings above. The water-bath, B, is mounted on a motor-operated, vertical jack-screw so that it can be raised or lowered easily, even when filled with water. It is agitated by two stirrers (not shown in the diagram) which are driven at 215 r. p. m. by the same sprocket chain which operates the calorimeter stirrers. The bath is heated by four bare nichrome coils (not shown in Fig. 1) each of five ohms resistance, connected in series to the 110-volt a. c. circuit. Each coil is 30 cm. long, loosely wound around a heavy copper wire serving as one of the leads, from which it is insulated by a length of glass tubing. The coils are equally spaced and mounted on the brass plate, P, by means of standard attachment plugs so that they project vertically down into the water. A cover, F, and lid, L, fit over the top of the bath. The entire apparatus is insulated with a 5-cm. layer of felt, H. Bare chromel wires, insulated between thin sheets of asbestos, are wound around the cover, lid and bath, under the felt. These surface heaters, connected through a rheostat to the 110-volt a. c. circuit, compensate for loss of heat when working at temperatures higher than that of the room. To maintain temperatures below that of the room, a regulated stream of cold water is allowed to drip into the bath. The surplus water escapes through the outlet tube, R, and the sight glass and overflow, D.

Submarine Jacket.—The heavy copper submarine jacket, J, was nickel plated and burnished on the inside. The bottom was detachable in order to expedite the process of plating and burnishing. Once this was accomplished, a gasket was put in place and the bottom was bolted on permanently. The top of the jacket was rigidly attached to the lid of the bath, P, by the heavy brass tubes through which the stainless steel stirrer shafts extended. The calorimeters were suspended entirely from this top plate, so that the lower part of the submarine jacket was easily detached at the point indicated by the gasket, G.

Calorimeters.—The calorimeters and lids were spun from an alloy of 20% platinum and 80% gold,[2] which combines chemical inertness with adequate mechanical strength. The lids were ground to fit their respective calorimeters and the joints were made vapor-tight by a thin coating of vaseline. Three wells for the thermel and heater cases were gold-soldered to each lid. Only the wells for the main and adiabatic thermels are shown in the horizontal section in Fig. 1. The third well, for the heater, was located directly behind the stirrer. Each lid was also provided with two conical openings. Into the center one was ground the lower end of a glass tube, E, through which passed the stirrer shaft. Toward one side was a second opening, not shown in Fig. 1, fitted with a ground plug. The calorimeter was filled through this second opening. All the ground joints were made vapor-tight by means of a thin coating of vaseline. The 3-stage propeller stirrers, S, S, made of platinum, were screwed into insulating sec-

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[1] (a) Richards and Gucker, THIS JOURNAL, **47**, 1876 (1925); (b) Gucker, *ibid.*, **50**, 1005 (1928); (c) Gucker and Schminke, *ibid.*, **54**, 1358 (1932); (d) **55**, 1013 (1933).

[2] The calorimeters were made by J. Bishop & Co.

tions machined from transparent Bakelite, indicated by cross-hatching in Fig. 1. This material has a low thermal conductivity. Since tests showed it is almost impervious to water, it is superior to the ivory sections used previously in this Laboratory. Unfortunately, it softens so much that it cannot be used above 40 or 50°. The lower end of the Bakelite was conical to fit a 60° conical seat in the bottom of the glass tube, E.

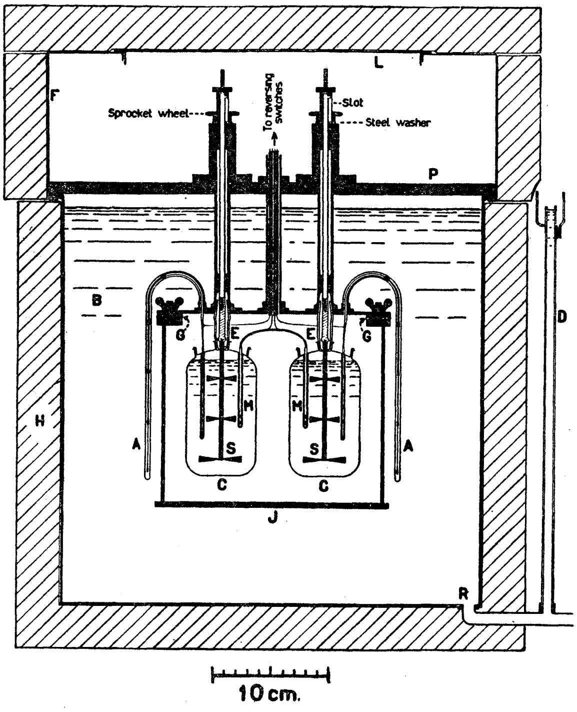


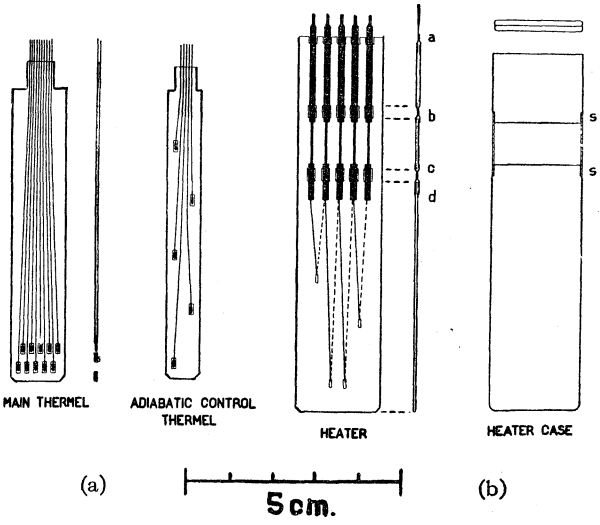
Fig. 1.—Calorimetric assembly.

In assembling the apparatus, the glass tube, E, was fitted into the lid of the calorimeter. The Bakelite section next was put in place and the stirrer screwed to it. The lid, carrying the stirrer, was put on the calorimeter, into which water or solution was then weighed. The conical joint between Bakelite and glass prevented evaporation during this process. The calorimeter was then raised until the top of the glass tube, E, fitted the conical base of the brass tube in the submarine lid, into which it had been ground. A temporary supporting frame held the calorimeter rigidly in this position. The bottom of the stainless steel shaft which carried the sprocket wheel was now screwed into the upper end of the Bakelite section, which was kept from turning by the friction between it and the conical seat in E. Finally the knurled knob above the sprocket wheel was screwed down, raising the shaft to the position shown in Fig. 1, where the Bakelite section is clear of the glass.

Each calorimeter was suspended from the top of the submarine jacket by four equally-spaced pieces of dental floss. The lower ends of these were tied to small wire loops, gold-soldered to the sides of the calorimeters near the top. The upper ends were slipped over small adjustable wire hooks which projected down from the top of the submarine jacket. Above the hook, each wire passed through a hole in the axis of a small machine screw, the lower end of which was knurled so that it could be turned with the fingers. Each screw was threaded vertically into a support fastened to the submarine lid. The top of the wire was bent horizontally, to fit into a vertical slot in the support, so that the hook did not rotate when the screw was turned. When the screws were tightened and the hooks raised, the calorimeters were held tightly against the glass tubes, E, E. Finally the temporary supporting frame was removed, leaving the calorimeters suspended with a very small avenue of heat exchange to the submarine jacket.

Two features in the calorimetric design are important. First, the air space above the liquid level in each calorimeter, including that inside the glass tube, E, is reduced to about 10 ml. This volume is so small that no trouble is caused by evaporation of water when the calorimeter is heated one degree. Second, since the stirrers are easily detachable at the bakelite–stainless steel joints, Fig. 1, the calorimeters and their contents can be removed completely and weighed with no loss of solution or water. The actual evaporation losses determined by this method are usually found to be only 2 or 3 mg. and hence completely negligible.

Thermels.—The constantan wire used in constructing the thermels was tested for homogeneity according to the method recommended by W. P. White[3] and only those sections were used which showed an e. m. f. of less than 1 μ v. over a thermal gradient of 70° in about 3 cm. The 20-junction copper–constantan main thermel, M, M, Fig. 1, was constructed in two halves of 10 junctions each so that the halves could be opposed in the usual manner. The general design is shown in Fig. 2a. Each junction was insulated from the others in a slot cut in a mica form, the No. 34 copper wires running up on one side of the mica and the No. 26 constantan on the other. The mica forms, 0.13 mm. thick, were about one centimeter longer than the corresponding wells in the calorimeter lid. Each 10-



(a) (b)

Fig. 2.—Details of thermels and heaters.

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(3) W. P. White, THIS JOURNAL, **36**, 2292 (1914).

junction unit was dipped in "razo-glass"[4] and sandwiched between two mica insulating strips about 0.08 mm. thick. Snugly fitting copper cases, thick enough for good thermal contact with the calorimeter well and long enough to cover the mica, were then slipped over each pair of completed units. The resistance of the insulation between the thermel wires and the copper cases was found to be about 100,000 megohms (50% relative humidity).

The five junctions of each adiabatic control thermel (A, A, Fig. 1) were staggered as shown in Figs. 1 and 2a in order to obtain a comparison of the average bath temperature with the average temperature inside the calorimeters.

The thermels were connected to the galvanometers through copper reversing switches by which parasitic currents in the galvanometer circuit could be eliminated.

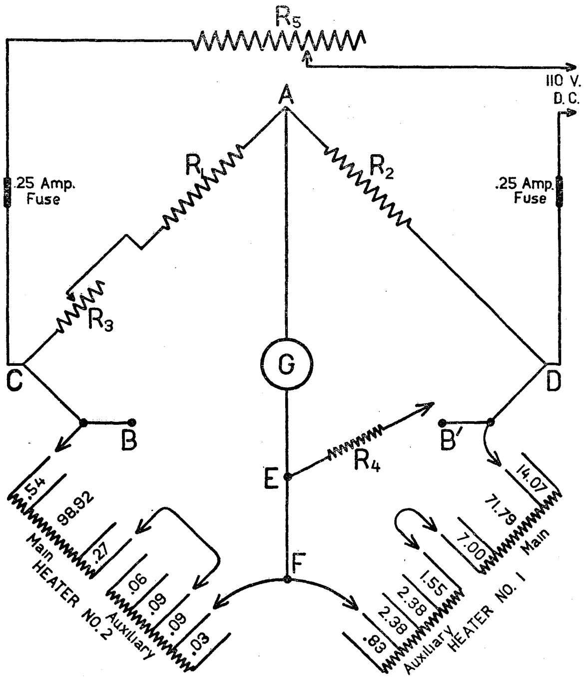

Fig. 3.—Bridge for measuring resistance ratio.

Variable Resistance Heaters.—The design of these heaters, allowing a measurement of the resistance ratio during an experiment, was the most important innovation in the present apparatus. Each consisted of 7 units with a total resistance of about 100 ohms. A large resistance, with a smaller one connected to each end, formed the *main heater* which was supplied with 4 leads. Four much smaller units, connected in series and supplied with 5 leads, formed the *auxiliary heater*. This arrangement gave a satisfactory flexibility in resistance with a minimum number of leads. In each main heater, connection could be made to the large resistance alone or in combination with either or both end coils. In order to keep the lead resistance constant, at least one unit of the auxiliary heater was always connected in series with the main. The 9 possible combinations of the auxiliary, combined with the 4 of the main, gave 36 resistances in each heater and 1296 resistance ratios for the two heaters. The values of the individual units, shown in Fig. 3, were so chosen as to give a series of resistance ratios progressing uniformly from 0.9800 to 1.3700 in steps of 0.0003 to 0.0004. In order to obtain a smooth progression, with no gaps, all the smaller steps were put in one heater (No. 2) and the larger in the other (No. 1).

The main and auxiliary heaters were mounted on separate strips of clear mica 0.13 mm. thick. The construction of auxiliary heater number 1 is shown in Fig. 2b, which is a scale drawing. The constantan resistance wires were No. 36 B and S gage, while those in auxiliary heater number 2, were No. 24 B and S gage, bent to shape and flattened to form a ribbon of the same thickness, 0.13 mm. These ribbons were annealed before assembly by the passage of a current of 6 amp. The large resistances of the main heaters were No. 40 B and S gage constantan. All the constantan wires were confined to the lower parts of the mica strips, 2.5 cm. or more below the surface of the liquid in the calorimeter.

The leads to the outside were No. 24 B and S gage copper wires. The lower end of each, flattened to form a ribbon 0.13 mm. thick, was carried down one side of the mica strip. It was fastened to the mica by means of a second copper strip carried down the opposite side and soldered to it in two slots at a and b, Fig. 2b. This arrangement ensured good thermal contact with the walls of the heater case, so that the heat generated in the coils is delivered to the calorimeter. One-centimeter lengths of flattened No. 36 B and S gage copper wire interposed between b and c, Fig. 2b, minimized the conduction of heat to the leads.

The heating units were made with slightly less than the desired resistance, mounted on the mica strips and soldered to the leads, using rosin flux. They were then annealed by passing through them a current appreciably larger than that which was used in the later experiments. The wires were then alternately scraped cautiously with a sharp knife and annealed until they were adjusted to within 0.01 ohm of the calculated value. Finally the heaters were washed thoroughly with carbon tetrachloride, to remove any rosin flux or grease from the hands, and rinsed several times in distilled water, to remove any salts which would increase the surface conduction of the mica. They were carefully dried and sandwiched between insulating strips of clear mica 0.08 mm. thick which had been cleaned in the same way. The total thickness of the heater with its two insulating strips was 0.9 mm. or less. Each heater was pushed into one side of a double case made from sheet copper 0.25 mm. thick, bent in the shape of a flattened S as shown in Fig. 2b and soldered together at the edges. A 1-cm. opening in the case, coinciding with the small wires bc of the heater leads, reduced conduction of heat up the heater case. The two copper sections of the case were held rigidly together by strips of stainless steel, s, s, 0.25 × 1.25 mm., soldered to shallow recesses filed in the edges of the case as shown in Fig. 2b.

The Resistance Ratio.—The heaters were incorporated in a conventional Wheatstone bridge circuit, Fig. 3, the measuring arms of which, AC and AD, consisted of much higher resistances than the heaters. R_1 and R_2 were 4000-ohm coils and R_3 consisted of a series of coils totaling 2000 ohms in series with a precision resistance box, variable in

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(4) "Razo-glass" is the trade name of a polymerized coumarone resin, obtained from the Marbro Products Corporation through the courtesy of the late Professor Eric von Gebauer-Fuelnegg. When dissolved in toluene, razo-glass is an excellent insulating varnish.

steps of 0.01 ohm. The individual Leeds and Northrup resistance coils, wound on metal spools, were mounted on brass rods in the usual manner. The coils were calibrated to within 0.01 ohm, using a set of Bureau of Standards type standard resistors as a basis of comparison. Calibration at intervals of several months showed no significant changes except in the 4000-ohm coils.

By means of this Wheatstone bridge, the resistance ratio was measured *during an experiment,* with a current of 0.19 ampere passing through the heaters, but only 0.005 ampere passing through the measuring arms—a current which they were designed to dissipate without an appreciable change in their calibration. The Leeds and Northrup pointer-type galvanometer G was sensitive to a change of 0.0003% in the resistance ratio.

The resistance ratio measured by the bridge is, of course, the ratio of the total resistances of the heater arms, from C to F and from F to D, respectively. The ratio of the resistances *effective in heating the calorimeters* can only be determined by applying a correction for the lead resistance. For this reason, every effort was made to keep the lead resistance small and constant. The 18 lead wires from the heaters were cut equal in length, and their upper ends were soldered to radio tip-jacks mounted on a shielded Bakelite disk immediately above the bath lid, P, Fig. 1. Connection between the jacks was made by short pieces of heavy stranded wire, soldered to phone tips, indicated by arrows in Fig. 3. Potentiometric measurement showed that the contact resistance of a pin-jack and phone-tip combination was about 0.0010 (±0.0002) ohm. This variation was negligible for the four contacts in each heater arm. Plugging all of the phone tips in and out several times in succession never produced a change in the measured resistance ratio of more than 0.0005%. In finding the value of the lead resistance, we assumed that only the lower half of the exposed leads within the air gap of the submarine jacket belonged to the heater and contributed to raising the temperature of the calorimeter. The resistance from this mid-point through the lead wires, phone connectors and external wires to the corners of the bridge made up the lead resistance, l, which we found by potentiometric measurement was 0.103 ohm for each heater. If the effective end of the heater is within 2 cm. of the center of the 9-cm. length of the lead wire in the gap, the uncertainty in l is not more than ±0.006 ohm. It can be shown easily that the *effective* resistance ratio, x' ($= r_2/r_1$) can be calculated from the *measured* resistance ratio X by the equation

$$x' = X + [l(X - 1)]/r_1 \tag{1}$$

where r_1 is the resistance of heater 1. This equation shows that the effective ratio equals the measured ratio when that ratio is unity, and differs by an increasing amount as the lead resistance and the resistance ratio increase. The lead correction amounts to +0.04% with the maximum ratio of 1.37, and the value of l found above. If l is known to 0.005 ohm and r_1 to 2 ohms, the maximum error in the lead correction will not exceed 0.002%.

Theory of the Measurements

In principle, the method consists in finding the balance point of the apparatus, first with equal weights of water (268.330 g. *in vacuo*) in the two calorimeters, and then with the same weight of water in the tare (number 2) and an equal *volume* of solution of known weight in the working calorimeter (number 1). The balance point is the effective resistance ratio for which the two calorimeters rise exactly the same amount when heated over an interval of 1°. Since the resistance ratio cannot be set *exactly* at the balance point, the small galvanometer deflection, Δg (due to a slight difference in temperature rise over a 1° range) is found by the graphical method used in our previous work.[1c] After two or more experiments, the values of Δg are plotted against the corresponding resistance ratios and the balance point is read from the graph, as shown in Fig. 4.

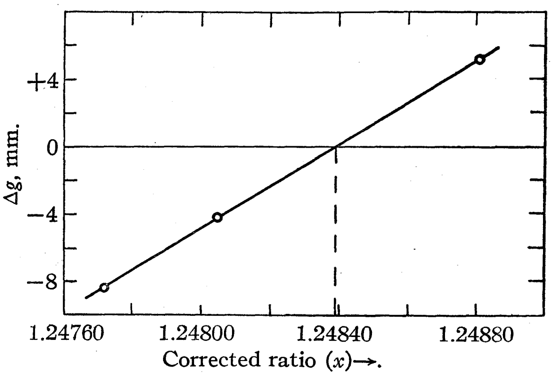

Fig. 4.—Graphical estimation of balance point: ($\Delta g = 0$ at $x = 1.24839$).

If the balance points corresponding to water and solution are designated respectively by x_0 and x, they are defined by the equations

$$x_0 = T/(C_w + c_1) \tag{2}$$

and

$$x = T/(C_s + c_1) \tag{3}$$

where T is the total heat capacity of the tare calorimeter and water, c_1 is the heat capacity of the working calorimeter and C_w and C_s the heat capacities of the weights of water and of solution in calorimeter 1 at balance. Dividing (2) by (3), and rearranging terms gives for the heat capacity of the solution

$$C_s = C_w x_0/x - c_1(x - x_0)/x \tag{4}$$

This equation shows that the effective heat capacity of the working calorimeter, c_1, must be known with an accuracy which becomes greater the more x increases—*i. e.*, the lower the heat capacity of the solution. If x_0 is unity and x has the extreme value of 1.37, c_1 must be known to 0.07 cal. per degree if C_s is to be determined to 0.01%. As the value of x decreases, the error in C_s caused by an error in c_1 becomes correspondingly less. In our experiments, the largest value of x was 1.25, hence an error of 0.1 calorie unit in c_1 causes an error of only 0.004% in C_s.

Although the value of c_1 need not be known more closely than 0.1 calorie unit, it must *remain constant* to 0.01 calorie unit or better. Preliminary experiments showed that the effective heat capacity c_1 decreased nearly linearly by about 0.015 calorie unit per ml. for the first 30 ml. of water removed from the calorimeter. In calculating the results of these experiments a correction was applied for the evaporation of water into the increased air space. The decrease in c_1 was probably due to a lag in the heat reaching the lid of the calorimeter, and an increased heat leakage down the heater leads to the calorimeter. In order to keep c_1 constant, the same volume of liquid (± 0.5 ml.) was always put into the working calorimeter.

In determining c_1, a hollow air-tight copper shell, displacing about 33 ml. of water, was fastened below the surface of the water in the calorimeter, which was then filled up to the usual level. From the balancing ratio x_0', the heat capacity of the water, C_w', and that of the displacer, the value of c_1 was found by eliminating T between equation (2) and a similar equation for x_0'. The heat capacity of the solid parts of the displacer was found by opening it, immersing the parts in the calorimeter filled to the usual volume with water, and finding the balancing ratio. The heat capacity of the air in the displacer was added to this value in calculating the value of c_1. The values of c_1 corresponding to the working volume of 268.3 ml. in the calorimeter, were 10.83 and 10.89 25°-calorie units—an average of 10.86 being used in subsequent calculations in experiments 1–5 inclusive. A slight alteration in one of the heater cases, made before the second series of measurements was started, necessitated a new set of calibration experiments. The new average value of c_1 was found to be 10.73 25°-calorie units. This value was used in all calculations following experiment number five.

The determination of the heat capacity of the calorimeter from the difference of two large heat capacities necessarily increases the percentage error in the value of c_1. However, the effect of this error upon the final results is reduced to negligible proportions, as we have already shown.

A Typical Experiment.—As an indication of the manner in which the measurements were carried out, the important data taken in connection with a typical experiment are given in Table I. The solution used in this experiment was the most concentrated of the series (23.998 molal). The change in galvanometer deflection, Δg, was found as before[1c] by recording the galvanometer deflections at one-minute intervals before and after the experiment and estimating the change graphically. The individual galvanometer deflections are not tabulated here.

TABLE I

Experiment Number 7, 12/24/35–12/26/35

Weight NH_4NO_3 231.670 g.
Weight solution 352.272 g. $m = 23.9978$

Heater settings (Nominal values) $\begin{cases} \text{No. 1} = 71.79 + 7.00 + 0.83 \text{ ohms} \\ \text{No. 2} = 98.92 + 0.54 + 0.06 \text{ ohms} \end{cases}$

	Time	Resistance
Balancing resistance during heating time ($R_1 + R_3$, Fig. 3)	9:43	4992.79 ohms
	44	.78
	45	.75
	46	.74
	47	.73
Average =		4992.76 ohms

Fixed resistance (R_2, Fig. 3) = 4002.47 ohms
Ratio = 4992.76/4002.47 = 1.24741 = X
Ratio, corrected for lead resistance
$= 1.24741 + [0.10(1.2471 - 1)]79.6 = 1.24772 = x_1$
$\Delta g' = -8.4$ mm. (galvanometer deflection for experimental temperature rise)

Platinum resistance thermometer $\begin{cases} \text{Final } R = 28.0808 \text{ ohms} \\ \text{Initial } R = 27.9799 \end{cases}$
$\Delta R = 0.1009$ ohm

$\Delta t = 9.957\Delta R = 1.005° =$ experimental temperature rise
Mean temperature = 24.99°
Δg_1, galvanometer deflection for 1° temperature rise = $-8.4/1.005 = -8.4$ mm.

Similarly, for two additional experiments using different heating ratios

$$\Delta g_2 = +5.2 \text{ mm.}, x_2 = 1.24881$$
$$\Delta g_3 = -4.2 \text{ mm.}, x_3 = 1.24805$$

From Fig. 4, $\Delta g = 0$, at $x = 1.24839$

$$C_s = \frac{1.00009(268.330) + (1.00009 - 1.24839)(10.73)}{1.24839}$$
$$= 212.826$$

$s = 212.826 \div 352.272 = 0.60481$ 25°-cal./deg.
$\Phi(C_{p_2}) = 31.945$ 25°-cal./deg.

Preparation of Ammonium Nitrate.—The ammonium nitrate used in these experiments was synthesized from pure ammonia and nitric acid by two slightly different methods, both based upon the procedure recommended by Archibald[5] for ammonium chloride. In both cases, C. P. nitric acid was distilled through a quartz condenser and the middle third was placed in quartz or platinum dishes. The first portions of ammonium nitrate were prepared by T. R. Rubin, who also measured the heat capacities of the corresponding solutions. The ammonia was obtained as follows. A hot solution of C. P. ammonium sulfate, dissolved in an equivalent weight of pure sulfuric acid, was treated with a few grams of finely powdered potassium permanganate and heated until it was colorless. This treatment ensures the oxidation of any organic matter. The purified ammonium bisulfate was cooled, dissolved in water and neutralized with a suspension of C. P. calcium oxide. It was then put in the bottom of a vacuum desiccator and mixed with excess lime, giving a slow evolution of ammonia. This was absorbed in the dishes of pure nitric acid which were placed on the shelf of the desiccator.

Subsequent tests showed that there were no oxidizable impurities in ammonium hydroxide of synthetic origin; hence the remaining portions were prepared by Robert Mueller using solutions of ammonium hydroxide made from synthetic ammonia in place of the lime and ammonium bisulfate mixture. The heat capacities of these solutions were measured by F. D. Ayres.

The ammonium nitrate resulting from either procedure was twice crystallized from water and dried *in vacuo* at 70–80°. The Hyvac pump was connected through a trap immersed in a mixture of carbon dioxide snow and acetone (about −78°). Pumping was continued until no more moisture collected in the trap. The salt was then ground in an agate mortar and dried again *in vacuo* at the same temperature for about six to ten hours. It was stored in a desiccator.

Experimental Results.

—The results for all the ammonium nitrate solutions are collected in

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(5) E. H. Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, 1932.

TABLE II

THE SPECIFIC HEATS AND APPARENT MOLAL HEAT CAPACITIES OF AMMONIUM NITRATE SOLUTIONS AT 25°

Expt.	m	c	$c^{1/2}$	s	$\Phi(C_{p2})$ obsd.	$\Phi(C_{p2})$ calcd.	Δs in (0.001%)
	0.0	0.0	0.0	1.00000		−3.64	
3	.1012	.1004	.3169	0.99211	1.5	0.8	− 7
2b	.1928	.1905	.4365	.98534	2.82	2.46	− 5
1a	.4065	.3975	.6305	.97044	4.96	5.14	+ 8
6	.5771	.5599	.7483	.95960	6.81	6.75	− 3
1	.8433	.8079	.8988	.94361	8.66	8.79	+10
2a	1.5093	1.4020	1.1841	.90907	12.52	12.58	+ 7
4b	2.4323	2.1672	1.4721	.87000	16.20	16.24	+ 9
2	3.2385	2.7855	1.6690	.84228	18.724	18.592	−35
9	3.2533	2.7962	1.6722	.84157	18.667	18.629	−10
5a	5.4142	4.2555	2.0629	.78362	22.761	22.790	+11
4a	7.5672	5.4761	2.3401	.74185	25.269	25.286	+ 8
8a	9.8764	6.5834	2.5658	.70781	27.074	27.081	+ 4
4	12.6314	7.6923	2.7735	.67681	28.590	28.596	+ 4
5	13.4508	7.9855	2.8258	.66918	28.971	28.961	− 6
7a	17.4353	9.2207	3.0366	.63850	30.376	30.385	+ 6
8	21.0845	10.1337	3.1833	.61792	31.341	31.337	− 3
7	23.9978	10.7495	3.2786	.60481	31.945	31.943	− 2

Table II. The experiments are numbered chronologically. Each solution made from weighed quantities of salt and water is given a consecutive number, while those made by quantitative dilution are designated by letters following the number of the concentrated solution from which they came. Experiments one to five inclusive were carried out by T. R. Rubin; the rest by F. D. Ayres. The molality, m, of the solution (moles solute per kg. water) was determined directly from the weights of the constituents. The molarity, c (moles solute per liter of solution) was then calculated from the equation[6]

$$\frac{c}{m} = d_1\left[1 - \frac{c\Phi(V_2)}{1000}\right]$$

The values of $\Phi\ (V_2)$, the apparent molal volume of ammonium nitrate, were calculated from the equation

$$\Phi(V_2) = 47.558 + 0.966\ c^{1/2} + 0.0474c$$

which was derived[6a] (p. 314) from the accurate density measurements of Adams and Gibson.[7] Successive approximations were made until two consecutive values of c agreed within 0.0001. The process was expedited, especially when successive values diverged, by taking the *average* of the two preceding values of c in making the later approximations. The value of the apparent molal heat capacity $\Phi(C_{p_2})$ was calculated from the usual equation

$$\Phi(C_{p_2}) = \left[\frac{1000}{m} + M_2\right] s - \frac{1000}{m}$$

where M_2 is the molecular weight of ammonium nitrate, 80.047 g. Since s is the specific heat at 25°, $\Phi(C_{p_2})$ is expressed in 25°-calories per degree.

One of our objects in studying ammonium nitrate was to compare the plots of the apparent molal heat capacity against $m^{1/2}$ and $c^{1/2}$ and to see if it was as nearly a linear function of the latter over the whole concentration range as we had already[6a] (p. 314) shown the apparent molal volume to be. Ammonium nitrate is particularly suitable for such a study. Its high solubility and large apparent molal volume give a great difference between the volume and weight concentrations. A plot of $\Phi(C_{p_2})$ against $m^{1/2}$, reproduced in Fig. 5, showed that up to 1.5 m the results could be reproduced with an accuracy of ±0.005% in s by means of the equation

$$\Phi(C_{p2}) = -2.90 + 12.56m^{1/2}$$

Above 1.5m the experimental points lay along a smooth curve which was concave downward.

A plot was next made, using $c^{1/2}$ as abscissa, but a linear equation reproduced the specific heat data adequately to no higher concentration than before. The equation

$$\Phi(C_{p2}) = -3.30 + 13.37c^{1/2}$$

reproduced the specific heats within ±0.004% on the average, up to c = 1.4. At higher concentrations the experimental points again lay along a smooth curve, concave downward, although the curvature was considerably less than in the plot against $m^{1/2}$.

In order to calculate values of the specific heat of the solution and of the partial molal heat ca-

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(6) (a) Gucker, *J. Phys. Chem.*, **38**, 312 (1934); (b) see also Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931).

(7) Adams and Gibson, THIS JOURNAL, **54**, 4520 (1932).

pacities of the salt and the water at any desired concentration, an equation connecting the apparent molal volume and the concentration was next sought. Calculations involving the weight concentration are simplest to make, so that we first attempted to obtain the apparent molal heat capacity as a function of the molality. Various equations giving $\Phi(C_{p_2})$ as an explicit function of $m^{1/2}$ were first tried, but none was found to reproduce the curve successfully. The large curvature near the center, with nearly straight portions at each end, suggested a section of a hyperbola.

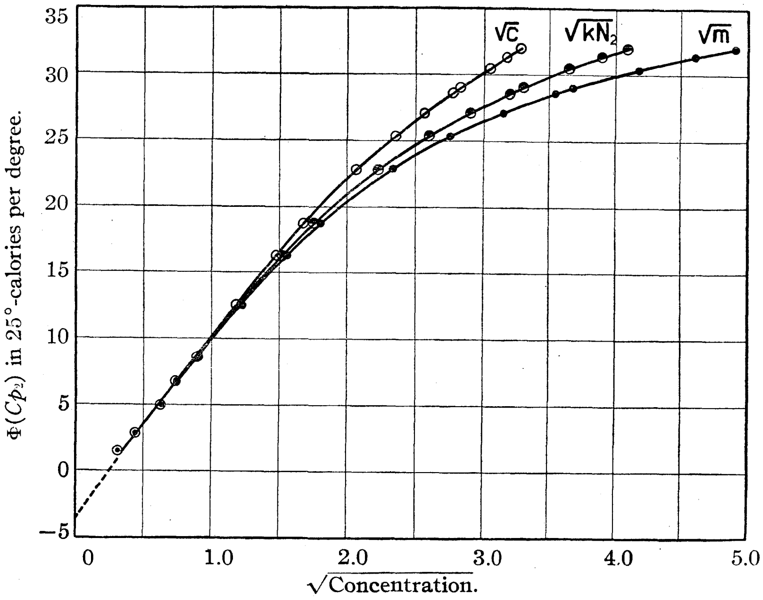

Fig. 5.—A comparison of abscissas.

Accordingly we tried a general equation of the second degree in $\Phi(C_{p_2})$ and $m^{1/2}$, and found that it gave a much better agreement. Such a function reproduced the curve with average deviations of ±0.0085% in s, but there were five deviations of more than 0.01% and the deviations were systematic at both ends of the curve. In order to reduce the curvature, still employing a function of the weight concentration, we next tried the same type of equation with the abscissa $\sqrt{1000\ N_2/M_1}$ where N_2 is the mole fraction of solute, and M_1 the molecular weight of water. This curve coincides with the previous one at low concentrations and in general lies about midway between the plot against $m^{1/2}$ and that against $c^{1/2}$ (see Fig. 5). The agreement was not appreciably improved. Finally we tried the equation

$$\Phi^2 + ac + b\Phi c^{1/2} + dc^{1/2} + e\Phi + f = 0$$

Substituting five values of the variables we evaluated the coefficients a, b, d, e, f. The equation was solved for Φ by the general algebraic formula. Calculated values of Φ were then compared with the experimental ones, and several successive solutions were tried to obtain the coefficients which gave best agreement at every point on the curve. The equation which we finally obtained was

$$\Phi(C_{p2}) = 6.036 + 9.991c^{1/2} - [93.644 - 78.79c^{1/2} + 19.683c]^{1/2}$$

From this equation we calculated the values of Φ which are included in Table II. The average deviation in the specific heat, Δs, is ±0.0075%, with only one of the seventeen observations showing a deviation exceeding 0.011%. In order to check this value, a final experiment, No. 9, was made at almost exactly the same concentration. It gave a value of the specific heat about 0.02% higher than the former one, but still 0.01% lower than the curve at this point. Since this was the largest discrepancy in the whole series, we may conclude that the experimental results, obtained by two experimenters using different samples of ammonium nitrate and making up solutions independently, are in very satisfactory agreement.

Using the last equation, we calculated the values of the apparent molal heat capacity of the salt at even values of c, which are collected in Table III. We also included the corresponding values of the molality and of the partial molal

TABLE III

THE SPECIFIC HEATS OF AMMONIUM NITRATE SOLUTIONS AND VALUES OF $\Phi(C_{p2})$, $\overline{C}_{p2}$ AND $\overline{C}_{p1} - \overline{C}^{\circ}_{p1}$ AT EVEN CONCENTRATIONS

c	m	s	$\Phi(C_{p2})$	$\overline{C}_{p2}$	$\overline{C}^{\circ}_{p1} - \overline{C}_{p1}$
0.0	0.0	1.00000	−3.6	−3.6	0.0000
.25	.2538	0.98092	3.3	6.8	.0156
1.0	1.0541	.93205	10.15	16.50	.1205
2.0	2.2239	.87818	15.52	23.47	.3184
3.0	3.5319	.83277	19.313	27.631	.5292
4.0	5.0066	.79314	22.171	30.146	.7194
5.0	6.6842	.75766	24.392	31.752	.8862
6.0	8.6120	.72539	26.179	32.927	1.0469
7.0	10.8529	.69586	27.678	33.893	1.2151
8.0	13.4928	.66874	28.979	34.726	1.3969
9.0	16.6522	.64379	30.142	35.452	1.5930
10.0	20.5044	.62083	31.203	36.083	1.8026
11.0	25.3099	.59966	32.183	36.624	2.0249

heat capacities of the solute and solvent. The partial molal heat capacity of the solute, $\bar{C}_{p_2}$, was obtained from the general equation which had been derived previously,[6a] namely

$$\bar{C}_{p2} = \Phi(C_{p2}) + \left[\frac{1000 - c\Phi(V_2)}{2000 + c^{3/2}\dfrac{\partial\Phi(V_2)}{\partial c^{1/2}}}\right] c^{1/2}\,\frac{\partial\Phi(C_{p2})}{\partial c^{1/2}}$$

Values of $\Phi(V_2)$ were calculated from the equation previously given, and $\partial\Phi(V_2)/\partial c^{1/2}$ from its derivative

$$\partial\Phi(V_2)/\partial c^{1/2} = 0.966 + 0.0948c^{1/2}$$

The values $\partial\Phi(C_{p_2})/\partial c^{1/2}$ were obtained from the derivative of our equation, which was

$$\frac{\partial\Phi(C_{p2})}{\partial c^{1/2}} = 9.991 + \frac{39.395 - 19.683c^{1/2}}{[93.644 - 78.79c^{1/2} + 19.683c]^{1/2}}$$

The partial molal heat capacity of the water was obtained from the equation

$$\bar{C}_{p1} = \bar{C}^{\circ}_{p1} - \frac{M_1}{d_1}\left[\frac{c}{2000 + c^{3/2}\dfrac{\partial\Phi(V_2)}{\partial c^{1/2}}}\right] c^{1/2}\,\frac{\partial\Phi(C_{p2})}{\partial c^{1/2}}$$

where M_1 is the molecular weight (18.0156 g.) of water and d_1 is its density (0.997077 g./ml.) at 25°. This equation is perfectly general, and would apply to any other partial molal property as well as to the heat capacity. In the case of the partial molal volume of the solute, it reduces to an equation analogous to that derived by Gibson[8] for the partial specific volume. Calculations involving the volume concentration are more complicated than those involving the weight concentration, but their use is justified when the apparent molal property may be expressed more exactly as a function of the volume than of the weight concentration.

In Fig. 6 we have plotted $\Phi(C_{p_2})$, $(\bar{C}_{p_2})$ and $\bar{C}_{p_1}$. The apparent molal heat capacity of the solute starts from the value −3.6 calories per mole per degree at zero concentration, with an initial slope of $\partial\Phi(C_{p_2})/\partial c^{1/2} = 14.06$, which decreases to 6.287 at $c = 11$. The corresponding partial molal heat capacity starts from the same point, with a slope half again as great. It is always greater than the apparent molal heat capacity, but the difference is greatest (8.3 calories per degree) at 3 molar and decreases steadily to 4.4 at 11 molar, where the *slope* of the curve is only about 55% of that of the apparent molal heat capacity curve.

The partial molal heat capacity of the water decreases regularly from the value in pure water, $\bar{C}^{\circ}_{p_1}$ = 18.0156 25°-calories per degree, to a value of 15.9907 in a saturated solution of ammonium nitrate (11 molar): a decrease of 11%.

Acknowledgments.—It is a pleasure to acknowledge our indebtedness to the National Research Council for a Grant-in-Aid which defrayed part of the cost of the apparatus used in this work; to Professor R. G. Bigelow and Mr. M. L. West of the Northwestern Engineering School for their advice and assistance in the construction of many parts of the apparatus; and to Mr. Robert J. Mueller who, working under an N. Y. A. project, assisted in the purification of much of the ammonium nitrate.

Summary

We have described the construction and operation of a new modification of the twin calorimetric apparatus for measuring specific heats. Special electrical heaters with resistances variable in small increments, mounted on mica strips, are used to supply energy proportional to the heat capacity in each calorimeter. The resistance ratio is measured during the experiment.

Solutions of ammonium nitrate were made from weighed amounts of purified dried salt and water, or from a single quantitative dilution. The specific heats of seventeen of these solutions, over

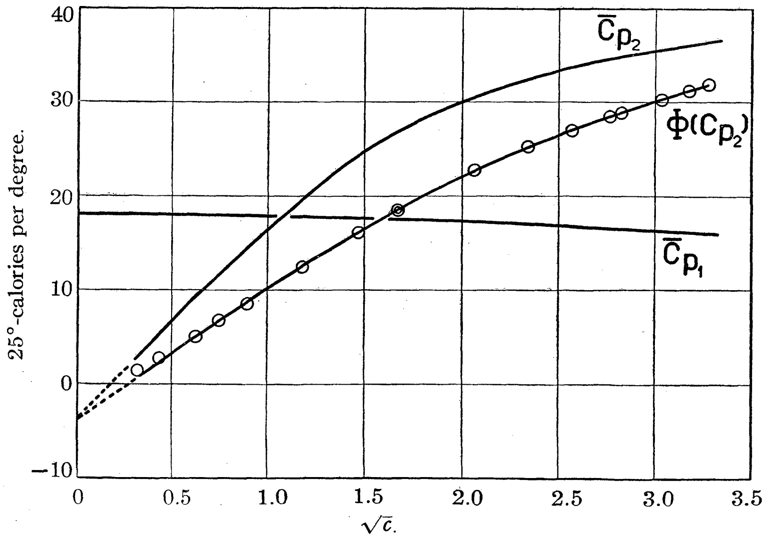

Fig. 6.—Apparent and partial molal heat capacities in solutions of ammonium nitrate at 25°.

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(8) Gibson, *J. Phys. Chem.*, **38**, 319 (1934).

the concentration range 0.1 to 10.75 moles per liter, were measured at 25°.

The apparent molal heat capacity is a linear function of $c^{1/2}$ (or $m^{1/2}$ or $N_2^{1/2}$) only up to about a 1.5 molal solution, above which the relation found by Randall and Rossini fails. A hyperbolic second degree equation for the apparent molal heat capacity as a function of the square root of the volume concentration reproduces the specific heats with an average deviation of ±0.0075%. Values of the partial molal heat capacity of the salt at round concentrations were calculated from an equation previously derived and values of the partial molal heat capacity of the water were calculated from a new equation which is generally applicable to all molal quantities. These values are tabulated, along with those of the specific heats of the same solutions.

EVANSTON, ILLINOIS RECEIVED JUNE 11, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Thermodynamics of Aqueous Indium Sulfate Solutions[1]

BY ERWIN M. HATTOX AND THOS. DE VRIES

Very little work has been done on the activity coefficients and other thermodynamic properties of aqueous solutions of the ter-bivalent salts. Hovorka and Rodebush[2] determined the freezing point lowering of dilute solutions of lanthanum sulfate, and from these data calculated the activity coefficients. Since their results dealt only with dilute solutions, it seemed desirable to study the behavior of indium sulfate in aqueous solutions over a wider range of concentrations and at several temperatures. E. m. f. measurements were made on cells of the type In (s) | $In_2(SO_4)_3$ (m) | Hg_2SO_4–Hg at 0, 15, 25 and 35°, and freezing point lowerings were determined for a few dilute solutions of indium sulfate. The degree of hydrolysis was also determined at room temperature.

Materials and Apparatus

All materials used in this investigation were very carefully purified. The water used for making the solutions and for making ice was prepared by double distillation of the ordinary laboratory distilled water. The first distillation was made from alkaline permanganate and the second from barium hydroxide. The water thus purified was stored in glass-stoppered Pyrex bottles.

Commercially pure indium (98.9%), obtained from W. S. Murray, Ithaca, New York, was purified in the following manner. The metal was dissolved in concentrated nitric acid, the solution diluted, and precipitated as indium hydroxide with dilute ammonium hydroxide. This was washed several times and dissolved in dilute hydrochloric acid. Spongy indium was plated out from this solution, using platinum electrodes and a current of about 0.3 ampere. The washed, spongy mass then served as an anode in another dilute hydrochloric acid solution, the indium being redeposited by electrolysis on a platinum cathode.[3] Indium sulfate was prepared from this indium by slowly evaporating a strong sulfuric acid solution of it at about 50°, washing the crystals that separated out with glacial acetic acid, and then heating in a furnace to a temperature of 450–500° for six hours.[4] By gravimetric analysis the product was shown to be anhydrous indium sulfate.

The mercury was purified by washing for several days with dilute nitric acid and distilling twice under reduced pressure in a current of air.

Mercurous sulfate was prepared by electrolysis from dilute sulfuric acid using a mercury anode and a platinum cathode, and a current density of 0.5 ampere per square decimeter. In order to prevent the formation of a yellow basic salt due to hydrolysis, the mercurous sulfate, along with the finely divided mercury mixed with it, was washed first with alcohol, then with ether. The product was dried and kept in a desiccator until ready for use.

The most concentrated indium sulfate solution was made up by weight from the prepared anhydrous salt. All the solutions of lower concentrations were made by successive weight dilutions, using an analytical balance of 2-kg. capacity.

After experimenting with complicated cells in which the air could be replaced by hydrogen, a simple cell was developed, made by sealing a platinum wire in the bottom of a 16-mm. Pyrex tube, and having a side-arm in which the indium electrode was placed.

The thermostat temperatures were maintained within ±0.01°. A two-liter size Dewar flask with crushed ice served very satisfactorily for the 0° bath. All temperatures were established with standard thermometers.

Electromotive forces of the cells were measured on a Leeds and Northrup Type K potentiometer.

Apparatus for the freezing point measurements was

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[1] Based upon a thesis submitted by Erwin M. Hattox to the Faculty of Purdue University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936. Presented before the American Chemical Society at its 92nd meeting in Pittsburgh, Pa., Sept. 7–11, 1936.

[2] Hovorka and Rodebush, THIS JOURNAL, **47**, 1614 (1925).

[3] Baxter and Alter, *ibid.*, **55**, 1943 (1933).

[4] Seward, *ibid.*, **55**, 2740 (1933).

essentially the same as that described by Hovorka and Rodebush,[2] the only change being that the two Dewar flasks were not sealed together. A twelve-junction thermel, carefully calibrated, and having a potential change of 461 microvolts per degree at 0°, was used for the determinations of the temperature differences. A very sensitive galvanometer set-up was arranged by making use of a lens of 1.22 meters focal length and focusing a straight edge image from the galvanometer mirror onto a ground glass plate. The distance from light source to the galvanometer, the same as that from the galvanometer to the plate, was 3.2 meters. The scale on the glass plate was calibrated and it was found that readings could be made with a precision of about 0.0001°. A White potentiometer, with the lower dials marked in 10 and 1 microvolts, was used to measure the voltage of the thermel.

Experimental

Mercury was placed in the bottom of the completely dried cell, and was then covered with a thin layer of the dry mercurous sulfate. The solution was poured down the side arm until it reached a height of about 2.5 cm. in the arm. After the cell had been tightly stoppered, it was allowed to stand for a period of from twenty-four to forty-eight hours in order for equilibrium to be reached. This time was found by experiment. When this time had elapsed, an indium electrode was prepared by plating a thin layer of the metal on a platinum spiral sealed in the end of a glass tube, using a current of about 0.2 ampere. After the electrode was washed and dried in a stream of air, it was placed in position in the side-arm, and held there by means of a rubber tubing which also served to keep the cell closed to the atmosphere. The cell was then placed in the 15° thermostat and allowed to reach equilibrium at that temperature, which usually required from three to six hours. After all the needed data at 15° had been recorded, the cell was transferred successively to the 25 and 35° thermostats. A separate cell was prepared for the measurements at 0°, but the procedure followed was the same.

The experimental technique used by Hovorka and Rodebush[2] was employed for the freezing point determinations.

Discussion of the Results

The molalities of the solutions used and the corresponding e. m. f.'s observed at the different temperatures are given in Table I. Two or more values were obtained for each concentration at each temperature. The voltages were reproducible to ±0.2 mv. in the concentrated solutions, but the deviations in the dilute solutions were about ±0.3 mv. The e. m. f.'s of the individual cells usually remained constant for eight to ten hours or longer.

In order to determine the absolute value of the activity coefficients, E_0 must be evaluated. This requires an extrapolation to infinite dilution, and the voltages of the dilute solutions are less reliable than those of the concentrated solutions. Evidently, then, an extremely accurate value of E_0 cannot be expected. However, from freezing point measurements the activity coefficients can be determined with considerable accuracy. Due to the formation of a precipitate resulting from hydrolysis it was possible to obtain only one point of any significance from such measurements. A 0.00631 molal solution gave a depression of 0.0316°, but solutions of 0.00198 molal and less developed precipitates upon standing. The one point that we were able to determine fits the data of Hovorka and Rodebush within the limits of experimental error. Assuming that indium sulfate and lanthanum sulfate give identical freezing point curves in very dilute solutions, which seems to be logical, we used 0.150 as the activity coefficient in 0.01 molal solution[5] and calculated E_0 to be 0.9747 volt at 0°. This agrees well with 0.974 obtained by an extrapolation from e. m. f. data.

TABLE I

ELECTROMOTIVE FORCE OF CELLS

In(s), $In_2(SO_4)_3(m)$, Hg_2SO_4-Hg

m, $\frac{\text{Moles } In_2(SO_4)_3}{1000 \text{ g. } H_2O}$	E. m. f., v. 0°	15°	25°	35°
0.4231		1.0473	1.0427	1.0382
.3132		1.0500	1.0456	1.0410
.2454		1.0528	1.0483	1.0439
.1676	1.0627	1.0560	1.0515	1.0470
.0999		1.0597	1.0553	1.0508
.0526	1.0700	1.0631	1.0591	1.0551
.0378		1.0673	1.0632	1.0590
.0281	1.0749	1.0698	1.0658	1.0617
.0221		1.0718	1.0677	1.0636
.0158	1.0800	1.0742	1.0703	1.0664
.0100	1.0838	1.0782	1.0744	1.0705
.00631	1.0885			
Values of E_0				
E_0	0.974	0.962	0.954	0.946

The electromotive force of the cell at any temperature T may be given by the equation

$$E = E_0 - (RT/6F) \ln 108\gamma^5 m^5 \qquad (1)$$

which may be written

$$k \log \gamma = E_0 - E - 0.4067k - k \log m \qquad (2)$$

In dilute solutions the logarithm of the activity coefficient may also be expressed by $\log \gamma = -6\,A\,\sqrt{\mu} + B\,\mu$ in which A and B are constants and μ is the ionic strength. When this relation is used in (2), the following expression is obtained

$$E + 0.4067k + k \log m - 6kA\sqrt{\mu} = E_0 - kB\mu \qquad (3)$$

Designating the left side of this equation as E_0', and plotting it against m, a curve is obtained for each temperature which may be extrapolated to

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[5] Rodebush, THIS JOURNAL, 48, 709 (1926).

infinite dilution to give a value for E_0. Harned and Ehlers' values[6] of A were used in evaluating E'_0. Curves of this type were drawn for the four temperatures. Although these were nearly straight lines and the curves did not have to be extrapolated very much, E_0 was not evaluated closer than 1 mv. The values are given in Table I. These were used in equation (1) to calculate the activity coefficients. Because of the uncertainty as to the degree of hydrolysis of indium sulfate, it is not feasible to determine the "true" activity coefficients. The "stoichiometrical activity coefficients"[7] were therefore determined. They are collected in Table II. The values, including those calculated by Rodebush[5] from the freezing point data for lanthanum sulfate, lie on a smooth curve when log γ is plotted againt $\sqrt{m}$. Since Halpern[8] questions the reliability of the La Mer, Gronwall and Greiff extension of the Debye–Hückel theory[9] to unsymmetric valence type of electrolytes, no attempt was made to make the Debye–Hückel equations fit the data. When extrapolated values of the La Mer, Gronwall and Greiff formulas were used, a value of about 5 Å. was obtained for "a," the mean distance of approach of the ions.

TABLE II

ACTIVITY COEFFICIENTS OF INDIUM SULFATE

m	0°	15°	25°	35°
0.4231		0.015	0.015	0.014
.3132		.018	.017	.017
.2454		.020	.020	.019
.1676	0.025	.025	.025	.024
.0999		.035	.035	.034
.0526	.056	.056	.055	.054
.0378		.064	.063	.063
.0281	(.081)	.076	.075	.075
.0221		.088	.088	.087
.0158	.111	.110	.109	.108
.0100	.145	.143	.142	.141
.00631	.181			

The normal potential of the In, In^{+++} electrode at 25° is +0.340 if the value −0.614 is used for the $Hg–Hg_2SO_4$, $SO_4^=$ electrode.[10]

The Partial Molal Heat Content

The partial molal heat content relative to the 0.01 M solution was computed by the Gibbs–Helmholtz equation

$$(\overline{H}_m - \overline{H}_{0.01}) = NF(E - TdE/dT) \quad (4)$$

The temperature coefficient of the cell was nearly constant. Since an error of ±0.01 mv. in the temperature coefficient means an error of approximately ±100 calories, the values given in Table III are merely good approximations. Because of insufficient data it was not possible to calculate $\overline{L}_2$, the relative partial molal heat content.

TABLE III

PARTIAL MOLAL HEAT CONTENT OF INDIUM SULFATE RELATIVE TO THE 0.01 M SOLUTION

m	$(\overline{H}_m - \overline{H}_{0.01})$ 0°	15°	Cal./mole 25°	35°
0.4231		−4280	−4390	−4470
.3132		−3900	−3990	−4080
.2454		−3520	−3610	−3680
.1676	−2920	−3070	−3170	−3250
.0999		−2560	−2640	−2730
.0526	−1910	−2090	−2120	−2130
.0378		−1510	−1550	−1590
.0281	(−1230)	−1160	−1190	−1220
.0221		− 890	− 930	− 950
.0158	− 530	− 550	− 570	− 570

Hydrolysis of Indium Sulfate

The pH values of nine solutions were determined at room temperature, 23°, using a quinhydrone electrode with a 0.1 N calomel cell as reference electrode.

Two series of hydrolysis constants were calculated from the pH values found at various molalities. These are designated in Table IV as K_h and K_h'. The K_h' was calculated on the assumption that the hydrolysis of In^{+++} may be represented

$$In^{+++} + H_2O \rightleftharpoons InO^+ + 2H^+ \quad (5)$$

The computed values of K_h' vary considerably at the different concentrations. If, however, the hydrolysis reaction is written

$$In^{+++} + H_2O \rightleftharpoons In(OH)^{++} + H^+ \quad (6)$$

and the constant calculated for this reaction, a much nearer approach to a constant value is obtained. The values headed K_h are the results

TABLE IV

HYDROLYSIS OF INDIUM SULFATE

m	pH	$K_h' \times 10^6$	$K_h \times 10^4$
0.2454	1.77	5.1	6.6
.0999	2.01	2.4	5.1
.0526	2.20	1.2	4.0
.0378	2.29	0.93	3.7
.0281	2.36	.79	3.7
.0221	2.41	.72	3.8
.0158	2.57	.34	2.5
.0100	2.69	.21	2.2
.00631	2.83	.14	2.0

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(6) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

(7) Brönsted, *ibid.*, **42**, 761 (1920).

(8) Halpern, *J. Chem. Phys.*, **2**, 85 (1934).

(9) La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

(10) Shrawder, Cowperthwaite and La Mer, THIS JOURNAL, **56**, 2348 (1934).

obtained. The results are not constant, but such could hardly be expected, since molalities instead of activities were used. There is indication, however, that a constant value will be approached in a very dilute solution.

Summary

1. Using cells of the type In(s), $In_2(SO_4)_3(m)$, Hg_2SO_4–Hg electromotive force measurements have been made at 0, 15, 25 and 35°.

2. The freezing points of dilute solutions of indium sulfate were investigated.

3. Calculations have been made of the activity coefficients of indium sulfate in aqueous solution, and of the partial molal heat contents relative to the 0.01 M solution.

4. *p*H values of solutions of indium sulfate have been determined at room temperature, using the quinhydrone electrode.

5. The constant for the hydrolysis of indium sulfate has been calculated assuming the reaction to be

$$In^{+++} + H_2O = In(OH)^{++} + H^+$$

LAFAYETTE, INDIANA RECEIVED AUGUST 1, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Presence of Free Radicals in the Thermal Decomposition of Diethyl Ether

BY C. J. M. FLETCHER AND G. K. ROLLEFSON

The decomposition of diethyl ether is a reaction for which a chain mechanism involving free radicals has been postulated.[1] The experimental results of previous investigations,[2–6] except for the recent results on the inhibition of the rate of reaction by small quantities of nitric oxide,[7] do not enable any decision to be made between the alternative theories of molecular rearrangement and such a chain mechanism. The present investigation provides definite evidence for the presence of free radicals since small amounts of ether are found to catalyze the decomposition of acetaldehyde. Quantitative estimations of the aldehydes, which are formed as intermediates, and a more detailed study of the kinetics of the over-all reaction have enabled the kinetics of the ether decomposition to be separated from those of secondary reactions.

Experimental Details.—The thermal reactions were studied in a Pyrex bulb, approximately 500 cc. in volume, placed in an electrically heated furnace. Fluctuations of the voltage were reduced by the use of Radiatron ballast tubes (U. V. 886 and 876), and the temperature was controlled by hand to within one degree. Pressures greater than 20 mm. were measured on a mercury manometer made from capillary tubing and heated by nicrome wire to prevent the condensation of organic vapors. The dead-space outside the furnace did not amount to more than 2% of the volume of the bulb. Pressures of less than 20 mm. were measured with a sulfuric acid manometer separated from the reaction by a click-gage. It was found that pressure equilibrium between the bulb and click-gage was not established instantaneously, so that the time lag was estimated with different pressures of air and a correction applied.

The reaction vessel was evacuated through a liquid air trap by a mercury vapor pump and oil pump to pressures of less than 10^{-3} mm. If at any time air was admitted to the reaction vessel, it was well washed out with the vapor of the substance in use.

The substances used were stored, if liquids, in small bulbs attached to the system; if gases, in a reservoir over mercury. Mixtures were made in a reservoir over mercury, and could be thoroughly mixed by changing the mercury level.

Gas analyses were carried out according to the micro methods of Blacet and Leighton.[8] The greater part of any aldehyde or ether present was removed in a trap at −70°. As it was found that the beads slowly absorb other gases than that for which they are used (*e. g.*, fuming sulfuric acid slowly absorbs carbon monoxide), the times of contact were carefully controlled.

In order to determine the amounts of aldehydes present the gas was withdrawn, shaken with water and (a) the total aldehydes found by titration with sodium bisulfite; (b) the formaldehyde estimated by the potassium cyanide method.[9] The bisulfite solution was stabilized with ethyl alcohol and frequently standardized against iodine. Blank experiments with acetaldehyde showed that it also slowly reacts with potassium cyanide for which interaction a correction was applied. Experiments with undecomposed acetaldehyde vapor withdrawn from the furnace showed the bisulfite method to be accurate.

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[1] F. O. Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

[2] Hinshelwood, *Proc. Roy. Soc.* (London), **A114**, 84 (1927).

[3] Newitt and Vernon, *ibid.*, **A135**, 307 (1932).

[4] Steacie and Solomon, *J. Chem. Phys.*, **2**, 503 (1934).

[5] O. K. Rice and Sickman, THIS JOURNAL, **56**, 1444 (1934).

[6] Steacie, Hatcher and Rosenberg, *J. Chem. Phys.*, **4**, 220 (1936).

[7] Staveley and Hinshelwood, *Proc. Roy. Soc.* (London), **A154**, 335 (1935).

[8] Blacet and Leighton, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 266 (1931).

[9] Romijn, *Z. anal. Chem.*, **36**, 19 (1897).

Diethyl ether (99.5%) was dried over sodium and freshly distilled in an all-glass apparatus. Acetaldehyde (Eastman Kodak) was distilled and the fraction boiling between 20.5 and 21° collected for use. A particularly pure specimen of helium, prepared for cryogenic work, was used. Ethylene was purified by fractionation at liquid air temperatures.

Experimental Results.—Analyses of the gaseous reaction products were made on samples for which the initial pressure, p_0, was 200 mm. at 507°, and which were allowed to proceed to various stages of completion, $\Delta p/\Delta p_\infty$. The results are given in Table I.

TABLE I

Gas Analyses: p_0 = 200 mm., Temp. = 507°

$\frac{\Delta p}{\Delta p_\infty}$	Hydrocarbons, % Unsatd.	Satd.	H_2, %	CO (obsd.), %	CO (calcd.), %
0.05	7.6	77.4	7.4	7.6	10
.075	10.0	74.8	7.0	8.2	12
.25	9.5	68.2	5.3	17.0	20
.40	8.5	68.5	4.0	19.0	24
.50	10.5	60.9	4.3	24.3	25
.90	8.5	57.9	4.3	29.3	32

It is known that formaldehyde and acetaldehyde are formed during the decomposition of diethyl ether,[3] and as their rates of decomposition are of the same order of magnitude as that of the ether, considerable quantities of the aldehydes are built up in the system. Quantitative estimations were carried out (a) at 507 and 552° for an initial pressure of 200 mm., and (b) at 552° for an initial pressure of 20 mm. In Fig. 1 the percentages of total aldehydes relative to the amount of ether originally present are plotted for comparable stages of completion. The ratio of formaldehyde to the total aldehydes is in each case from 20 to 25%. The almost exact agreement between the two curves for 200 and 20 mm. means that the order of the reaction that produces the aldehyde is the same as that by which it decomposes: results to be described later show that the former is 1.4. The amounts of aldehyde present do, however, show a definite increase with temperature (Table II) for which allowance must be made in deriving the energy of activation of the ether decomposition from pressure measurements.

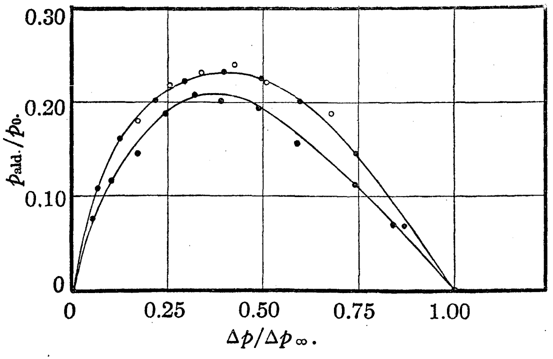

Fig. 1.—Amounts of aldehydes built up at different stages of completion: ●, p_0 200 mm., temp., 552°; ⊙, p_0 20 mm., temp., 552°; ◉, p_0 200 mm., temp., 521°.

TABLE II

Aldehydes Present at $\Delta p/\Delta p_\infty$ = 0.40

Temp., °C.	p_0, mm.	$p_{ald.}/p_0$ × 100	$p_{form.}/p_{ald.}$ × 100
552	380	22.9	23
552	200	23.4	24
552	53	23.5	..
552	20	23.6	23
507	200	21.0	21
490.5	200	21.0	19
473.5	200	20.4	..
442	200	18.8	18
490	4636	18.0	32 (Newitt and Vernon)

Irrespective of the mechanism by which the ether decomposes, it is possible, *a priori*, (a) that the ether decomposes directly to carbon monoxide, *e. g.*

$$C_2H_5OC_2H_5 \longrightarrow C_2H_6 + CH_4 + CO$$

or (b) that an aldehyde is formed as an intermediate, *e. g.*

$$C_2H_5OC_2H_5 \longrightarrow CH_3CHO + C_2H_6$$

and that the aldehyde subsequently decomposes to carbon monoxide and methane. If all the ether decomposes in the former manner, the percentage of carbon monoxide in the products would be constant throughout the reaction; if all in the latter manner, the percentage would be very small in the early stages and increase as the reaction proceeds. Further, assuming that all the ether does actually form an aldehyde as an intermediate, it is possible, knowing the amounts of aldehyde present (Fig. 1), to calculate at any stage of the reaction the amount of aldehyde which has decomposed and therefore the percentage of carbon monoxide in the reaction products. The agreement between the calculated and observed amounts of carbon monoxide (Table I) justifies the conclusion that virtually all the ether forms an aldehyde as an intermediate step in its decomposition.

The question arises as to whether the aldehydes decompose at the same rate as in the pure state. At 552°, the maximum amounts of aldehyde are present when the pressure increase is 40% complete: at this stage the rate of production of aldehyde equals its rate of destruction. For an initial ether pressure of 197 mm. the rate of destruction of ether, which equals the rate of formation of aldehyde, is 0.374 mm./sec. From Fig. 1 it is seen that $p_{\text{ald.}}/p_0$ is 0.234, so that the aldehyde pressure is 46.1 mm. For this temperature and pressure it may be calculated from the results on the decomposition of pure acetaldehyde[10] that the rate of aldehyde disappearance is 0.122 mm./sec.; for formaldehyde the value is very similar.[11] When, therefore, these aldehydes are formed as intermediates in the decomposition of ether they react at a rate approximately three times greater than in its absence. This is too great a difference to be accounted for by cross activation by collisions with ether, and indicates a definite catalytic action of ether which has been confirmed by comparing the rates of decomposition of pure acetaldehyde with those of mixtures containing small percentages of ether.

The Decomposition of Acetaldehyde Catalyzed by Diethyl Ether.—Experiments with acetaldehyde were alternated with those of the aldehyde–ether mixtures. In both cases, after allowing for the ether decomposition, the shapes of the pressure–time curve were similar, and the end-point was nearly double the initial pressure. The rates have, therefore, been compared from the half-times, after applying a correction for the rate of decomposition of the ether: this is comparatively small as the rates of reaction of ether and acetaldehyde are similar (at 552° and 200 mm. they are 0.79 mm./sec. for ether and 1.15 mm./sec. for acetaldehyde). Table III gives the temperature, the percentage of ether to the total gas, the initial acetaldehyde pressure and the ratio of $1/t_{1/2}$ to that for the same initial pressure of pure acetaldehyde. The increase in $1/t_{1/2}$, which represents the catalyzed reaction, is independent of temperature, and nearly proportional to the percentage of ether. It may be noted that the addition of 5% of acetaldehyde does not change the initial rate of the ether decomposition.

TABLE III

THE CATALYSIS OF ACETALDEHYDE BY DIETHYL ETHER

Temp., °C.	% Ether	$p_{\text{ald.}}$, mm.	% increase $1/t_{1/2}$
552	1.9	179	5.3
	5.2	161	15.5
	5.2	90	21.7
	5.2	20.3	25.0
	18.5	156	55.2
507	5.2	178	15.8
	11.3	164	32.2
	11.3	85	38.9
	11.3	23.2	40.0
490.5	5.2	174	16.1

The catalysis of acetaldehyde by ether may be explained on the hypothesis that the decomposition of ether produces free radicals which then set up a chain in acetaldehyde. The uncatalyzed reaction of acetaldehyde cannot involve free radicals to any appreciable extent or the introduction of a few free radicals from ether, at temperatures at which the acetaldehyde is already decomposing as fast as the ether, would not increase the rate appreciably. At temperatures around 550°, therefore, the uncatalyzed reaction is

$$CH_3CHO \longrightarrow CH_4 + CO$$

If free radicals are present, however, the chain decomposition

$$CH_3CHO + R \longrightarrow CH_4 + CH_3CO$$
$$CH_3CO \longrightarrow CH_3 + CO$$

can also occur.

The chain length, λ, can be found in terms of the fraction of free radicals, x, produced from ether. At 552° the addition of 9 mm. of ether to 161 mm. of aldehyde causes an increase in $1/t_{1/2}$ of 15.5%: the initial rate may be assumed to increase by the same amount. In the absence of ether this rate is 0.82 mm./sec., so that the increase is 0.13 mm./sec. The initial rate of disappearance of ether, assuming no cross activation by acetaldehyde, is 0.011 mm./sec.; if collisions with acetaldehyde are equally as effective as collisions with ether in causing activation, the rate of disappearance is 0.031 mm./sec. The value of λ therefore lies between $12/x$ and $4/x$. The results with nitric oxide on ether[7] indicate that at this temperature the inhibited reaction is about 0.3 of the total reaction, so that for ether the chain length is $0.7/x$. The value of x may be very considerably smaller than 0.3 as ether molecules not only produce free radicals but also decompose directly to molecules without the formation of such radicals.

The Rate of Pressure Increase.—Deductions about the rate of disappearance of ether can only be made from measurements on the rate of pressure increase if (a) the final pressure increase at any temperature and pressure is known, and if (b) allowance is made for the undecomposed aldehydes present. Newitt and Vernon[3] at pressures

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[10] Fletcher and Hinshelwood, *Proc. Roy. Soc.* (London), **A141**, 41 (1933).

[11] Fletcher, *ibid.*, **A146**, 357 (1934).

greater than atmospheric have estimated the aldehydes and corrected for them.

The final pressure increase, Δp_∞, at any initial ether pressure, p_0, does not vary with temperature, but at any temperature there is a marked decrease with pressure. The values obtained at different pressures at temperatures from 495 to 565° are plotted in Fig. 2. A similar variation has been found for other molecules[11] and has been correlated with condensation reactions.

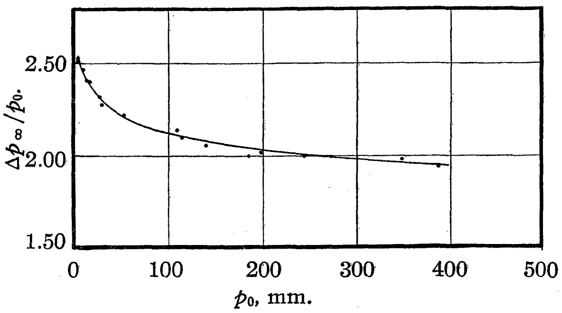

Fig. 2.—Variation of end-point with initial pressure.

The rates at different initial pressures were compared by taking the times, $t_{1/4}$ and $t_{1/2}$, in seconds, for one-quarter and one-half of the pressure increase at completion. The variations of $1/t_{1/4}$ with p_0 at 552 and 521° are plotted in Fig. 3.

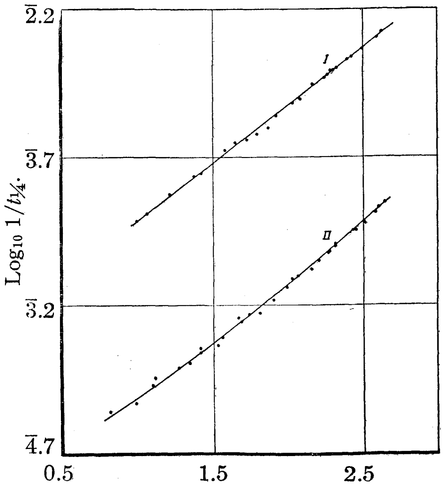

Fig. 3.—I, 552°; II, 507°.

As the amounts of aldehydes present throughout the reaction have been estimated, a pressure–time curve, such as would be obtained if the aldehyde present were completely decomposed, can be constructed (it has been assumed that unit pressure of aldehyde gives 1.95 units of products). This has been done in Fig. 4 for p_0 = 198 mm. at 552°, and it is seen that the induction period noticeable in the uncorrected curve is in this way removed. The uncorrected values of $t_{1/4}$ and $t_{1/2}$ are 102 and 232.5 sec., respectively; from the corrected curve they are 68.2 and 167 sec., so that as the correction for the aldehydes at this temperature is the same at all pressures (Fig. 1), the observed values of $t_{1/4}$ at 552° must all be decreased by the factor 68.2/102 = 0.669. The corrected value of $t_{1/2}/t_{1/4}$ is 2.45, which is very close to that for a unimolecular reaction (2.41). The unimolecular constant, $k_{\text{uni.}}$, is connected at 552° with $t_{1/4}$ by the relation, $k_{\text{uni.}} = 0.43/t_{1/4}$.

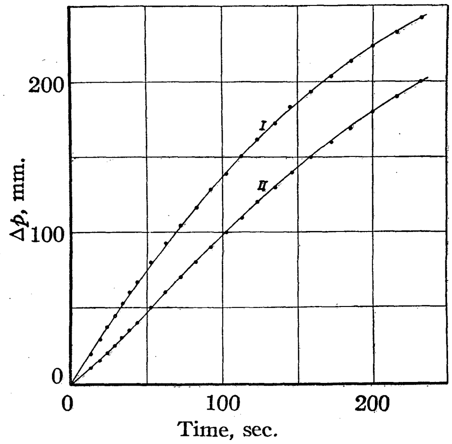

Fig. 4.—Pressure–time curve: p_0 197 mm., temp. 552°; I, corrected for aldehydes present; II, uncorrected for aldehydes.

The slope of log $1/t_{1/4}$: log p_0 (Fig. 3) gives directly the order of the ether decomposition with respect to the initial pressure, as the correction to be applied for the aldehydes is the same at all pressures. This gives an order of 1.40 at 552°, and at 521° a similar value, though at this temperature the order increases somewhat with pressure, as has been found by Rice and Sickman at lower temperatures and pressures.[5] It is known that the non-chain reaction, *i. e.*, that in which small quantities of nitric oxide eliminate the chain reaction, varies with the initial pressure from 50 to 500 mm. in the same manner as the uninhibited reaction.[7] It follows, therefore, that the orders of both the chain and non-chain reactions are approximately 1.4. At much higher pressures (30 to 300 atm.), Steacie, Hatcher and Rosenberg[6] derive an order of 1.35, though they make no allowance for any variation in the end-points.

The Variation of the Energy of Activation with Pressure.—Theories of quasi-unimolecular reactions predict an increase in the energy of activation with pressure, which have been verified for azomethane.[12] In other cases, *e. g.*, the aldehydes,[13] the reverse has, however, been found, and has been correlated with chemical and physical complexities of the reactions. For diethyl ether, in which the greater number of molecules decompose by a chain mechanism, our results show that the energy of activation, E_1, decreases slightly but definitely with pressure (Table IV). The values of E are those derived directly from the slopes of $\log 1/t_{1/4}$ against $1/T$; the quarter times for constant concentrations were compared (Fig. 5). These energies of activation represent composites of the individual energies of activation of the reactions which contribute to the pressure increase. The smaller amounts of aldehydes formed at lower temperatures indicate a lower energy of activation for their destruction than for their formation. At 552° it has been found that $k = 0.43/t_{1/4}$; a similar calculation for $p_0 = 200$ mm. at 507° gives $k = 0.412/t_{1/4}$. If $k = x/t_{1/4}$, the energy of activation, E_1, for the initial decomposition of ether is

$$\begin{aligned} E_1 &= (E + R)\ \mathrm{d} \ln x/d(1/T) \\ &= E + 1200 \text{ cal.} \end{aligned}$$

and at 200 mm., $k = 1.6 \times 10^{13}\ e^{-58,600/RT}$.

TABLE IV

THE ENERGY OF ACTIVATION OF DIETHYL ETHER

p_0, mm.	E, cal.	E_1, cal.
400	56,900	58,100
200	57,400	58,600
100	58,200	59,400
50	58,700	59,900
25	59,000	60,200
12	58,700	59,900

Our results lie between those of Hinshelwood[2] (53,000 cal.), and those of Rice and Sickman[5] (62,000 cal.).

Discussion

The decomposition of diethyl ether was at first thought to be a simple quasi-unimolecular reaction;[2] later Rice and Sickman[5] postulated the existence of two or more unimolecular reactions or selective types of internal activation. The chain mechanism of Rice and Herzfeld[1] can now in part be accepted as the present work has demonstrated the existence of free radicals, and the retardation by nitric oxide shows that chains are set up by the radicals.[7] We have also found that the retardation of the rate by the reaction products[2] is due to ethylene, which can act as a chain breaker. Further, it is known that free radicals produced photochemically from acetone[14] or thermally from ethylene oxide[15] can also set up chains in diethyl ether at lower temperatures.

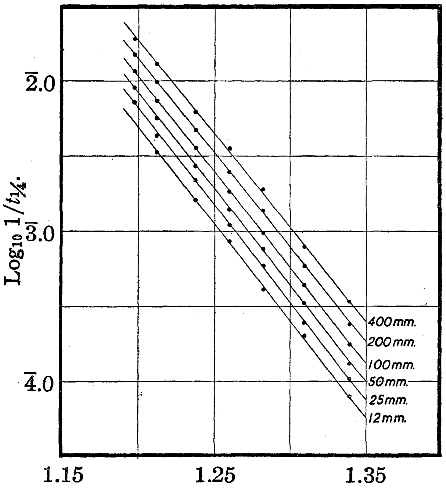

Fig. 5.—Variation of energy of activation with initial pressure.

Although the chain mechanism is thus firmly established, there is evidence that a certain fraction of ether molecules decompose by an intramolecular rearrangement directly to an aldehyde and other molecules.[15] Thus there are three general ways in which ether molecules may break down:

(1) By rearrangement to molecules

$$C_2H_5OC_2H_5 \longrightarrow C_2H_6 + CH_3CHO$$
$$C_2H_5OC_2H_5 \longrightarrow C_2H_4 + CH_4 + HCHO$$

(2) By the formation of free radicals

$$C_2H_5OC_2H_5 \longrightarrow C_2H_5 + C_2H_5O$$

(3) By interaction with free radicals (R)

$$R + C_2H_5OC_2H_5 \longrightarrow RH + C_2H_4OC_2H_5$$

followed by

$$C_2H_4OC_2H_5 \begin{cases} \nearrow CH_3CHO + C_2H_5 \\ \searrow HCHO + CH_3 + C_2H_4 \end{cases}$$

and subsequent chain decomposition of the aldehydes. Our results indicate that an aldehyde is always formed as an intermediate, so that there is no direct production of carbon monoxide from such a reaction as

$$C_2H_5OC_2H_5 \longrightarrow C_2H_6 + CH_4 + CO$$

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[12] O. K. Rice and Ramsperger, THIS JOURNAL, **50**, 617 (1928).

[13] Hinshelwood, Fletcher, Verhoek and Winkler, *Proc. Roy. Soc.* (London), **A146**, 327 (1934).

[14] Leermakers, THIS JOURNAL, **56**, 1899 (1934).

[15] Fletcher and Rollefson, *ibid.*, **58**, 2135 (1936).

The proportion of the three types of reaction will vary with the pressure and temperature; thus from the relative energies of activation the chain reaction predominates more at lower temperatures.[7] The formation of free radicals by a unimolecular process, and chain termination by the recombination of two small (ethyl and methyl) radicals best accounts for the observed order of the chain reaction of approximately 1.4.[16] The inhibited reaction is probably composed of a number of quasi-unimolecular components of types 1 and 2, so that the order with respect to the initial pressure will, as in the aldehydes,[10] have no simple value. It is at first sight surprising that the order during the course of a run is first order, as the ethylene produced, which retards the rate of reaction, would be expected to raise the order. However, as the reaction proceeds there will be an increase in the relative proportions of methyl to ethyl radicals due to such a reaction as

$$C_2H_5 + CH_3CHO \longrightarrow C_2H_6 + CO + CH_3$$

and methyl radicals may react more easily with ether than do ethyl radicals.

The indecisive influence of inert gases is in agreement with the complex nature of the reaction. Such gases have been found slightly to retard the rate of chain reactions,[15] while they accelerate that of quasi-unimolecular reactions.[17] We have found that helium, when present in a 2:1 ratio, does not change the rate by more than ±2%.

The Evidence for Chains in Related Compounds.—The decomposition of dimethyl ether has been studied by Hinshelwood and Askey,[18] and the results justify a chain mechanism. Formaldehyde is formed as an intermediate ($CH_3OCH_3 \longrightarrow CH_4 + HCHO$) and its rate of decomposition is considerably faster than that of the pure substance. Making a calculation similar to that for diethyl ether, it is found that for an initial ether pressure of 312 mm. at 504°, the rate of disappearance of formaldehyde when its pressure is 38 mm. is 0.10 mm./sec. If it is assumed that there is no cross-activation by other molecules, the value extrapolated from the data on pure formaldehyde[11] is 6.8×10^{-3} mm./sec., *i. e.*, some fifteen times slower. Free radicals will account for the catalysis of the formaldehyde decomposition which does not normally involve a chain mechanism: part of the dimethyl ether reacts therefore through a chain mechanism, as it has been found that chains exist in the presence of free radicals.[14] As in other chain reactions the rate is retarded by inert gases.

Quantitative analyses of the amounts of acetaldehyde present at different stages of the reaction have not been made for methyl ethyl ether. Ure and Young[19] assumed that 65% of the ether decomposed to acetaldehyde, and in this way obtained a rate constant for the aldehyde decomposition similar to that from direct measurement. If, as in the other simple ethers, virtually all the ether forms an aldehyde as an intermediate, the velocity constant for the aldehyde will be greater than in the absence of ether, in agreement with a free radical mechanism. Glass and Hinshelwood[20] found that both methyl ethyl and methyl propyl ether decompose more rapidly in the presence of their respective reaction products. This effect may not have been due to inert gases but rather to traces of iodine compounds, introduced during the preparation of the ethers.

Methyl alcohol bears a structural resemblance to the methyl ethers, and formaldehyde is formed in the course of its decomposition.[21] Its rate of reaction has, however, been explained without postulating the existence of free radicals. The reaction of methyl alcohol in the presence of ethylene oxide shows that the alcohol does not easily form chains even in the presence of comparatively large concentrations of free radicals:[15] further, the decomposition of methyl alcohol is not retarded by nitric oxide and decomposes faster in the presence of its reaction products.[22] There is no evidence, therefore, for a chain mechanism though the formation of free radicals has not been disproved definitely.

The kinetics of the individual reactions which constitute the different steps in the chain decompositions of the ethers must await the determination of the chain-lengths and the percentage of molecules which produce free radicals. In view of the considerable proportion of molecules which decompose without interacting with free radicals, the values assumed by Rice and Herzfeld for the separate steps may need considerable modification.

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(16) F. O. Rice, *Chem. Rev.*, **17**, 53 (1935).

(17) O. K. Rice and Sickman, *J. Chem. Phys.*, **4**, 242 (1936).

(18) Hinshelwood and Askey, *Proc. Roy. Soc.* (London), **A115**, 215 (1927).

(19) Ure and Young, *J. Phys. Chem.*, **37**, 1169 (1933).

(20) Glass and Hinshelwood, *J. Chem. Soc.*, 1804 (1929).

(21) Fletcher, *Proc. Roy. Soc.* (London), **A147**, 119 (1934).

(22) Fletcher, unpublished results. The increase in rate is 21% when the reaction products are present in the ratio 2.5:1 and 60% for a 7:1 ratio.

We wish to thank Mr. D. H. Etzler for assistance with part of the experimental work, and one of us (C. J. M. F.) is grateful to the Commonwealth Fund for a Fellowship which has made this work possible.

Summary

The decomposition of diethyl ether has been studied over the pressure range of 6 to 450 mm., and at temperatures from 473 to 562°. Gas analyses indicate that an aldehyde is always formed as an intermediate, and from the amounts of aldehydes present it is found that their rates of decomposition are greater than in the pure state. In confirmation of this the decomposition of acetaldehyde is catalyzed by small amounts of ether, which is explained by the formation of free radicals from diethyl ether, and the initiation of a chain decomposition of the aldehyde. The ether decomposition is interpreted in terms of the three simultaneous processes of molecular rearrangement, free radical formation and chain decomposition, and the importance of these processes in the decomposition of analogous substances is discussed.

BERKELEY, CALIF. RECEIVED AUGUST 5, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Production of Free Radicals from Ethylene Oxide and the Catalysis of Other Reactions by Them

BY C. J. M. FLETCHER AND G. K. ROLLEFSON

The investigations of F. O. Rice and his coworkers have shown that free radicals are produced from a number of organic substances when they are passed through a hot tube. In the majority of cases the energy of activation for the production of the free radicals is considerably higher than that for the thermal decomposition of the substance, but for ethylene oxide the two energies of activation are similar.[1] Therefore, the fraction of free radicals present in the thermal decomposition of ethylene oxide should be relatively higher than in other compounds. In confirmation of this, we have found that small amounts are very effective in promoting the chain decomposition of other compounds,[2] and can be used to initiate chain reactions from 400 to 450°, just as azomethane has been used around 300°.[3] The catalysis of acetaldehyde by ethylene oxide is of special interest, firstly, as it is formed from ethylene oxide by isomerization and so any investigations on the decomposition of ethylene oxide must necessarily consider the chain decomposition of acetaldehyde, and secondly, because the kinetics are simplified by the fact that only one type of radical, the methyl radical, need be considered.

The kinetics of the decomposition of ethylene oxide were first studied by Heckert and Mack[4] and their results have recently been interpreted in terms of the free radical theory.[5] Thompson and Meissner[6] have shown that the decomposition is not a simple unimolecular reaction and that the variation of the rate with the initial pressure indicates a number of simultaneous reactions.

Experimental Procedure.—The reactions were followed in a manner similar to those described with diethyl ether.[7] The organic materials were purified by distillation, except for ethylene which was purified by fractionation after condensation at liquid air temperatures. Nitric oxide was formed *in situ* in the reaction vessel from ethyl nitrite, which under the experimental conditions decomposes instantaneously.[8]

$$2C_2H_5ONO \longrightarrow 2NO + CH_3CHO + C_2H_5OH$$

The Decomposition of Ethylene Oxide.—The pressure increase at completion is equal to the initial pressure, and the reaction is strictly homogeneous.[4] Aldehydes are formed as intermediate products of the decomposition and in order to obtain sufficiently large amounts with which to carry out tests, moderately large pressures were used and the gases removed at an early stage of the reaction. Acetaldehyde was detected by Rimini's test, formaldehyde by the resorcinol test, while a solution had a definite odor of acrolein; the ratios of unsaturated aldehydes and of formaldehyde to acetaldehyde were small. For an initial pressure of 380 mm., the total aldehyde

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[1] F. O. Rice and Johnson, THIS JOURNAL, **56**, 214 (1934).

[2] Fletcher, *ibid.*, **58**, 534 (1936).

[3] Allen and Sickman, *ibid.*, **56**, 2031 (1934).

[4] Heckert and Mack, *ibid.*, **51**, 2706 (1929).

[5] Sickman, *J. Chem. Phys.*, **4**, 297 (1936).

[6] Thompson and Meissner, *Nature*, **137**, 870 (1936).

[7] Fletcher and Rollefson, THIS JOURNAL, **58**, 2129 (1936).

[8] Steacie and Shaw, *J. Chem. Phys.*, **2**, 243 (1934).

pressure was 8.8 ± 1.0 mm. after 8% pressure increase, and 3.8 ± 1.0 mm. after 25% pressure increase.

TABLE I

THE DECOMPOSITION OF ETHYLENE OXIDE

Temp., °C.	p_e, mm.	$10^3/t_{1/2}$, sec.$^{-1}$	$t_{1/2}/t_{1/3}$	$\frac{10^3}{p_e}\left(\frac{dp}{dt}\right)_{\max.}$ sec.$^{-1}$
474	283	5.85	1.86	4.2
	200	5.46	1.87	4.0
	163	5.18	1.87	4.0
	99	4.77	1.86	3.5
	96	4.76	1.86	3.6
	52.5	4.10	1.83	3.2
	48.1	4.05	1.85	3.3
	28.1	3.64	1.83	2.5
457	56.4	1.78	1.86	1.36
	46.9	1.67	1.85	1.34
441	145	0.93	1.89	0.73
	54.8	.790	1.92	.60
	52.0	.794	1.85	.63
428	53.3	.386	1.86	.28
414	52.1	.178	1.85	.13

The rate, as measured by the reciprocal of the half-time, $1/t_{1/2}$, is seen from Table I to decrease with the initial pressure, p_e; Heckert and Mack's results indicate that the rate is more nearly first order above 300 mm. The results of Table I have been used (Fig. 1) to calculate the energy of activation for initial pressures of 50 mm., and give the value 53,300 ± 800 cal., while at different temperatures

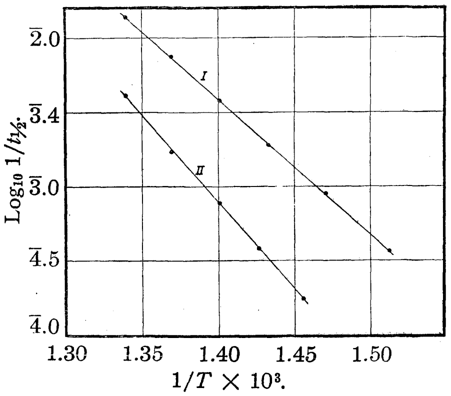
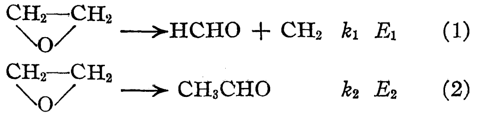


Fig. 1.—I, Acetaldehyde and ethylene oxide; II, ethylene oxide.

$$1/t_{1/2} = 1.8 \times 10^{13} \times e^{-53{,}300/RT}\ \text{sec}^{-1}$$

The pressure–time curves show an induction period at the beginning of the reaction similar to that in other decompositions (*e. g.*, ethers, methyl alcohol) in which aldehydes are formed as intermediates. With ethylene oxide, however, its duration is proportionately less in agreement with the small fraction of aldehydes formed.

The kinetics may be interpreted on the assumptions that ethylene oxide partly decomposes to formaldehyde, and partly isomerizes to acetaldehyde: small amounts of acrolein may be produced as a side reaction by the decomposition of dioxane formed by a polymerization reaction.



No methylene radicals have been detected,[9] so that they probably react extremely rapidly to form methyl radicals, which in turn lead to a chain decomposition of the aldehydes.

$$CH_2 + C_2H_4O \longrightarrow 2CH_3 + CO \qquad k_3\ E_3 \quad (3)$$
$$CH_3 + CH_3CHO \longrightarrow CH_3 + CH_4 + CO \quad k_4\ E_4 \quad (4)$$

Methyl radicals may be removed by direct recombination either alone or in the presence of a third body.

$$2CH_3 \longrightarrow C_2H_6 \qquad k_5\ E_5 \qquad (5)$$
$$2CH_3 + M \longrightarrow C_2H_6 + M \quad k_6\ E_6 \qquad (6)$$

Sickman[5] has assumed that methyl radicals recombine only at ternary collisions; the experimental results on the induced decomposition of acetaldehyde indicate, however, that a direct bimolecular association also occurs. Let the pressure of ethylene oxide be x_1, of methylene radicals be x_2, of acetaldehyde be x_3, of methyl radicals be x_4, and let the total pressure, including that of inert gases, be P; then, when steady concentrations of methylene and methyl radicals are established, if reaction 1 is first order

$$x_4 = \sqrt{\frac{2k_3x_1x_2}{k_5 + k_6P}} = \sqrt{\frac{2k_1x_1}{k_5 + k_6P}} \qquad (1)$$

It is justifiable to assume that $k_2 > k_1$, as the ratio of formaldehyde to acetaldehyde is small, and the amount of hydrogen, which would be formed from the decomposition of formaldehyde, is only 7% of the reaction products. Furthermore, as the amounts of aldehyde built up are in general agreement with the assumption that there is no direct formation of carbon monoxide and methane from ethylene oxide (see later), it is apparent that the pressure increase is mainly due to reaction 4. The observed rate of pressure increase, (dp/dt), is thus given by

$$\left(\frac{dp}{dt}\right) \sim k_4x_4x_3 \sim k_4x_3\sqrt{\frac{2k_1x_1}{k_5 + k_6P}} \qquad (2)$$

This rate increases (during which time there is an induction period) until the acetaldehyde pressure

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[9] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Maryland, 1935 ,p. 161.

is a maximum, x_3'. As this occurs at a very early stage, one may put $x_1 = p_e$, and at this time, $t_{\text{max.}}$

$$k_2p_e = k_4x_4x_3' \qquad (3)$$

so that

$$x_3' = \frac{k_2p_e}{k_4}\sqrt{\frac{k_5 + k_6P}{2k_1p_1}} \qquad (4)$$

and

$$(\mathrm{d}p/\mathrm{d}t)_{\text{max.}} \sim k_2p_e \qquad (5)$$

The maximum rate is actually (see Table I) proportional to rather more than the first power of the ethylene oxide pressure, and so inert gases may slightly increase $(\mathrm{d}p/\mathrm{d}t)_{\text{max.}}$ if they help to maintain the Maxwell–Boltzmann distribution of activated molecules. Hydrogen, which is usually far more effective in this way than other gases, has been found to increase the rate of reaction. On the other hand, it follows from equation 4 that inert gases which contribute to the term P, or substances such as nitric oxide which remove free radicals,[10] should increase the maximum amounts of aldehydes and, therefore, of $t_{\text{max.}}$ and of $t_{1/2}/t_{1/3}$. The effect of inert gases found by Heckert and Mack,[4] and the results with small amounts of nitric oxide, p_{NO}, given in Table II are in agreement with these deductions. The fact, however, that $(\mathrm{d}p/\mathrm{d}t)_{\text{max.}}$ is not changed by small amounts of nitric oxide, indicates that not the isomerization of ethylene oxide, but only the subsequent decomposition of acetaldehyde is a chain reaction.

TABLE II

THE EFFECT OF NITRIC OXIDE ON THE DECOMPOSITION OF ETHYLENE OXIDE

Temp. 441°C.

p_e, mm.	p_{NO}, mm.	$t_{\text{max.}}$, sec.	$(\mathrm{d}p/\mathrm{d}t)_{\text{max.}}$, mm./sec.	$t_{1/2}/t_{1/3}$	$t_{1/2}$, sec.
180	..	60	0.14	1.87	960
182	3	240	.15	1.74	980
177	6	330	.14	1.69	1030

The Catalysis of Organic Reactions by Ethylene Oxide.—As ethylene oxide produces relatively to most other organic compounds a copious supply of free radicals, it is extremely suitable for the study of the extent to which chain reactions involving free radicals may occur. It is possible to invent a chain mechanism for the decomposition of nearly every organic molecule but without knowledge of the kinetics of the separate steps it is often impossible to predict whether such mechanisms will take place. Our experiments contrast the ease with which acetaldehyde and diethyl ether may be made to undergo chain decompositions, compared to the difficulty with which acetone and methyl alcohol decompose in the presence of free radicals. The induced decomposition of acetaldehyde has been used to test for chain-breakers as well as to illustrate the efficiency of inert gases in promoting the recombination of methyl radicals at ternary collisions.

(1) The Decomposition of Acetaldehyde.—Mixtures were made up in which the ratio of the pressure of ethylene oxide, p_e, to acetaldehyde, p_a, was small, and the rates of pressure increase were measured at a number of different initial pressures, p_0. The rate of the uncatalyzed acetaldehyde decomposition was always negligible in comparison with that of the catalyzed reaction. The relative rates of reaction have been compared from the half-times, *i. e.*, the times for a pressure increase of 50%, as the "end-points" are double the total initial pressure, p_0. Figure 2 shows the variation of $1/t_{1/2}$ with p_0 at 441°, and it is seen from Table III that $1/t_{1/2}$ is proportional to the square root of the ethylene oxide pressure, but for a constant ethylene oxide pressure decreases slightly with p_0. It has been shown previously that some recombination of free radicals occurs at ternary collisions, and the present results indicate that ethylene oxide or acetaldehyde can act as the third body. Substituting in equation 2, the initial rate, $(\mathrm{d}p/\mathrm{d}t)'$, of the induced reaction is given by

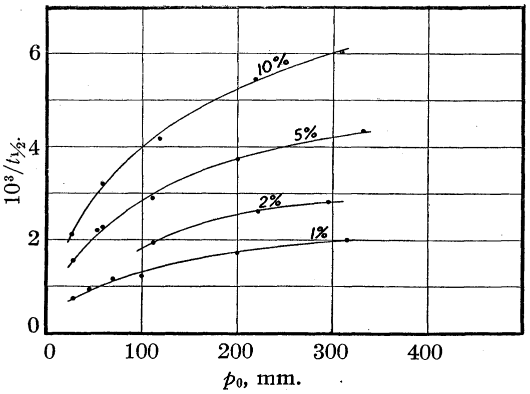

Fig. 2.—Rates of reaction of acetaldehyde with various percentages of ethylene oxide. Temp. 441°C.

$$\left(\frac{\mathrm{d}p}{\mathrm{d}t}\right)' = k_4\sqrt{p_e} \times p_a \times \sqrt{\frac{2k_1}{k_5 + k_6p_0}} \qquad (6)$$

Approximate values of the constants may be obtained by a comparison with the experimental

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[10] Staveley and Hinshelwood, *Proc. Roy. Soc.* (London), **A154**, 335 (1936).

results, on the assumption that the correction due to the decomposition of the ethylene oxide is small. The mean values of $1/(t_{1/2}\sqrt{p_e})$ may be expressed in the form

$$\frac{1}{t_{1/2}\sqrt{p_e}} = \frac{1.39 \times 10^{-3}}{(1 + 1.93 \times 10^{-3} p_0)^{1/2}} \qquad (7)$$

from which the calculated results of Table III have been derived. As the initial rate is found by experiment to equal approximately 0.77 $p_a/t_{1/2}$, it follows that

$$k_4\sqrt{2k_1}/\sqrt{k_5} = 1.07 \times 10^{-3}, \text{ and } k_6/k_5 = 1.93 \times 10^{-3}$$

Table III

Values of $10^3/t_{1/2}\sqrt{p_e}$ for Different Mixtures of Acetaldehyde and Ethylene Oxide at Different Initial Pressures, Temp. 441°

p_e/p_0	p_0 = 300 mm.	200 mm.	100 mm.	50 mm.
0.10	1.09	1.18	1.23	1.32
.05	1.09	1.19	1.25	1.33
.02	1.15	1.22	1.24	..
.01	1.13	1.21	1.26	1.31
Mean	1.115	1.20	1.245	1.32
Calculated	1.11	1.18	1.27	1.33

Table IV

The Retardation of the Chain Decomposition of Acetaldehyde by Various Substances

Gas	Temp., °C.	p_e/p_0	p_0, mm.	p_g, mm.	$t_{1/2}$, sec.	$t_{1/2}'/t_{1/2}$
Helium	441	0.10	120	222	264	0.90
		.10	55.3	115	342	.90
		.05	119	240	385	.87
		.05	121	120	351	.95
		.05	53.5	121	502	.90
		.01	69.0	153	995	.90
Nitric oxide		.05	208	2.3	804	.32
		.05	199	5.0	1548	.17
		.05	148	18	8100	.036
Ethylene		.05	102	102	1160	.31
Diethyl ether	465	.05	196.5	10	111.5	1.00
Acetone		.05	114.7	19.8	150	0.99
		.05	67.2	88.8	236.5	.81
Methyl alcohol		.05	33.2	10.0	364	.72
		.048	97.8	100.5	327	.45
		.048	94.7	100.8	325	.45

The term k_6P of equation 1 is composite when more than one type of molecule is present, but the value of k_6/k_5 just obtained will refer predominantly to acetaldehyde. The rate of reaction has been found to be retarded by helium (Table IV), and the increase in $t_{1/2}$ by approximately 10% with a 2–1 helium ratio, indicates that for helium k_6/k_5 is 1.4×10^{-3}. It follows from equation 7 that for the pressures used, the number of free radicals which combine at ternary collisions is rather smaller than the number which combine directly either on the surface or in the gas phase.

Experiments carried out at 446° in a reaction vessel packed with tubes showed the rate to be slower by about 30%, although the surface–volume ratio was increased by a factor of eleven: it is evident, therefore, that at this temperature the recombination of free radicals is mainly a homogeneous reaction. At temperatures around 300°, Allen and Sickman[3] have found that the induced decomposition of acetaldehyde is retarded by over 50%. This decrease in the retardation by the surface at higher temperatures agrees with the investigations of Paneth, Hofeditz and Wunsch[11] who have found that the heterogeneous recombination of free radicals decreases with the temperature. At temperatures and pressures sufficiently low for heterogeneous recombination to predominate, inert gases, by impeding the diffusion of radicals to the walls will, therefore, increase and not decrease the rate of reaction.

The energy of activation of the induced reaction was determined for a mixture containing 5% of ethylene oxide at initial pressures of approximately 200 mm. (Fig. 1). The half-times satisfy the equation

$$1/t_{1/2} = 2.1 \times 10^{10} \times e^{-41,500/RT} \text{ sec.}^{-1}$$

The energy of activation (41,500 ± 500 cal.) can be lower than that for ethylene oxide as the rate has been found to depend upon the square root of the ethylene oxide concentration.

Now that the rate of the induced acetaldehyde decomposition is known, it is possible to compare the amounts of acetaldehyde actually formed from ethylene oxide with those calculated on the assumption that practically all of the ethylene oxide isomerizes to acetaldehyde. From equations 1, 3, 5 and 6, the initial rate of the induced reaction, and the maximum rate of the ethylene oxide decomposition with the same ethylene oxide pressure are related by the expression

$$\left(\frac{dp}{dt}\right)' \Big/ \left(\frac{dp}{dt}\right)_{\text{max.}} \sim p_a/x_3'$$

Comparing these rates at 441° for p_e = 30 mm., $x_3' \sim 3$ mm. However, from equation 4, it follows that x_3' is roughly proportional to $\sqrt{p_e}$, so that for p_e = 380 mm., $x_3' \sim 11$ mm. The aldehydes determined experimentally at an early stage of the reaction were 8.8 mm. for this initial pressure.

The chain length of the acetaldehyde induced reaction may be expressed in terms of the fraction,

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(11) Paneth, Hofeditz and Wunsch, *J. Chem. Soc.*, 372 (1935).

z, of methyl radicals produced from ethylene oxide. At 441° with a mixture containing 20 mm. of ethylene oxide and 180 mm. of acetaldehyde $(dp/dt)' = 1.34$ mm./sec. At the same temperature extrapolation of the results with ethylene oxide alone gives for $p_e = 20$ mm. a maximum rate of 0.012 mm./sec. Therefore, the chain length is approximately $100/z$. Assuming that the hydrogen and ethane that are present in the reaction products from ethylene oxide are formed solely by way of reaction 1, the observed products (CO, 50%; CH_4, 36%; H_2, 7%; C_2H_6, 7%) would indicate that 14% of the ethylene oxide decomposes to methylene and formaldehyde. The fraction decomposing in this way may, of course, vary with the initial pressure, but if it is not very different at lower pressures, z will be approximately 0.3 as two methyl radicals are formed by reaction 3 from each methylene radical.

It has recently been found that small quantities of nitric oxide can retard certain reactions, due to the elimination of any chain reactions by the removal of free radicals by the nitric oxide.[10] Table IV, which gives the ratio of the half-time, $t_{1/2}'$, in the absence of nitric oxide to the half-time, $t_{1/2}$, in the presence of nitric oxide, shows that the chain decomposition of acetaldehyde is retarded markedly. Organic substances such as acetone and methyl alcohol, when present in large quantities, can also act as chain-breakers (Table IV); this indicates that they can compete effectively with acetaldehyde for methyl radicals, but that the re-formation of a methyl radical is less frequent, either on account of the relative stability of the radicals CH_3O and CH_2COCH_3, or due to their relative ease of recombination with other radicals, *e. g.*

$$CH_3 + CH_3OH \longrightarrow CH_4 + CH_3O$$
$$CH_3O \longrightarrow HCHO + H$$
$$CH_3O + CH_3 \longrightarrow CH_3OCH_3$$

Ethylene also retards the rate of pressure increase but its influence is complicated by the decrease in pressure which must occur from its polymerization.

(2) **Diethyl Ether.**—With a mixture containing 5% of ethylene oxide the initial rate at 441° for an ether pressure of 180 mm. is increased by a factor of twenty and the reaction goes 82% toward completion. If the chain length of the ethylene oxide catalyzed reaction is not very different from that of the chains in the normal ether decomposition, it is apparent that the proportion of free radicals produced directly from ether is only about one four-hundredth of the proportion from ethylene oxide: considerably less than one ether molecule in a thousand, therefore, forms a free radical. Extrapolation of the ether decomposition inhibited by nitric oxide[10] indicates that some 15% of the ether decomposes by a non-chain reaction, so that it follows that in the uncatalyzed reaction there is an appreciable decomposition which takes place neither to free radicals nor by a chain reaction, but rather by a direct molecular rearrangement.[7] Further, the chains must be few and long rather than numerous and short.

(3) **Ethylene.**—The rate of polymerization of 176 mm. of ethylene is twenty times greater in the presence of 3.7 mm. of ethylene oxide at 441°.

(4) **Acrolein.**—The rate of decomposition at 470° is increased by a factor of four with 10% of ethylene oxide.

(5) **Methyl Alcohol.**—Some interaction between free radicals and methyl alcohol occurs which (a) decreases the rate of pressure increase as compared to that for the pure ethylene oxide, and (b) leads to the decomposition of some fraction of the methyl alcohol. Thus at 465° for $p_e = 98$ mm., $t_{1/3} = 173$ sec. In the presence of 105 mm. of methyl alcohol, $t_{1/3} = 211$ sec., but the final end-point indicates that 24.5% of the methyl alcohol has decomposed. The uncatalyzed reaction is inappreciable at this temperature.[12]

We wish to thank Dr. O. K. Rice for many helpful discussions, and one of us (C. J. M. F.) is grateful to the Commonwealth Fund for a Fellowship, which has made this work possible.

Summary

The main reaction of ethylene oxide when heated to temperatures around 450° is an isomerization to acetaldehyde. Free radicals are also formed at the same time and decompose the acetaldehyde by a chain mechanism though they do not affect the isomerization process. Though the fraction of free radicals formed from ethylene oxide is comparatively small, it is relatively much higher than for most other organic compounds, and small amounts effectively catalyze the decomposition of other substances. The induced decomposition of acetaldehyde has been studied in detail, and the rate varies with the square root of the ethylene oxide concentration and with rather less than the first power of the acetaldehyde concentration; it is retarded slightly by helium,

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(12) Fletcher, *Proc. Roy. Soc.* (London), **A147**, 119 (1934).

moderately by acetone and methyl alcohol and considerably by nitric oxide. The energy of activation of this induced reaction is 41,500 ± 500 cal., and the kinetics have been explained by a chain decomposition initiated by free radicals, which disappear partly at ternary collisions and mainly in the gas phase.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Photochemical Reaction of Chlorine with Formic Acid

BY HELEN L. WEST[1] AND G. K. ROLLEFSON

Introduction

A study of the photochemical reaction between formic acid and chlorine was undertaken because it offered the possibility of proceeding in stages involving the formation of an intermediate substance, less stable than that found in the formaldehyde chlorine reaction,[2] but stable enough to exist in appreciable concentrations in the reacting mixture. Furthermore, on account of the measurable equilibrium existing between single and double molecules of formic acid, it was possible to test the relative reactivity of the two forms. The results presented in this paper show the formation of the expected intermediate, chloroformic acid, but do not show any appreciable difference in reactivity between the single and double molecules.

Materials and Apparatus

Anhydrous formic acid was prepared from Merck 90% C. P. acid by a preliminary dehydration with copper sulfate followed by repeated distillations *in vacuo* from finely pulverized boric anhydride. Before each of three distillations the acid remained in contact with the boric anhydride for at least one day. In order to prevent any slow thermal decomposition, the purified formic acid was kept in a trap immersed in a liquid air bath. The purity of the acid was evidenced by the agreement of the vapor pressures with those reported by Ramsperger and Porter[3] and Coolidge.[4]

The melting point determined from the vapor pressure-temperature curve was 8.3 ± 0.05°.

The chlorine was prepared by heating anhydrous cupric chloride. The supply used for the second series of experiments was purified by fractional distillation and stored in a three-liter bulb. It was admitted to the reaction vessel by means of a stopcock lubricated with Shell Apiezon grease (this was found to be practically inert toward both chlorine and formic acid). The absorption coefficient of this chlorine was found to be 26 at 3650 Å. in good agreement with the values given by Gibson and Bayliss.[5]

Comparison of data obtained under similar conditions using this chlorine and also chlorine prepared directly from copper chloride showed no essential differences provided the copper chloride had been heated to the decomposition temperature numerous times. Unless this treatment were followed, an inhibitory effect upon the reaction resulted.

A sample of Eastman Kodak Co. C. P. methyl formate was vacuum distilled from phosphorus pentoxide.

In the first series of experiments a spherical Pyrex reaction vessel of 250 cc. capacity was employed. Although the temperature coefficient of the reaction is negligible, some thermostating was necessary to prevent variations in the equilibrium constant for the relation of single to double molecules of formic acid. Water at temperatures from 20–25° was allowed to run over the cell. The light source was a 500-watt tungsten lamp, placed 80 cm. from the reaction bulb. The course of the reaction was determined by the pressure change. Due to the reactivity of formic acid, the pressure had to be read indirectly by means of a click gage connected externally to a sulfuric acid manometer. All pressures are recorded in cm. of sulfuric acid.

In order to provide an independent method for the determination of the amount of chlorine which had reacted, a second series of experiments was performed in which in addition to measuring the pressure change a simultaneous measurement of the absorption of light by chlorine could be made. These experiments were carried out using a cylindrical Pyrex reaction vessel, 15 cm. long with plane windows at the ends, which was immersed in a water-bath. The bath could be thermostated accurately at any desired temperature between 20 and 30°. The light both for the absorption measurements and the photoactivation process was supplied by a quartz Hereaus mercury arc focused by a pair of quartz lenses and passed through a Corning violet ultra filter No. 586 so as to isolate the groups of lines near 3650 Å. After the light had passed through the reaction vessel, it was focused on a Moll surface thermopile connected to a sensitive galvanometer. Variations in intensity of the arc were corrected for by taking simultaneous readings on another thermopile illuminated by a beam which had not passed through the reaction vessel. Quantum yields were calculated from these data after the

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(1) Swarthmore Sigma Xi Fellow, 1934–1935.

(2) Krauskopf and Rollefson, THIS JOURNAL, **56**, 2542 (1934).

(3) (a) Ramsperger and Porter, *ibid.*, **48**, 1267 (1926); (b) Ramsperger and Porter, *ibid.*, **50**, 3036 (1928).

(4) Coolidge, *ibid.*, **50**, 2166 (1928).

(5) Gibson and Bayliss, *Phys. Rev.*, **44**, 188 (1933).

surface thermopile had been calibrated by means of a standard lamp.

Results and Discussion

The net reaction between formic acid and chlorine may be represented by the equations

$$HCOOH + Cl_2 = 2HCl + CO_2 \qquad (1)$$
$$(HCOOH)_2 + 2Cl_2 = 4HCl + 2CO_2 \qquad (2)$$

Both of these equations and the equilibrium between the two types of molecules must be taken into consideration in order to calculate the composition of the mixture after any observed pressure change. These reactions are strictly photochemical at the temperatures used, and blank tests showed that formic acid is not affected by light of the wave lengths involved in these experiments.

That hydrogen chloride and carbon dioxide are the only products formed in appreciable amounts is shown by the fact that under no conditions were any gases obtained which could not be condensed by liquid air. In addition, the equilibrium constants $K = (HCOOH)^2/((HCOOH)_2)$ calculated on the assumption that the products are as shown above compare favorably with those reported by Ramsperger and Porter.[3] These constants were computed from the over-all pressure change in experiments carried to completion in the presence of excess chlorine.

TABLE I

RATE CONSTANTS FOR DIFFERENT PRESSURES OF CHLORINE AND FORMIC ACID

A. 500-Watt Lamp Light Source

% Formic acid reacted	Residual cm.		Slope	Temp., °C.	K used	$k_I(I_0)^{1/2} \times 10^2$	$k_{II}(I_0)^{1/2} \times 10^2$
	Formic acid	Cl_2					
0.43	7.4	76.4	0.200	21	1.5	0.86	0.31
.48	5.2	16.0	.105	23	1.6	1.19	.50
.41	3.4	102.0	.128	22	1.55	0.78	.37
.39	2.5	8.8	.029	24	1.7	.72	.40
.44	3.7	20.1	.085	21	1.5	1.11	.51
[.29	7.8	7.0	.029	22	1.55	0.40	.14]
					Average	.93	.42

B. Hg Arc Light Source; $K = 2.1$; temp. 27°

% Formic acid reacted	Residual cm.		Slope	$k_I(I_0)^{1/2} \times 10^2$	$k_{II}(I_0)^{1/2} \times 10^2$
	Formic acid	Cl_2			
0.32	7.1	13.4	0.036	0.33	0.138 (1)
.29	5.3	25.6	.029	.24	107
.22	15.8	11.0	.057	.36	.108 (2)
.22	10.5	23.3	.050	.27	.097
.29	9.0	12.1	.038	.32	.122
.24	7.2	23.4	.042	.29	.120 (3)
[.21	15.3	8.4	.032	.23	.073]
			Average	.30	.115

A comparison of the amounts of chlorine which have reacted at various stages of the reaction as determined from the change in light absorption and from the over-all pressure change is given in Table II. The fourth column gives the difference between the actually observed deflection of the thermopile galvanometer and that which would have been observed if an amount of chlorine had reacted corresponding to the observed pressure change. The first example shows no discrepancies other than might be expected due to experimental errors; the second shows a definite difference which starts at zero and increases regularly as the reaction progresses; the third shows a discrepancy which increases to a maximum and then disappears as the reaction goes to completion. Whenever such a difference appears it is always such that the residual chlorine pressure as calculated from the pressure change is greater than that found by the absorption measurements. This behavior could be expected if the first reaction forms an intermediate substance such as chloroformic acid which then decomposes to give the final products, carbon dioxide and hydrogen chloride. If the conditions are such that the rate of decomposition of this intermediate is sufficiently slow compared to the rate of formation, an appreciable amount of it will be built up during the course of the reaction. By analogy to the behavior of formyl chloride in the reaction between formaldehyde and chlorine, we expect the decomposition of chloroformic acid to be catalyzed by chlorine in the light and by the walls of the reaction vessel. If such conditions prevail, we should expect the greatest discrepancy in the presence of excess formic acid as is actually the case. The variability of the behavior with excess chlorine as shown by experiments 1 and 3 in Table II may be attributed to variations in the rate of the heterogeneous reaction similar to that found with formyl chloride.

Another fact which supports the hypothesis of an unstable intermediate was obtained by heating the reaction vessel after a reaction had been run with relatively low chlorine. Under these conditions, an additional pressure change of approximately one centimeter was observed. Blank experiments showed that this change could not be ascribed to the excess formic acid.

The pressure–time curves (*cf.* Fig. 1) are essentially the same whether excess chlorine or excess formic acid were present. Under no conditions

TABLE II

CHARACTERISTIC EXPERIMENTS SHOWING THE EFFECT OF THE FORMATION OF CHLOROFORMIC ACID

Time, sec.	% Formic acid reacted	Cm. Cl_2 absorption	ΔP	$D_{abs.} - D_{\Delta P}$	$k_I(I_0)^{1/2} \times 10^2$	$k_{II}(I_0)^{1/2} \times 10^2$
1. Initial Pressure, 10.5 cm. Formic Acid, 19.5 cm. Cl_2						
30	0.12	17.6	17.4	−0.2	0.43	0.16
60	.22	15.8	15.4	− .4	.41	.16
105	.32	13.5	13.4	0	.33	.14
155	.41	11.6	12.0	.4	.29	.12
220	.49	10.2	10.5	.4	.27	.12
330	.59	8.7	8.7	0	.25	.12
720	.74	6.2	6.1	− .2		
2. Initial Pressure, 20.3 cm. Formic Acid, 19.3 cm. Cl_2						
8	0.03	18.0	18.3	0.1	0.43	0.12
23	.07	16.4	16.8	.4	.43	.12
38	.10	15.0	15.5	.3	.43	.12
93	.22	10.0	11.0	1.9	.36	.11
154	.29	7.1	8.1	2.0	.26	.08
335	.37	4.3	5.5	3.2	.12	.04
1200	.50	1.5	2.8	3.3	..	..
3. Initial Pressure, 9.4 cm. Formic Acid, 27.3 cm. Cl_2						
30	0.16	23.9	24.6	0.4	0.39	0.16
60	.24	22.5	23.4	.6	.29	.12
90	.35	20.6	21.6	.9	.29	.12
120	.40	19.8	20.7	.7	.27	.12
180	.50	18.5	19.2	.6	.23	.11
300	.65	16.3	16.8	.6	.19	.095
600	.82	14.1	14.3	.3	.16	.091
3600	.94	12.6	12.6	0		

do they show an initial "foot" which could be attributed to the time required to build up the intermediate (*cf.* the reaction between formaldehyde and chlorine[2]). This is in accord with the data in Table II which show that the concentration of the intermediate does not attain its maximum value until a considerable amount of reaction has occurred.

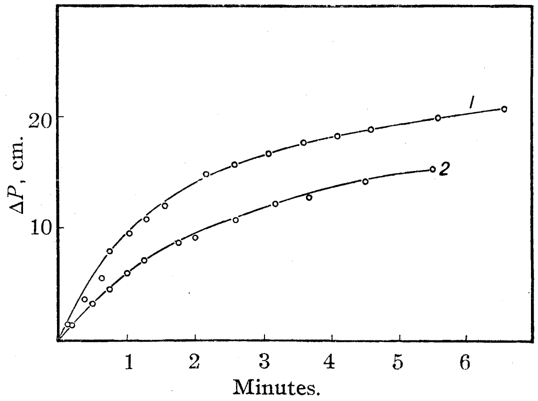

Fig. 1.—Pressure change–time curves: (1) initial pressure, 20.3 cm. formic acid, 19.3 cm. Cl_2; (2) initial pressure, 10.5 cm. formic acid, 19.5 cm. Cl_2.

The rate law for the reaction was deduced from an analysis of the data represented by curves of the type shown in Fig. 1, and separate tests in which the light intensity was varied by the use of calibrated screens. The constants tabulated in Tables I and II are calculated from the equations

$$\frac{-\mathrm{d}(Cl_2)}{\mathrm{d}t} = k_I(I_{abs.})^{1/2}(HCOOH) = k_I(I_0)^{1/2}(Cl_2)^{1/2}(HCOOH) \quad (1)$$

$$\frac{-\mathrm{d}(Cl_2)}{\mathrm{d}t} = k_{II}(I_{abs.})^{1/2}[H(COOH) + (HCOOH)_2] = k_{II}(I_0)^{1/2}(Cl_2)^{1/2}[(HCOOH) + (HCOOH)_2] \quad (2)$$

The exponent of $(I_{abs.})$ was found to change from one-half to one as the chlorine pressure or the light intensity was lowered. This effect manifests itself in the data shown in the tables as a falling off in the values of k_I and k_{II}. The results in brackets in Table I and those in Table II illustrate this behavior. The decrease in the constants can be attributed partly to the formation of chloroformic acid which makes the actual chlorine less than that calculated from the pressure change and the initial pressure. In experiments in which relatively large amounts of the intermediate appear, this effect is especially noticeable. It is obvious, however, that the influence of the change of the exponent of $I_{abs.}$ is much greater. With light intensities such as were used in these experiments, the square root law held for chlorine pressures of 10–15 cm. of sulfuric acid or greater.

A comparison of values of k_I and k_{II} listed in Tables I and II shows a slight preference for the law involving k_{II}. The most strenuous tests are those experiments with excess chlorine in which a large fraction of the formic acid was used up (1 and 3, Table II). In these both constants show a decrease as the run progresses but k_I shows a drop of roughly 45% over the same range that k_{II} drops only 25%.

These constants are calculated by plotting the residual chlorine pressure against time, drawing tangents to the curves at the desired points and using the slopes of these tangents in the rate laws (1) and (2). They represent constants derived from differential rates rather than averages over the range indicated. It is concluded from the data which have been acquired that the single and double molecules react with approximately the same speed.

As has been mentioned, the second experimental arrangement used, permitted a determination of the quantum yield. Some of the values obtained are listed in Table III. It is to be noted that even at the relatively low pressures employed in these experiments, the maximum quantum yields are around two thousand. This value is comparable with the chain length of the hydrogen–chlorine reaction under similar conditions.

TABLE III

QUANTUM YIELDS OF CHLORINE–FORMIC ACID REACTION AT 3650 Å. AND 27°

Initial cm. formic acid	Initial cm. Cl_2	Cm. Cl_2 reacted	Time, sec.	Yield
6.41	22.7	3.0	49	2145
		6.6	172	1413
9.4	27.3	6.7	90	2106
		7.5	120	1794
13.5	30.3	5.6	82	1981
		11.7	230	1595
6.4	15.3	5.8	140	1712
10.5	19.5	7.9	155	2230
		9.3	220	1659

The light sensitized reaction between methyl formate and chlorine has been reported[6] as forming methyl chloroformate followed by substitution in the methyl groups in the presence of excess chlorine. Therefore, a quantitative study of this reaction was undertaken in the possibility of observing the stages in the chlorination of the formate radical in a case the intermediate of which had been isolated. A typical chlorine–time curve is shown in Fig. 2. From this curve it is apparent that no discrete steps in the chlorination can be detected. Substitution is occurring in the methyl group simultaneously with substitution in the formate radical. The absence of any pressure change indicated that there was no decomposition of the chlorine derivatives.[7] The quantum yields for the chlorine–methyl formate experiments are of the same order of magnitude as those of the formic acid reaction.

The facts which have been presented show that the photochemical reaction between chlorine and formic acid is a chain reaction which proceeds at least partially through chloroformic acid; the final products are carbon dioxide and hydrogen chloride. The following set of reactions will account for all of the observed facts including the rate laws

$$Cl_2 + h\nu = Cl + Cl^* \qquad (1)$$
$$Cl + HCOOH = COOH + HCl \qquad (2)$$
$$COOH = CO_2 + H \qquad (3a)$$
$$COOH + Cl_2 = ClCOOH + Cl \qquad (3b)$$
$$H + Cl_2 = HCl + Cl \qquad (4a)$$
$$ClCOOH = CO_2 + HCl \qquad (4b)$$
$$Cl + Cl + (M) = Cl_2 \qquad (5)$$

Step (5) becomes $Cl + (M) = {}^1/_2Cl_2$ when $I_{abs.}$ replaces $I_{abs.}{}^{1/2}$. For the double molecules (2) and (3) are replaced by

$$(HCOOH)_2 + Cl = (HCOOH)(COOH) + HCl \qquad (2')$$
$$(HCOOH)(COOH) = (HCOOH) + CO_2 + H \qquad (3'a)$$
$$(HCOOH)(COOH) + Cl_2 = HCOOH + ClCOOH + Cl \qquad (3'b)$$

The failure to obtain higher concentrations of chloroformic acid may be attributed to 3a and 3′a since they supply a path to the final products which does not involve this intermediate. The competition between 3a and 3b and 3′a and 3′b requires that larger amounts of chloroformic acid should be obtained with high chlorine concentrations unless there is a chlorine catalyzed decomposition as well. Apparently such a situation exists as is shown by experiments made in the presence of excess chlorine.

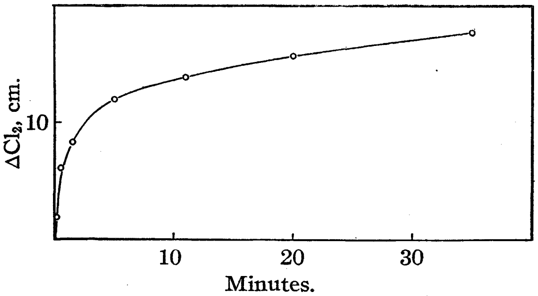

Fig. 2.—Chlorine reacted–time curve for initial pressures: 15.3 cm. $HCOOCH_3$, 58.5 cm. Cl_2.

The theoretical rate law calculated from the mechanism by the usual procedure is

$$\frac{-d(Cl_2)}{dt} = \frac{\sqrt{2}k_2}{\sqrt{k_5}} (I_{abs.})^{1/2} (HCOOH) \text{ or}$$
$$(\sqrt{2}k_2'/\sqrt{k_5}) (I_{abs.})^{1/2} ((HCOOH)_2)$$

Since reactions 3, 3′ and 4 do not affect the final form of the rate law, they may be replaced by any others which will allow for the formation of some chloroformic acid and give carbon dioxide and hydrogen chloride as the final products.

Summary

An investigation of the photochemical reaction between chlorine and formic acid has shown (1) there is no marked difference in the reactivity of the single and double molecules, (2) the reaction proceeds through a chain mechanism involving

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[6] Kling, Florentin, Lassieur and Schmutz, *Compt. rend.*, **169**, 1046 (1919).

[7] A small white deposit appeared on the walls of the reaction vessel when water vapor was admitted after the reaction of chlorine with either formic acid or methyl formate had started. No effect was observed with moisture and the initial reactants. Amounts of this white substance sufficient for analysis could not be obtained, and its formation affected the reaction chiefly through a diminution in rate.

the formation of appreciable quantities of an intermediate, probably chloroformic acid. If excess chlorine is present or if the reaction vessel is heated to destroy any residual intermediate, the products are solely carbon dioxide and hydrogen chloride. A mechanism which will account for the observations has been presented.

Berkeley, Calif. Received August 11, 1936

[Contribution from the Chemical Laboratory of the University of California]

The Heat Capacity and Entropy of Potassium Permanganate from 15 to 300° Absolute. The Entropy and Free Energy of Permanganate Ion

By Oliver L. I. Brown, Wendell V. Smith and Wendell M. Latimer

As part of a general program for the evaluation of the entropies of the common inorganic ions, the entropy of potassium permanganate has been determined.

Material.—Kahlbaum "For analysis with guarantee" grade potassium permanganate was used in the first series of heat capacity runs. These measurements demonstrated that the sample contained water. The material was removed from the calorimeter, ground in a mortar, and dried over sulfuric acid in a darkened desiccator. The sample was then analyzed by titration with sodium oxalate solution. Within experimental error (±0.1%) the sample was 100% potassium permanganate.

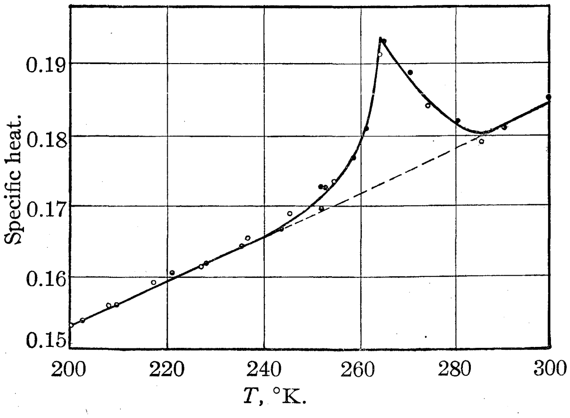

Fig. 1.—Specific heat of wet sample of potassium permanganate.

Heat Capacity Measurements.—The heat capacities were determined by the experimental method used by Latimer and Greensfelder.[1] One calorie was assumed equal to 4.1833 int. joules. The molecular weight of potassium permanganate was taken as 158.03. Measurements on Series I were made on a sample of 133.034 g. (weight *in vacuo*). An anomaly was found in the heat capacities, which appeared to be due to the presence of considerable water included in the sample. On removing the sample from the calorimeter the crystals were found to decrepitate upon heating, confirming the presence of water. The specific heats of the sample in the neighborhood of the melting point of water are presented in Table I and plotted as a function of temperature in Fig. 1. The half filled circles represent runs 1–7 (Oct. 14, 1933), the filled circles runs 8–16 (March 28–29, 1934), the open circles runs 17–26 (April 4, 1934). The area between the dotted curve and the solid curve corresponds to 0.28 cal., and after subtracting 0.02 cal. for the heat absorbed by the solution of potassium permanganate in the liquid water formed, corresponds to the melting of 0.0033 g. of water in each gram of sample. Although the eutectic of ice and potassium permanganate occurs at about 272.5°K., the maximum of the observed "hump" occurs at 265°K. and the abnormal specific heats persist even down to about 245°K. In view of the large amount of water present it was decided to dry the sample as described above, and repeat the entire series of measurements, even though it appeared reasonable that the heat capacity of dry potas-

Table I

Specific Heat of Series I (Wet Sample)

Run	T, °K.	C_p, cal./gram/deg.	ΔT
1	202.67	0.1539	6.426
2	209.69	.1561	6.176
3	221.15	.1605	6.898
4	228.15	.1619	6.678
5	235.37	.1643	7.542
6	243.53	.1667	8.417
7	251.76	.1696	8.060
8	251.69	.1727	7.538
9	258.37	.1768	7.236
10	265.00	.1931	7.573
11	252.58	.1726	9.776
12	261.24	.1809	9.162
13	270.26	.1887	9.460
14	280.40	.1819	9.640
15	290.41	.1808	10.520
16	300.04	.1851	11.149
17	200.34	.1532	7.234
18	208.12	.1560	9.132
19	217.34	.1592	10.281
20	227.06	.1614	9.836
21	236.47	.1654	9.320
22	245.35	.1689	8.898
23	254.39	.1732	9.586
24	264.14	.1912	9.720
25	274.10	.1840	10.885
26	285.55	.1789	11.895

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[1] Latimer and Greensfelder, This Journal, **50**, 2202 (1928).

sium permanganate could be calculated by correcting these measurements for the amount of water present.

Series II (made on the dry sample) is shown in Table II and plotted as a function of temperature in Fig. 2. The measurements on series I, after being corrected for 0.33% of water,[2] are shown in Table III. A few of these measurements selected at random are plotted as filled circles in Fig. 2. The measurements on the wet sample were not used in computing the entropy, but the excellent concordance of these two sets of data indicates that it is quite feasible to correct for water impurity in a salt crystal by assuming the water present as ice. This conclusion is important in cases where the instability of the substance under investigation precludes rigorous drying, although working with wet samples is not recommended as a general practice.

TABLE II

MOLAL HEAT CAPACITY OF POTASSIUM PERMANGANATE

T, °K.	C_p, cal./mole/deg.	T, °K.	C_p, cal./mole/deg.
14.79	1.55	138.11	20.12
16.49	2.01	145.07	20.59
18.03	2.43	152.22	21.11
20.20	3.01	158.93	21.55
22.76	3.70	166.09	21.98
25.13	4.39	173.62	22.45
27.62	5.00	181.51	22.77
35.57	7.26	189.59	23.33
39.13	8.06	198.42	23.89
42.25	8.85	204.45	24.37
46.73	9.69	206.81	24.40
51.36	10.67	209.80	24.51
55.92	11.52	214.69	24.83
61.20	12.33	218.53	25.03
72.77	13.91	222.21	25.14
78.87	14.64	226.43	25.38
84.24	15.22	229.90	25.66
90.31	15.86	238.67	25.91
94.27	16.21	247.12	26.07
101.34	16.98	255.44	26.82
108.59	17.67	264.87	27.18
116.77	18.30	272.74	27.14
123.28	18.89	283.87	27.53
130.78	19.56	295.24	28.42

TABLE III

MOLAL HEAT CAPACITY OF SERIES I (WET SAMPLE) OF $KMnO_4$

T, °K.	C_p, cal./mole/deg.	T, °K.	C_p, cal./mole/deg.
37.56	7.77	136.01	19.90
41.89	8.82	141.36	20.29
46.69	9.85	147.12	20.68
51.52	10.82	153.36	21.14
56.80	11.66	160.29	21.64
62.12	12.49	165.72	22.12
72.06	13.89	177.78	22.73
77.52	14.52	184.01	23.13
83.42	15.10	190.10	23.53
88.82	15.83	196.27	23.77
94.67	16.54	202.67	24.19
100.86	16.97	209.68	24.59
106.70	17.50	221.15	25.22
112.60	18.03	228.15	25.44
118.69	18.54	235.37	25.82
124.64	18.97	243.53	26.19
130.44	19.55	251.76	26.63

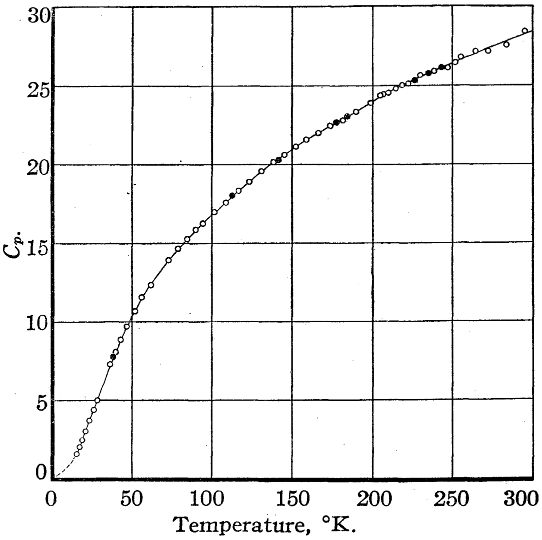

Fig. 2.—Molal heat capacity of potassium permanganate.

Entropy of Potassium Permanganate.—The entropy was calculated by graphical integration of the integral $S = \int_0^T C_p \, d \ln T$ combined with an extrapolation using the Debye specific heat equation. A summary of the entropy calculation is given in Table IV.

TABLE IV

MOLAL ENTROPY OF POTASSIUM PERMANGANATE

0–14.79°K.	Debye extrapolation	0.53
14.79–298.1°K.	Graphical from data	40.51 ± 0.1
	Entropy at 298.1°K.	41.04 E. U.

Heat and Free Energy of Solution.—Roth and Becker[3] have measured the integral heats of solution of potassium permanganate at several different temperatures and concentrations. Heats of dilution to very low concentrations have been determined[4] for the similar salt, potassium perchlorate, but not for potassium permanganate. Since the heats of dilution calculated from the measurements of Roth and Becker are almost identical with those for potassium perchlorate over the same range of concentration, we may assume that the heats of dilution remain the same down to very low concentrations. The heat of

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(2) Giauque and Stout, THIS JOURNAL, **58**, 1144 (1936).

(3) Roth and Becker, *Z. physik. Chem.*, **A159**, 27 (1932).

(4) Andauer and Lange, *ibid.*, **A165**, 89 (1933).

solution of potassium permanganate in an infinite amount of water is, then, 10,620 cal. per mole at 298.1°K.

The solubility[5] of potassium permanganate in water at 298.1°K. is 0.482 M. By extrapolation of the activity coefficients of potassium permanganate obtained from freezing point lowering,[6] γ at 0.482 M is 0.49. The free energy change when potassium permanganate dissolves to form a hypothetical one molal solution is, therefore

$$\Delta F^0_{298.1} = -1363.8 \log (0.482 \times 0.49)^2 = 1710 \text{ cal./mole}$$

Entropy of Solution.—Substituting the above values in the equation $\Delta S^0 = (\Delta H^0 - \Delta F^\circ)/T$ we have for the reaction $\text{KMnO}_4\text{(s)} = \text{K}^+ + \text{MnO}_4^-$ (hypothetical one molal solution); $\Delta S^0_{298.1} = 29.9$ E. U.

Entropy of Permanganate Ion.—The entropy of potassium ion has previously been taken[7] as 24.6 E. U. as an average of the values obtained from the entropies of solution of potassium chloride and potassium bromide, and the entropy change of the potassium electrode reaction. Since the time that this value was calculated, improved data for the first two reactions have become available, so that we now regard the entropy change of the potassium electrode as inferior in accuracy to the values 24.3 E. U. and 24.1 E. U. calculated from the entropies of solution of potassium chloride and potassium bromide, respectively.[7b] As an average we shall adopt 24.2 E. U. as the entropy of potassium ion. The entropy of permanganate ion is given by the expression

$$S^0_{\text{MnO}_4^-} = \Delta S^0 + S_{\text{KMnO}_4} - S_{\text{K}^+} = 29.9 + 41.0 - 24.2 = 46.7 \text{ E. U.}$$

This value, as well as the value of the entropy of potassium permanganate, may be somewhat in error due to the possibility that the paramagnetic nature of potassium permanganate may contribute to the heat capacity below the lowest temperatures obtained in this investigation. No trace of this behavior was found, and the heat capacity appeared to be rapidly approaching the limiting T^3 law. The paramagnetism of potassium permanganate is without temperature coefficient, and no theory has yet been proposed which adequately accounts for this type of magnetic behavior. Further work on the entropies of paramagnetic ions, and particularly the study of reactions in which the products have a different magnetic behavior than the reactants, should help to settle this difficult question of magnetic entropy.

Free Energy of Potassium Permanganate and Permanganate Ion.—Bichowsky and Rossini[8] have selected −192,900 cal. as the ΔH of formation of solid potassium permanganate at 18°. Since the correction to 25° amounts to only 14 cal. it may be neglected. Using the entropies of potassium, manganese and oxygen as given by Kelley[9] we find ΔS of formation to be −79.5 E. U., from which the free energy of formation of solid potassium permanganate is −169,200 cal. per mole. Combining this value with the free energy of solution computed above, and subtracting the free energy of potassium ion[10] (−67,431), the free energy of formation of permanganate ion is found to be −100,060 cal./mole.

The authors wish to thank Dr. Philip W. Schutz of this Laboratory for assistance in the experimental work and calculations on Series I.

Summary

The heat capacity of potassium permanganate has been measured from 15 to 300°K., and the entropy of the salt determined by graphical integration to be 41.04 E. U. Coupling this value with the entropy of solution, and the entropy of potassium ion herein adopted, the entropy of permanganate ion has been determined to be 46.7 E. U.

The free energy of formation of potassium permanganate and of permanganate ion have been computed from the known entropies and heat of formation.

BERKELEY, CALIF. RECEIVED JUNE 15, 1936

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[5] Flöttmann, *Z. anal. Chem.*, **73**, 1 (1928).

[6] Landolt-Börnstein, "Physikalisch-chemische Tabellen," Eg. IIb, p. 1122.

[7] (a) Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934); (b) Latimer, *Chem. Rev.*, **18**, 349 (1936). These references contain complete summaries of all previous work in this field.

[8] Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Co., New York, 1936, p. 162.

[9] Kelley, Bull. 350, Bureau of Mines, 1932.

[10] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 434.

[A CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Action of Diethylmagnesium upon the Methyl Substituted Derivatives of Epoxyethane[1,2]

BY F. H. NORTON AND H. B. HASS

Recently, Bartlett and Berry[3] have shown that dimethyl- and diethylmagnesium react with 1,2-epoxycyclohexane to form when hydrolyzed the products *trans*-2-methyl- and *trans*-2-ethylcyclohexanol. The present paper presents the results obtained by extending the use of dialkylmagnesium as a reagent into the field of epoxyalkanes.

The reactions of epoxyalkanes with Grignard reagents may be summarized as follows. Epoxyethane and 1,2-epoxypropane are known to react by simple splitting of the oxygen-to-carbon linkage; but the more highly substituted epoxyalkanes rearrange to produce alcohols which can be obtained from the corresponding aldehyde or ketone by use of the same alkylmagnesium halide.[4]

The authors have allowed diethylmagnesium to react with the methyl substituted derivatives of epoxyethane. Their purpose was to discover whether or not there is rearrangement when a dialkylmagnesium is allowed to react with epoxyalkanes and to determine the difference in activity of the two carbon to oxygen valences in the epoxyalkane. To ensure identification of the alcohols synthesized by this method, the authors allowed ethylmagnesium bromide to react with the same epoxyalkanes. Reference alcohols also were prepared by other Grignard reagents.

Quite accidentally, the authors discovered and separated *cis* and *trans* 2,3-epoxybutane. The identification was performed before the authors ascertained through a private communication that Lucas and Wilson[5] had synthesized these compounds in order to prove Lucas' identification of *cis* and *trans* 2-butenes.

Experimental

Purification of Organic Liquids.—All organic liquids were carefully rectified at atmospheric or reduced pressure in a Podbielniak column or in a rectifying column[6] packed with Penn State glass spirals. A reflux ratio of 20 to 1 or higher was maintained in all distillations.

Cis and trans 2,3-epoxybutane were synthesized from 2-butanol. Eight hundred and fourteen grams of 2-butanol was converted to *cis* and *trans* 2-butene.[7] The mixture of butenes was allowed to react with a cold solution of hypochlorous acid to form 3-chloro-2-butanol, 245 g., b. p. 76–79° at 100 mm.;[8,9] yield 20.6%. The crude 2,3-epoxybutanes were prepared by treatment with solid potassium hydroxide,[10] and were separated by rectification. Sixty-one and one-half grams of *trans*-2,3-epoxybutane distilled from 52–53° at 741 mm., and 43.5 g. of *cis*-2,3-epoxybutane boiled from 58–59° at 745 mm. (yield of combined *cis* and *trans* isomers, 66% based on chlorohydrin).

2,3-Epoxy-2-methylbutane was prepared from 2-methyl-2-butanol by pyrolysis[11] to 2-methyl-2-butene which was converted to the epoxyalkane as described above. Ninety-six grams of 2,3-epoxy-2-methylbutane distilled from 73.0–74.2° at 753 mm.; yield, 8.6% based on alcohol; 74% based on chlorohydrin.

2,3-Dimethyl-2,3-epoxybutane was prepared from acetone. The following reactions were carried out: the conversion of acetone to pinacol hydrate,[12] the dehydration of pinacol hydrate by a benzene distillation,[13] the treatment of 909 g. of anhydrous pinacol with molar proportions of anhydrous hydrogen chloride,[14] crystallization and filtration of the resulting chlorohydrin, 3-chloro-2,3-dimethyl-2-butanol[15] and treatment as above with potassium hydroxide to produce the corresponding epoxyalkane. One hundred and fifteen grams of 2,3-dimethyl-2,3-epoxybutane distilled from 90.2–91.4° at 753 mm. Yield of oxide was 15% based on anhydrous pinacol.

Preparation of Diethylmagnesium.—An ether solution of diethylmagnesium was prepared from ethylmagnesium bromide made from 109 g. of bromoethane, 24.5 g. of magnesium and 150 ml. of ether. The Grignard reagent was treated while refluxing with 110 g. of 1,4-dioxane in 300 ml. of ether.[16, 17] The mixture was centrifuged, the clear ether layer decanted and analyzed for diethylmagnesium[18] and for bromide ion. The solution was concentrated by distillation of about 60% of the ether.

Reactions of Diethylmagnesium upon Epoxyalkanes (Table I).—A general procedure was used in this reaction, typified by the case of 1,2-epoxypropane. The sample of epoxypropane in an equal volume of ether was added

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(1) Presented at the Kansas City Meeting of the American Chemical Society, April, 1936.

(2) This paper is an abstract of a thesis submitted by F. H. Norton to the Faculty of Purdue University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

(3) Bartlett and Berry, THIS JOURNAL, **56**, 2683 (1934).

(4) Schlenk, "Houben–Weyl," 2d Ed., Vol. IV, 1924, p. 781.

(5) Private communication with Dr. H. J. Lucas, California Institute of Technology, March 23, 1936.

(6) Hass, McBee and Weber, *Ind. Eng. Chem.*, **27**, 1195 (1935).

(7) Lucas and Young, THIS JOURNAL, **52**, 1964 (1930).

(8) Beilstein, Vol. I, 1918, p. 373.

(9) Fourneau and Puyal, *Bull. soc. chim.*, **31**, 424 (1922).

(10) Beilstein, Vol. XVII, Part II, 1933, p. 11.

(11) Matignon, Moureu and Dode, *Compt. rend.*, **196**, 973 (1933).

(12) "Organic Syntheses," Coll. Vol. I, 1932, p. 448.

(13) King and Stewart, *C. A.*, **25**, 1799 (1931).

(14) Delacre, *Bull. soc. chim.*, [4] **3**, 203–12 (1908).

(15) Nilsson and Smith, *Z. physik. Chem.*, **166**, 145 (1933).

(16) Noller and Hilmer, THIS JOURNAL, **54**, 2506 (1932).

(17) Cope, *ibid.*, **57**, 2238 (1935).

(18) Gilman, *ibid.*, **45**, 150 (1923).

TABLE I

REACTIONS OF DIETHYLMAGNESIUM UPON EPOXYALKANES

Epoxyalkane	G.	Di-Et-Mg, eq.	Product	G.	Yield, % on oxide	B. p. °C.	Mm.
1,2-Epoxypropane[a]	25.2	0.47	2-Pentanol	9	23	118.0–119.5	763.4
1,2-Epoxy-2-methylpropane	29	.37	2-Methyl-2-pentanol	11.3	27.5	64.8–65.6	70
cis-2,3-Epoxybutane	19	.4	3-Methyl-2-pentanol	16.5	61	75.4–75.8	70
trans-2,3-Epoxybutane	21	.4	3-Methyl-2-pentanol	6.5	21.8	73.0–74.0	70
2,3-Epoxy-2-methylbutane	25.8	.4	2,3-Dimethyl-2-pentanol	7	21	71–73	50
2,3-Dimethyl-2,3-epoxybutane	20	.4	2,3,3-Trimethyl-2-pentanol	9	34.6	81.8–83.2	50

[a] B. p. 34.1–34.6°.

TABLE II

REACTION OF ETHYLMAGNESIUM BROMIDE UPON THE EPOXYALKANES

EtMgBr + reactant	G.	Product	G.	Yield, % on oxide	B. p. °C.	Mm.
1,2-Epoxypropane[a]	45	2-Pentanol	8	11.7	117–118	756
1,2-Epoxy-2-methylpropane	135	2-Methyl-3-pentanol	39	21	67.0–67.2	70
cis-2,3-Epoxybutane	14	3-Methyl-3-pentanol	3.5	17.5	62.6–64.6	70
trans-2,3-Epoxybutane	15	3-Methyl-3-pentanol	10.5	49	63.7–64.9	70
2,3-Epoxy-2-methylbutane	40	2,3-Dimethyl-3-pentanol	27	50	67.8–68.6	50
2,3-Dimethyl-2,3-epoxybutane	50	2,2,3-Trimethyl-3-pentanol	25	38	76.6–77.2	50

[a] This fraction was obtained from the third rectification and its 3,5-dinitrobenzoate indicated that it was still impure. The impurity probably was 3-pentanol.

TABLE III

PREPARATION OF REFERENCE ALCOHOLS

Prepared from Grignard reagents and aldehydes or ketones in the usual manner

Reactants					Product				
I	G.	II	G.	Mg., G.	Pentanol	G.	% on I	B. p. °C.	Mm.
Acetone	36.5	1-Bromopropane	86.1	17.1	2-Methyl-2-	37.3	72	64.8–65.3	70
2-Methylpropanal	33	Bromoethane	56	12.5	2-Methyl-3-	28	68	67.4–68.2	70
Acetaldehyde	79	2-Bromopropane	362	63	3-Methyl-2-	31	16.9	74.0–75.8	70
2-Butanol	68	Bromoethane	109	24.5	3-Methyl-3-	43	44.5	63.6–64.1	70
Acetone	113	2-Bromobutane	378	65.7	2,3-Dimethyl-2-	17.4	7.7	70.0–70.8	50
2-Butanone	61	2-Bromopropane	123	24.5	2,3-Dimethyl-3-	26	26.4	68.0–68.6	50
Acetone	130	2-Chloro-2-methylbutane	542	120	2,2,3-Trimethyl-2-	17.5	6	78.9–80.1	50
3,3-Dimethyl-2-butanone	93	Bromoethane	109	24.5	2,2,3-Trimethyl-3-	41	34	76.9–77.1	50

slowly to the diethylmagnesium which had been prepared from bromoethane. The mixture was refluxed for twenty minutes, cooled, poured into ice, treated with only enough dilute sulfuric acid to dissolve the precipitate and then separated. The water layer was extracted with ether. The combined ether solutions were dried with anhydrous potassium carbonate for twelve hours. The ether was distilled off slowly in a packed column and the residue then rectified in a Podbielniak column, the fraction distilling from 113–120° being again distilled.

Reaction of Ethylmagnesium Bromide upon the Epoxyalkanes.—The epoxyalkanes (Table I) were allowed to react with ethylmagnesium bromide. The products were treated in the same manner as for those formed with diethylmagnesium (Table II).

Determination of Physical Constants.—The boiling point at atmospheric pressure,[19] the density at 25° (Ostwald pycnometer, vol. 1.1134 ml.), and the refractive index (Abbé) at 25° of all the alcohols were determined in a ten-day period. The reaction rate with zinc chloride-hydrochloric acid was determined at 27.4° in a three-hour period. The reagent was prepared as described in the literature.[10]

It is very evident from this table that diethylmagnesium reacts with the epoxyalkane to produce 2-pentanol. In the case of the corresponding Grignard reagent there is evidence that two products are formed. The alcohol prepared from ethylmagnesium bromide was rectified repeatedly and still gave a 3,5-dinitrobenzoate melting at 72°. A mixture of this derivative and the 3,5-dinitrobenzoate of 3-pentanol melted from 69–71°, which is very nearly the melting point of both derivatives. The 3-pentanol was a commercial product prepared by a distillation of a mixture of pentanols. It probably contained 2-pentanol.

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(19) Willard and Crabtree, *Ind. Eng. Chem., Anal. Ed.*, **8**, 79 (1936).

It is apparent from Table V that diethylmagnesium and ethylmagnesium bromide form different alcohols when they react with 1,2-epoxy-2-methylpropane.

TABLE IV

ALCOHOLS FROM 1,2-EPOXYPROPANE

Source	B. p. °C.	B. p. Mm.	n^{25}_{D}	d^{25}_{4}	R$_L$	ZnCl$_2$–HCl sec.	Derivative M. p., °C.	Derivative Mixed m. p., °C.
			2-Pentanol					
Lit.	118.9	760	1.4127^{20}	0.811^{19}			61	60
Ref. cpd.	117.8	750	1.4051	.8082	26.72	210	*a* 59	60 *a* + *b*
Et$_2$Mg	118.0	749	1.4042	.8085	26.66	285	*b* 61	59 *b* + *e*
EtMgBr	116.1		1.4061	.8121	28.64	65	*c* 72	59–66 *a* + *c*
			3-Pentanol					
Lit.	116		1.4057	0.8157			*d* 97	
Ref. cpd.							*e* 71	69–71 *c* + *e*

TABLE V

ALCOHOLS FROM 1,2-EPOXY-2-METHYLPROPANE

Source	B. p. °C.	B. p. Mm.	B. p. 70 mm.	n^{25}_{D}	d^{25}_{4}	R$_L$	ZnCl$_2$–HCl sec.	Derivative M. p., °C.	Derivative Mixed m. p., °C.
				2-Methyl-2-pentanol					
Lit.	122.0	758			0.8194				
Ref. cpd.	119.3	748	65.0	1.4089	.8051	31.39	0		
Et$_2$Mg	119.4	748	65.2	1.4089	.8071	31.27	0		
				2-Methyl-3-pentanol					
Lit.	127.2	721		1.4134	0.8243				
Ref. cpd.	124.6	747	67.8	1.4151	.8193	31.22	50	*a* 79	80 *a* + *b*
EtMgBr	124.5	747	67.1	1.4150	.8207	31.16	10	*b* 80	

TABLE VI

ALCOHOLS FROM *cis* AND *trans*-2,3-EPOXYBUTANE[a]

Source	B. p. °C.	B. p. Mm.	B. p. 50 mm.	n^{25}_{D}	d^{25}_{4}	R$_L$	ZnCl$_2$–HCl sec.	Derivative M. p., °C.	Derivative Mixed m. p., °C.
				3-Methyl-2-pentanol					
Lit.	134	760		1.4205	0.8307				
Ref. cpd.	134.2	749	74.9	1.4178	.8264	31.13	65	*a* 41	40 *a* + *b*
Et$_2$Mg *cis*	134.4	749	75.6	1.4179	.8235	31.24	55	*b* 45	41 *b* + *c*
Et$_2$Mg *trans*	133	749	73	1.4180	.8240	31.23	10	*c* 51	40–44 *a* + *c*
				3-Methyl-3-pentanol					
Lit.	121.8	758			0.8494				
Ref. cpd.	120.0	749	63.8	1.4165	.8240	31.13	0		
EtMgBr *cis*	117.5	751	63.6	1.4161	.8245	31.09	0		
EtMgBr *trans*	121.3	749	64.3	1.4161	.8234	31.13			

[a] *Trans* is the lower boiling oxide.

TABLE VII

ALCOHOLS FROM 2,3-EPOXY-2-METHYLBUTANE

Source	B. p. °C.	B. p. Mm.	B. p. 70 mm.	n^{25}_{D}	d^{25}_{4}	R$_L$	ZnCl$_2$–HCl sec.
				2,3-Dimethyl-2-pentanol			
Lit.	Not reported in the literature						
Ref. cpd.	139.0	744	70.4	1.4234	0.8285	35.72	0
Et$_2$Mg	139.7	744	72	1.4231	.8276	35.74	0
				2,3-Dimethyl-3-pentanol			
Lit.	139	750			0.8329^{21}		
Ref. cpd.	138.5	743	68.3	1.4263	.8366	35.59	0
EtMgBr	137.7		68.2	1.4262	.8382	35.51	0

Anal. Calcd. for $C_7H_{16}O$: C, 72.34; H, 13.88. Found: C, 72.01; H, 13.86.

TABLE VIII

ALCOHOLS FROM 2,3-DIMETHYL-2,3-EPOXYBUTANE

Source	Boiling point, °C.	mm.	50 mm.	$n^{25}\text{D}$	d^{25}_4	RL	$ZnCl_2$–HCl sec.
			2,3,3-Trimethyl-2-pentanol				
Lit.			79	1.4410^{20}			
Ref. cpd.	159.4	750	78.5	1.4360	0.8151	41.75	0
			2,2,3-Trimethyl-3-pentanol				
Lit.	151	760	76^{40}	1.4353^{20}			
Ref. cpd.	152.4	743	77.0	1.4330	0.8423	40.16	0
EtMgBr	151.8	743	76.9	1.4330	.8434	40.10	0

Table VI is the basis for the following discussion. 3-Methyl-2-pentanol is the only alcohol obtained from *cis* or *trans* 2,3-epoxybutane and diethylmagnesium. There are four possible isomers: the *cis* should give one set of racemic forms while the *trans* yields the other set. The reference compound should be a mixture of the four isomers. The physical properties of the 3-methyl-2-pentanols check each other closely. The melting points and mixed melting points of their derivatives also tend to show that they are 3-methyl-2-pentanols.

3-Methyl-2-pentanol is obtained from ethylmagnesium bromide. All of the physical properties are very nearly identical with the exception of the boiling point of the alcohol produced from the *cis* form. In this case only 3.5 g. of the alcohol was obtained from the distillation at reduced pressure. This quantity was insufficient for an accurate determination of the boiling point.

The alcohols listed in Table VIII are identified entirely by their physical properties. All the alcohols which were isolated were tertiary derivatives, as shown by the zinc chloride–hydrochloric acid method.

It is evident from the data compiled in Table V that diethylmagnesium reacts with 2,3-dimethyl-2,3-epoxybutane to produce 2,3,3-trimethyl-2-pentanol. Ethylmagnesium bromide, on the other hand, forms 2,2,3-trimethyl-3-pentanol.

In the reaction of diethylmagnesium upon the unsymmetrical expoxyalkanes only one product was isolated. In every case there is a possibility of two products. The alcohol formed by the reaction is tertiary if possible, and secondary if there is a choice and tertiary is impossible.

Summary

1. Dialkylmagnesiums react with epoxyalkanes to form addition products which yield alcohols when hydrolyzed. These alcohols are the result of the splitting of the oxide linkage and not of rearrangement such as occurs with alkylmagnesium halides.

2. Diethylmagnesium reacts with 1,2-epoxypropane to give 2-pentanol, 1,2-epoxy-2-methylpropane to form 2-methyl-2-pentanol, *cis*-2,3-epoxybutane to produce a stereoisomeric mixture of 3-methyl-2-pentanols, *trans*-2,3-epoxybutane to yield a different racemic mixture of 3-methyl-2-pentanols, 2,3-epoxy-2-methylbutane to make 2,3-dimethyl-2-pentanol, and 2,3-dimethyl-2,3-epoxybutane to engender 2,3,3-trimethyl-2-pentanol.

3. When there is a difference between the two carbon valences holding the epoxy oxygen atom, the primary valence breaks rather than the secondary or tertiary and the secondary rather than the tertiary.

4. Ethylmagnesium bromide reacts with 2,3-dimethyl-2,3-epoxybutane to produce 2,2,3-trimethyl-3-pentanol.

5. Certain physical properties of ten alcohols have been determined.

6. A new alcohol, 2,3-dimethyl-2-pentanol, has been synthesized for the first time.

7. The synthesis of Bartlett and Berry, namely, the reaction of dialkylmagnesium upon an alpha epoxy compound has been extended to the epoxyalkanes and has been shown to be widely applicable as a method of synthesizing secondary and tertiary alcohols free from isomers.

LAFAYETTE, INDIANA

RECEIVED JULY 23, 1936

[CONTRIBUTION NO. 145 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

The Compound of Cuprous Chloride with Phosphorus Trichloride[1]

BY TENNEY L. DAVIS AND PERCY EHRLICH

More than fifty years ago in a series of brilliant papers Schutzenberger,[2] and Schutzenberger and Fontaine,[3] described the preparation of carbonyl derivatives of platinous chloride and reported that phosphorus trichloride displaced carbon monoxide from these substances to form compounds which retained their essential structure through a variety of chemical transformations. Their experiments, demonstrating the chemical equivalence of carbon monoxide and phosphorus trichloride in complex formation, suggest that phosphorus trichloride may perhaps in general displace carbon monoxide from the carbonyls and that it may in general combine with the elements and compounds with which carbon monoxide enters into direct combination. The interesting possibilities do not appear to have been investigated.

Cuprous chloride forms complex compounds with ammonia and with carbon monoxide. Tropsch and Mattox[4] have recently reported that it combines with ethylene in which, it may be noted, the two valences available for coördination are on different atoms. Phosphorus trichloride, like ammonia and carbon monoxide, has two available valences on its central atom. We find that it also combines directly with cuprous chloride. When phosphorus trichloride is poured upon a quantity of cuprous chloride in a test-tube, the solid immediately commences to swell, heat enough is evolved to produce incipient boiling, and at the end of two hours the solid material occupies two or three times its original volume. On standing overnight, if an excess of phosphorus trichloride is present, the material swells still further, but the reaction appears to be complete after twenty-four hours. In certain experiments in which bottles were used, the material formed hard cakes which by their swelling broke the bottles. Some samples of cuprous chloride reacted more readily than others. When purified cuprous chloride was used, the complex was procured as a white powder having a strong odor of phosphorus trichloride. Washed with benzene or with some other inert solvent, warmed in a stream of carbon dioxide or left to itself in a vacuum desiccator, the compound lost much of its phosphorus trichloride.

The complex is attacked by atmospheric moisture, and cannot be weighed in the ordinary manner because of its high dissociation pressure. Samples for analysis were secured by allowing cuprous chloride undersaturated with phosphorus trichloride to take up more of that material from the vapor phase, and by allowing cuprous chloride oversaturated with phosphorus trichloride to give up a portion of that material through the vapor phase to other cuprous chloride and by introducing samples of the resulting materials into weighing tubes at the temperature of dry ice. The results of analysis showed that the complex has the composition $(CuCl)_2 \cdot PCl_3$.

The dissociation pressures of the complex at various temperatures were determined by the static method which has been used in this Laboratory for determining the dissociation pressures of metal pyridine thiocyanates, etc.[5] The measurements were rendered difficult by the circumstances (1) that the phosphorus trichloride attacked the mercury of the manometer, and (2) that the rate of dissociation of the complex when it was warmed was much greater than the rate of re-association of the components when they were cooled together. The first difficulty was met to some extent by working rapidly, but the second difficulty became more important when the work was rapid. The experimental results were plotted, a smooth curve drawn, and the figures for the dissociation pressures at the even temperatures were read from the curve and found to be 16 mm. at 0°, 28 mm. at 10°, 47 mm. at 20°, 73 mm. at 30°, 117 mm. at 40° and 170 mm. at 50°. These data plotted on a semilogarithmic chart, ln p *vs.* $1/T$, gave a straight line practically parallel with the straight line corresponding to Regnault's[6] data

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(1) For financial aid in this work we wish to make grateful acknowledgment of a grant from the Permanent Science Fund of the American Academy of Arts and Sciences.

(2) Schutzenberger, *Bull. soc. chim.*, **14**, 97, 178 (1870); *Compt. rend.*, **70**, 1414, 1287 (1870).

(3) Schutzenberger and Fontaine, *Bull. soc. chim.*, **17**, 386, 482 (1872); **18**, 148, 529, 1287 (1872).

(4) Tropsch and Mattox, THIS JOURNAL, **57**, 1102 (1935).

(5) Davis and Batchelder, *ibid.*, **52**, 4069 (1930); Davis and Ou, *ibid.*, **56**, 1061, 1064 (1934).

(6) Regnault, *Jahresber.*, 65 (1863). Other data by Antoine, *Compt. rend.*, **36**, 676 (1853); **167**, 681, 778, 836 (1888).

for the vapor pressure of phosphorus trichloride, a fact which shows that the affinity which holds the phosphorus trichloride in combination with the cuprous chloride is practically constant over the temperature range 0 to 50°.

The complex reacts violently with a small quantity of water and goes entirely into solution. With a solution of aniline in benzene its reaction is vigorous enough to cause the benzene to boil. It reacts vigorously with methyl and ethyl alcohols, less vigorously with isopropyl, *n*-butyl and isoamyl alcohols, and with phenol in benzene solution only very slowly in the cold and more strongly on warming. The product of the reaction with methyl alcohol is a mixture of cuprous chloride with a compound having the formula $CuCl \cdot P(OCH_3)_3$, m. p. 216–217°, crystals from acetone or methyl alcohol, identical with the material prepared by Arbusow[7] by the direct combination of cuprous chloride with methyl phosphite. Arbusow reported m. p. 190–192°. He reported complexes of cuprous chloride, bromide and iodide with a number of alkyl phosphites, complexes generally having the formula $CuX \cdot P(OR)_3$, but in a few cases the formula $CuX \cdot [P(OR)_3]_2$. In our experiments with alcohols other than methyl, no solid products except cuprous chloride could be isolated from the reactions of $(CuCl)_2 \cdot PCl_3$ with the alcohols.

The white crystalline compound $CuCl \cdot P(OCH)_3$ oxidizes slowly in the air, turning green and finally black, but appears to be otherwise stable and odorless. The tendency toward its formation is so great that powdered cuprous chloride added to an ether solution of methyl phosphite wholly deprives it of its offensive odor. The compound dissolves in ammonia water to yield a colorless solution which quickly turns blue in the air, and it produces at the same time an extremely offensive carbylamine-like odor. It dissolves in warm aniline or dimethylaniline without the production of any odorous substance, and the solution on boiling deposits a copper-colored material. It hisses with strong nitric acid. On pyrolysis the compound does not decompose into cuprous chloride and methyl phosphite as might be expected, but leaves a residue which contains metallic copper, and produces methyl chloride and volatile compounds of phosphorus. The latter are now being studied further in this Laboratory.

Experiments

Analysis of the Complex $(CuCl)_2 \cdot PCl_3$.—Although it was not found possible to procure the complex in a state of complete purity, satisfactory indications of its composition were secured by approaching the equilibrium from both sides and analysing the resulting materials. A quantity of freshly purified, finely powdered cuprous chloride was introduced into a short tube open at the top and this was placed within a wide tube which contained some liquid phosphorus trichloride; the wide tube was stoppered and allowed to remain in the refrigerator for ten days. A similar arrangement was set up with cuprous chloride in the outer tube and cuprous chloride plus an excess of phosphorus trichloride in the inner one. After ten days the smaller tubes which contained the complex were removed and cooled in dry ice. Samples of the complex were introduced quickly into previously weighed small glass tubes which had also been cooled in dry ice. These tubes were immediately sealed at the blast lamp, weighed again and marked with identifying marks. In making the analyses, the tubes were scratched with a file, warmed at the scratch with a blowpipe flame and dropped into strong ammonia water, whereupon they cracked open and the contents dissolved in the liquid. Chlorine was determined in the usual way by precipitation as silver chloride in the presence of dilute nitric acid. The samples to be analyzed for copper and phosphorus were evaporated to dryness; concd. nitric acid was added and the mixtures were again evaporated to dryness, the residues were taken up in dilute nitric acid, and the copper in them was determined electrolytically. Phosphorus was determined in the residual solution by precipitation as magnesium ammonium phosphate and the ignition of this material to magnesium pyrophosphate. The results of the analyses, indicated in Table II, correspond fairly closely to the composition, two molecules of cuprous chloride and one of phosphorus trichloride, and differ widely from the composition, one molecule of each of the two.

TABLE I

ANALYSIS OF THE COMPLEX, $(CuCl)_2 \cdot PCl_3$

	Found, %				
					Average
Chlorine	51.88	53.91	51.02	49.75	51.39
Copper	36.33	35.80	40.52	40.79	38.36
Phosphorus	9.71	9.00	8.13	8.23	8.77

	Calcd. for	
	$(CuCl)_2 \cdot PCl_3$	$CuCl \cdot PCl_3$
Chlorine	52.89	59.99
Copper	37.88	26.88
Phosphorus	9.23	13.13

The Complex Methyl Ester $CuCl \cdot P(OCH_3)_3$.—When the complex $(CuCl)_2 \cdot PCl_3$ was treated with absolute methyl alcohol, a violent reaction ensued, clouds of hydrogen chloride were evolved and a heavy, white, crystalline powder remained in the bottom of the vessel. Extraction of the solid with boiling methyl alcohol, ethyl acetate or acetone yielded liquids which on cooling deposited white prismatic crystals of the crude complex ester. Acetone is the best solvent which we have found; on cooling it deposited, sometimes in handsome needles, about one-

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(7) Arbusow, *Ber.*, **38**, 1121 (1905).

half of the material which it dissolved at boiling temperature. In methyl alcohol or ethyl acetate solution the methyl ester tended to oxidize readily and to turn green. The crude ester melted at about 180–190° and did not appear to decompose at this temperature. At distinctly higher temperatures it decomposed to yield a red residue and to produce a very offensive odor. Recrystallization from acetone or methyl alcohol raised the melting point of the material, 197–202°, 202–207°, 203–209°, etc., and in one instance 216–217°. The latter material showed almost no red color when heated to its melting point.

Chlorine was determined by dissolving a sample of the ester in ammonia water and precipitating as silver chloride in the presence of dilute nitric acid. Copper was determined electrolytically in the solution which resulted from treating the ester with concd. nitric acid and diluting with water. The residual liquid gave no test for phosphate with ammonium molybdate, for the trivalent phosphorus had not been oxidized by the cold concd. nitric acid. Experiment showed that evaporation to dryness with concd. nitric acid, or evaporation to fuming with concd. sulfuric acid, would not accomplish the result. Satisfactory phosphorus determinations were finally made by evaporating the sample with a mixture of nitric and sulfuric acids until fumes of sulfuric acid were given off, or by evaporating with fuming sulfuric acid until the liquid boiled freely, and then diluting with water, precipitating as magnesium ammonium phosphate, etc.

Anal. Calcd. for $CuCl \cdot P(OCH_3)_3$: Cl, 15.89; Cu, 28.49; P, 13.91. Found: Cl, 15.36, 16.26, 16.00; Cu, 28.69, 28.63; P, 13.60, 13.59, 14.22, 13.87, 13.41.

Summary

Phosphorus trichloride combines directly with cuprous chloride to form the compound $(CuCl)_2 \cdot PCl_3$.

The dissociation pressure of this compound has been measured from 0 to 50°. The affinity which holds the phosphorus trichloride in combination with the cuprous chloride is practically constant over that temperature range.

The complex reacts with methyl alcohol, losing one of its molecules of cuprous chloride and forming a complex ester $CuCl \cdot P(OCH_3)_3$.

The pyrolysis of the complex ester yields metallic copper, methyl chloride and volatile compounds of phosphorus which we have not yet identified.

CAMBRIDGE, MASS. RECEIVED JULY 28, 1936

[CONTRIBUTION NO. 144 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

Metal Pyridine Complex Salts. V.[1] Volume Change During Formation of Cyanates and Thiocyanates

BY TENNEY L. DAVIS AND ALBERT V. LOGAN

The fact that cobaltous thiocyanate forms compounds only with two and with four molecules of pyridine, while cobaltous cyanate forms compounds with two, with four, and with six molecules, has suggested that the affinity of pyridine for the metal in complex thiocyanates is probably less than it is in the complex cyanates. Experiments reported in the second and third papers of this series showed that cobaltous, cupric and nickelous pyridine cyanates have lower dissociation pressures than the corresponding thiocyanates containing the same number of pyridine molecules—and support the conclusion that the pyridine coördinately attached to the metal is held in the complex cyanates by a stronger affinity than it is held in the complex thiocyanates. The substitution of an oxygen atom in place of a sulfur at the remote end of the electrovalently connected acid radical considerably increases the residual affinity of the metal atom available for combination with pyridine through its coördination valence.

We now find that the greater forces of affinity at work in the complex cyanates, by pulling the parts of the molecules more closely together, produce greater contractions than do the forces which hold together the complex thiocyanates. The proportionate decrease in volume when the complex cyanate is formed from the simple salt plus pyridine is greater than when the complex thiocyanate is similarly formed. The cyanate radical, then, exhausts to a less extent than the thiocyanate radical the total affinity of the metal atom, and leaves more of it available for holding the pyridine with those internal forces which reduce both the dissociation pressure and the volume of the resulting compounds.[2]

The fact that water and all organic liquids (ex-

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[1] Earlier papers of this series: I, Davis and Logan, THIS JOURNAL, **50**, 2493 (1928); II, Davis and Batchelder, *ibid.*, **52**, 4069 (1930); III and IV, Davis and Ou, *ibid.*, **56**, 1061, 1064 (1934).

[2] Compare the ideas of T. W. Richards on compressible atoms developed in his Faraday Lecture, delivered before the Chemical Society of London June 14, 1911, and in his Presidential Address to the American Chemical Society, published in THIS JOURNAL, **36**, 2417–2439 (1914), where a bibliography of his papers on the subject is also printed.

cept pyridine) which we have tried removed some of the pyridine from the complex salts, and also dissolved more or less of them, greatly limited the choice of liquids which might be used in the density determinations, and practically confined the choice to saturated solutions of the complexes in pyridine itself. This meant that it was generally possible to work only with the most highly pyridinated of the compounds. We have therefore determined the densities at 25° of cupric, nickelous and cobaltous hexapyridine cyanates and tetrapyridine thiocyanates, by measuring in a pycnometer the amount of a saturated solution of the complex in pyridine (the density of that solution having been determined previously) which was displaced by a known weight of each of the complex salts. The densities of the simple cyanates and thiocyanates were determined similarly under benzene. From the densities, the molecular volumes at 25° of the complexes, of the simple salts, and of the pyridine with which the latter combine to form the complexes have been calculated, and the shrinkages which occur during the formation of the complexes have been determined, and are reported in Table I.

TABLE I

VOLUME CHANGE DURING FORMATION OF COMPLEX CYANATES AND THIOCYANATES

	Molecular volumes at 25°, cc.					
	Components					
	Pyridine	Salt	Total	Complex	Volume Decrease	Decrease, %
$Cu(NCO)_2 \cdot 6Pyr.$	485.0	61.0	546.0	486.3	59.7	10.9
$Co(NCO)_2 \cdot 6Pyr.$	485.0	58.8	543.8	474.7	69.1	12.7
$Ni(NCO)_2 \cdot 6Pyr.$	485.0	62.0	547.0	469.2	77.8	14.2
$Cu(NCS)_2 \cdot 4Pyr.$	323.3	76.2	399.5	366.7	32.8	8.2
$Co(NCS)_2 \cdot 4Pyr.$	323.3	73.9	397.2	354.5	42.7	10.7
$Ni(NCS)_2 \cdot 4Pyr.$	323.3	73.2	396.5	352.7	43.8	11.1

From these data it appears that the absolute shrinkage in cc. and the per cent. shrinkage calculated on the basis of the volume of the components are both greater for the hexapyridine cyanates than for the tetrapyridine thiocyanates. The per cent. shrinkage during the formation of cupric hexapyridine cyanate (10.9) is 1.33 times the per cent. shrinkage during the formation of cupric tetrapyridine thiocyanate (8.2); the ratio for the cobaltous compounds is 1.19, for the nickelous compounds 1.28; average 1.27; that is, the per cent. shrinkage during the formation of cupric, cobaltous and nickelous hexapyridine cyanates from the simple salts and pyridine is about 1.27 times the per cent. shrinkage during the formation of the corresponding tetrapyridine thiocyanates. The shrinkage, however, in the case of the hexapyridine cyanates involves six molecules of pyridine while that in the case of the tetrapyridine thiocyanates involves only four. If each molecule of pyridine in all of the compounds were compressed by the respective chemical forces in exactly the same amount, the absolute shrinkage in cc. during the formation of the hexapyridine cyanates would be 1.5 times the absolute shrinkage during the formation of the tetrapyridine thiocyanates. The ratios calculated from the data are for the cupric compounds 1.82, for the cobaltous 1.62, and for the nickelous 1.78; average 1.74, or about 16% more shrinkage for each molecule of pyridine combined in the complex cyanates than for each molecule combined in the complex thiocyanates. The absolute shrinkages per mole of combined pyridine are shown in Table II where they are compared with the dissociation pressures of the several substances.

TABLE II

SHRINKAGE DURING COMBINATION WITH PYRIDINE COMPARED WITH DISSOCIATION PRESSURE OF THE COMPLEX

	Shrinkage, cc., per mole of combined pyridine	Dissociation pressure, mm.			
		20°	25°	30°	50°
$Cu(NCO)_2 \cdot 6Pyr.$	9.9	7.0	10.0	13.4	49.6
$Co(NCO)_2 \cdot 6Pyr.$	11.5	5.8	(7.7)	10.0	25.7
$Ni(NCO)_2 \cdot 6Pyr.$	13.0	...	5.0	..	7.3
$Cu(NCS)_2 \cdot 4Pyr.$	8.2	5.1	(8.4)	12.0	58.0
$Co(NCS)_2 \cdot 4Pyr.$	10.7	1.9	(2.6)	3.4	10.6
$Ni(NCS)_2 \cdot 4Pyr$	11.0	5.0	(5.4)	6.1	9.8

The shrinkage per mole of pyridine during the formation of the complexes of the three metals is least for the cupric salt, next for the cobaltous, and most for the nickelous salt—both in the hexapyridine cyanate and in the tetrapyridine thiocyanate series. For the cyanates the dissociation pressures at 25° (the figures in parenthesis being estimated) fall in the inverse order; the complex showing the greater shrinkage has the lower dissociation pressure. The dissociations of the thiocyanates at 25° do not fall in line; at 50°, however, they are in the inverse order of the shrinkages.

Correction.—The facts that cupric, cobaltous, and nickel cyanates behave alike in forming complexes with six molecules of pyridine, and that cobaltous and nickelous thiocyanates behave alike in forming complexes with four, have led us to believe, contrary to previously existing information, that cupric thiocyanate also forms a complex with four molecules of pyridine. In the second paper of this series Davis and Batchelder[1] reported analyses and dissociation pressures for the complexes of cupric thiocyanate with one and with two molecules of pyridine. We now find that the dissociation pressures which they reported for the dipyridine compound are actually those of the tetrapyridine compound. They isolated and analyzed the dipyridine compound but failed to observe its dissociation pressure. Their data for the monopyridine compound are correct. The correct data for the three complexes are now summarized in Table III.

TABLE III

DISSOCIATION PRESSURES OF CUPRIC PYRIDINE THIOCYANATES

	Dissociation pressures, mm.					
Temp., °C.	20	30	40	50	60	70
$Cu(NCS)_2 \cdot 4Pyr.$	5.1	12.0	27.0	58.0	106.0	..
$Cu(NCS)_2 \cdot 2Pyr.$	...	5.0	10.0	23.0	...	..
$Cu(NCS)_2 \cdot Pyr.$	...	3.4	5.0	10.1	20.0	36.0

Experiments

The pyridine was fractionated twice, and the portion boiling between 115.25 and 115.40° taken for the density determination.

The complex salts were prepared as described in earlier papers, crystallized from chloroform containing pyridine, dried superficially between filter papers, and kept in desiccators containing pyridine and potassium hydroxide.

Cupric tetrapyridine thiocyanate exists in very dark moss-green crystals which lose pyridine rapidly in the air to produce the dipyridine compound. *Anal.* Calcd. for $Cu(NCS)_2 \cdot 4Pyr$: Cu, 12.82; pyridine, 63.77. Found: Cu, 13.05, 12.99; pyridine, 63.98, 64.96. Cupric dipyridine thiocyanate has an emerald-green color and loses pyridine slowly to form the monopyridine compound. *Anal.* Calcd. for $Cu(NCS)_2 \cdot 2Pyr$: Cu, 18.80. Found: Cu, 18.74, 18.90. The change to the monopyridine compound is hastened by subjecting the dipyridine compound to reduced pressure. *Anal.* Calcd. for $Cu(NCS)_2 \cdot Pyr$: Cu, 24.58. Found: Cu, 24.34, 23.56. The compounds are only moderately soluble in chloroform, but dissolve more readily if pyridine is added. The substances which were described by Davis and Batchelder were the mono- and dipyridine compounds.

Cupric, cobaltous and nickelous cyanates were prepared by warming the complex salts and pumping off the pyridine. It was found that temperatures above 80° caused decomposition with the production of carbon dioxide and the cyanides of the metals. At lower temperatures it was necessary to continue the pumping for several days in order to remove all of the pyridine. Cupric cyanate has a dark moss-green color, nickelous cyanate pale green, and cobaltous cyanate pale lavender.

Cobaltous thiocyanate was prepared as a yellow-brown powder by heating the pyridine complex in vacuum at about 300° at which temperature no decomposition of the salt was found to occur. Nickelous thiocyanate, mustard yellow, was procured by heating the pyridine complex in a well ventilated oven at 250° for two or three hours.

Cupric thiocyanate could not be prepared by any of these methods. It breaks down at slightly elevated temperatures to produce a reddish-brown compound which has been described by Speter[3] as having the composition $Cu(CNS)_2 \cdot CuCNS$. When precipitated from aqueous solution, it decomposes to a greater or less extent forming cuprous thiocyanate. We have prepared the substance by treating freshly precipitated and moderately dry cupric hydroxide with the very strong thiocyanic acid procured by distilling potassium thiocyanate, phosphorus pentoxide and concd. sulfuric acid in an atmosphere of hydrogen at about 60 mm. pressure.[4] The intensely black cupric thiocyanate was transferred quickly to a suction filter, the excess acid was removed, and the unwashed solid was dried in a desiccator over concd. sulfuric acid.

The composition of the salts was verified by analysis for the metals. Cobalt was determined as sulfate, copper by titration with iodide and sodium thiosulfate, and nickel by titration with potassium cyanide. Results are summarized in Table IV.

TABLE IV

ANALYSIS OF CYANATES AND THIOCYANATES

	Metal, % Found			Calcd.
Cupric cyanate	42.84	43.47	...	43.08
Nickelous cyanate	41.24	41.09	41.51	41.13
Cobaltous cyanate	41.16	41.98	...	41.23
Cupric thiocyanate	35.59	35.50	...	35.40
Nickelous thiocyanate	33.50	33.57	33.70	33.59
Cobaltous thiocyanate	33.61	33.55	...	33.69

The densities at 25° of the simple salts, and of the complexes except nickelous tetrapyridine thiocyanate, were determined as has been described briefly in the early part of the present paper. Nickelous tetrapyridine thiocyanate when allowed to stand in contact with pure pyridine forms the heptapyridine derivative which has been described in the second paper of this series.[1] It is unaltered even by long standing in contact with its solution in a 60/40 mixture of pyridine and benzene, and its density was determined by the use of this solution. The density determinations are summarized in Table V.

TABLE V

DENSITIES AT 25°

	Experimental values		Average
Pyridine	0.9774	0.9772	0.9773
$Cu(NCO)_2$	2.4195	2.4172	2.418
$Ni(NCO)_2$	2.3018	2.3021	2.302
$Co(NCO)_2$	2.4325	2.4322	2.432
$Cu(NCS)_2$	2.3589	2.3536	2.356
$Ni(NCS)_2$	2.3866	2.3845	2.386
$Co(NCS)_2$	2.3673	2.3656	2.366
$Cu(NCO)_2 \cdot 6Pyr.$	1.2781	1.2780	1.278
$Ni(NCO)_2 \cdot 6Pyr.$	1.3142	1.3147	1.314
$Co(NCO)_2 \cdot 6Pyr.$	1.2995	1.2994	1.299
$Cu(NCS)_2 \cdot 4Pyr.$	1.3511	1.3509	1.351
$Ni(NCS)_2 \cdot 4Pyr.$	1.3922	1.3901	1.391
$Co(NCS)_2 \cdot 4Pyr.$	1.3846	1.3844	1.384

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[3] Speter, *Z. Med. Chem.*, **3**, 14; *Chem. Zentr.*, **96**, I, 2069 (1925).

[4] Rosenheim and Levy, *Ber.*, **40**, 2166 (1907).

Summary

The decreases in volume which occur at 25° when cupric, cobaltous and nickelous cyanates and thiocyanates combine with pyridine to form hexapyridine cyanates and tetrapyridine thiocyanates have been determined.

The shrinkage in cc. during the formation of the hexapyridine cyanates is about 1.74 times as great as during the formation of the tetrapyridine thiocyanates. This corresponds to about 16% more shrinkage for each molecule of pyridine in the complex cyanates than for each molecule in the complex thiocyanates. This fact, and the fact that the complex cyanates have the lower dissociation pressures, both indicate that the pyridine in the complex cyanates is held by greater forces of chemical affinity than in the complex thiocyanates. The thiocyanate radical to a greater extent than the cyanate radical exhausts the total affinity of the metal atom and leaves less of it available for coördinative combination with pyridine.

For the three cyanates and thiocyanates alike, the shrinkage during combination with pyridine is least in the case of the cupric compounds, next in the case of the cobaltous, and most in the case of the nickelous compounds.

CAMBRIDGE, MASS. RECEIVED JULY 28, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Heats of Dissociation of Hexaarylethanes

BY CHARLES BUSHNELL WOOSTER

In a recent paper Conant[1] has estimated the heats of dissociation of a number of substituted ethanes from cryoscopic data on the basis of the following assumptions: (1) that the heat of dissociation, ΔH, the free energy of dissociation, ΔF, and the corresponding entropy change, ΔS, were all approximately independent of the nature of the solvent in which the ethane was dissolved; (2) that ΔH and ΔS were independent of the temperature over the range involved in the experiments and (3) that ΔS was independent of the substituents attached to the two carbon atoms which dissociate from each other, at least in solution in organic solvents. The work of Ziegler,[2] on hexaphenylethane had furnished confirmation of the first two assumptions, but Conant offered no experimental basis for the third. The last assumption has also been made by Pauling and Wheland[3] but, on the other hand, Hückel[4] states that variations in the entropy change may be expected to accompany alterations in the structure of the molecules.

As a matter of fact, it is possible to calculate values for the heats of dissociation of four hexaarylethanes by independent and somewhat more direct methods from data at present available in the literature. It is the purpose of this paper to present and discuss the results of such calculations.

The Heat of Dissociation of Di-β-naphthyltetraphenylethane.—Gomberg and Sullivan[5] have measured the intensity of color of solutions of di-β-naphthyltetraphenylethane over a wide temperature range in toluene and in chloroform solutions. A sufficiently close approximation to the dissociation constant K, expressed in mole fractions, may be obtained from these measurements by the use of equation 1

$$K = \frac{4N(I/I_0)^2}{1 - I/I_0} \qquad (1)$$

where N is the concentration in moles of the ethane per mole of solvent, I is the intensity of color per mole of the ethane (in arbitrary units) and I_0 is the limiting value of I on dilution.[6] In order to test the consistency of the data, ΔH is best determined graphically by plotting values of $-\log K$ against $1/T$ which should yield a straight line in accordance with equation 2

$$-\log K = (\Delta H/2.303RT) + \text{const.} \qquad (2)$$

when ΔH is independent of the temperature. The value $I_0 = 195$ was obtained from equation 1 by setting K equal to the value 3.50×10^{-4} based on Ziegler's photometric measurements at 20° in

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[1] Conant, *J. Chem. Phys.*, **1**, 427 (1933).

[2] Ziegler, *Ann.*, **373**, 163 (1929).

[3] Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

[4] Hückel, "Free Radicals, a General Discussion," The Faraday Society, 1933, p. 40.

[5] Gomberg and Sullivan, THIS JOURNAL, **44**, 1810 (1922).

[6] The value of I_0 is assumed to be independent of the temperature and of the nature of the solvent. These assumptions were also made by Ziegler in his study of hexaphenylethane.

cyclohexane[7] and substituting the observed value of I at that temperature. A plot of $-\log K$ against $1/T$ appears in Fig. 1. The points obtained in the two solvents lie on the same curve which is linear within the limits of error over a range of 56° in toluene and 52° in chloroform. The value of ΔH corresponding to the slope of this line is 12.9 kcal.

The method suggested for the estimation of I_0 neglects any variation in K which might occur as a result of changing the solvent from cyclohexane to toluene and to chloroform. Some justification for neglecting this variation may be found in the correspondence between the measurements in toluene and chloroform which shows that the values of K in these two solvents do not differ sufficiently to influence appreciably the value of ΔH. However, Ziegler found much wider differences in the values of K for hexaphenylethane in various solvents, so it is necessary to examine carefully the influence of the choice of I_0 on the value of ΔH as calculated from the data of Gomberg and Sullivan.

As a matter of fact, ΔH is not very sensitive to the choice of I_0 when this constant is not too small. The expression for ΔH may be written

$$\Delta H = RT^2(\mathrm{d}\ln K/\mathrm{d}T) = RT^2\frac{\mathrm{d}}{\mathrm{d}t}[2\ln I - \ln(1 - I/I_0)] \qquad (3)$$

and in the limiting case when I_0 is sufficiently great, $1 - I/I_0$ may be replaced by unity so that on integration a linear relation between $\log I$ and $1/T$, similar in form to equation 2, is obtained.

$$-\log I = (\Delta H/4.606RT) + \text{const.} \qquad (4)$$

Plots of $\log I$ against $1/T$ for the β-naphthyl compound in toluene and in chloroform are actually linear in accordance with equation 4 and the value of ΔH thus obtained is 12.3 kcal. The term $1-I/I_0$ cannot exceed unity so the neglected term always makes a positive contribution to ΔH when I increases with the temperature. Therefore, the value 12.3 kcal. may be regarded as a reliable *minimum* within the limits of experimental error, regardless of the true value of I_0.[8]

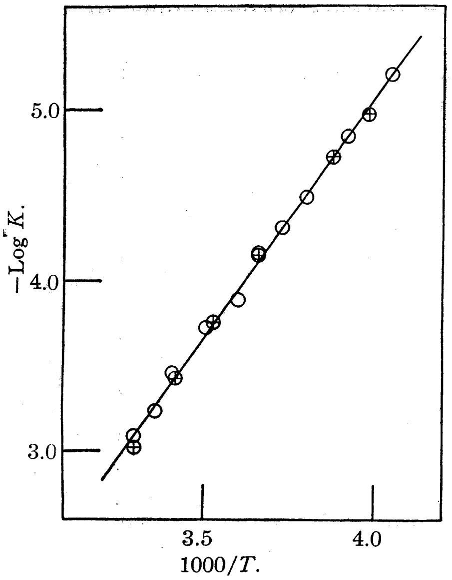

Fig. 1.—Plot of $-\log K$ against $1/T$ for di-β-naphthyltetraphenylethane in toluene (open circles) and in chloroform (crossed circles).

A third method of approximation may be used to set a maximum limit for ΔH. Gomberg and Sullivan also gave data regarding the intensity of color of solutions of the ethane in *cyclohexane* at its freezing point 5.8°. Taking the value of K in cyclohexane at 293°K. as 3.50×10^{-4} and using the minimum value of $\Delta H = 12.3$ kcal., a maximum value of 1.22×10^{-4} may be calculated for K in cyclohexane at 279°K. By the use of equation 1 the value of I_0 may be determined[9] from the values of I in cyclohexane at 5.8°. Unfortunately, these values of I and consequently the resulting values of I_0 are not expressed in the same units as those given for the toluene and chloroform solutions. This difficulty may be circumvented in the following way. From the data on benzene solutions at the freezing point, 5.3°, neglecting the temperature difference of 0.5°, the

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[7] This value of the equilibrium constant is somewhat uncertain because Ziegler did not determine the concentration of his solution by direct analysis. The concentration has been estimated from the amount of triarylmethyl chloride used, assuming a theoretical yield of the ethane. Since Gomberg and Sullivan obtained the yields 99.6, 102 and 100% in three quantitative studies of this reaction, it is believed that the error thus introduced is actually quite small; in any event, this value of K in cyclohexane may be regarded as a reliable *maximum*.

[8] The solutions used by Gomberg and Sullivan were about 0.034 molar with respect to the ethane and the values of I increased approximately ten-fold in passing from the lowest to the highest temperature so that the degree of dissociation, $\alpha = I/I_0$, in toluene, calculated on the basis $I_0 = 195$, varies from 0.0205 at −26° to 0.2100 at +30°. Although it may seem a very arbitrary procedure to set $1-\alpha$ equal to unity when $\alpha = 0.21$, this simplification is justified by the fact that the extreme variation in $1-\alpha$ from 0.979 to 0.790 is accompanied by a variation in α^2 from 4.2×10^{-4} to 4.4×10^{-2} and, accordingly, the neglected variation in $1-\alpha$ contributes but 4.4% of the total variation in $-\log K$.

[9] It has been pointed out previously [Wooster, THIS JOURNAL, **51**, 1163 (1929)] that these measurements are not sufficiently accurate to permit the determination of I_0 by direct extrapolation because the concentration range is so narrow that the moderate experimental errors are greatly magnified by the process of extrapolation. A similar magnification of the experimental errors is not involved in the direct calculation of I_0 from I and K.

ratio of K_b (the dissociation constant in benzene) to K_c (the dissociation constant in cyclohexane) may be calculated by the use of equation 5.

$$K_b/K_c = (N_b/N_c)(I_b/I_c)^2(I_0 - I_c)/(I_0 - I_b) \quad (5)$$

where I_b and I_c are the color intensities in the respective solvents corresponding to the concentrations (in moles ethane per mole solvent) N_b and N_c. The three available intercomparisons yield the value $K_b/K_c = 1.14 \pm 0.06$.

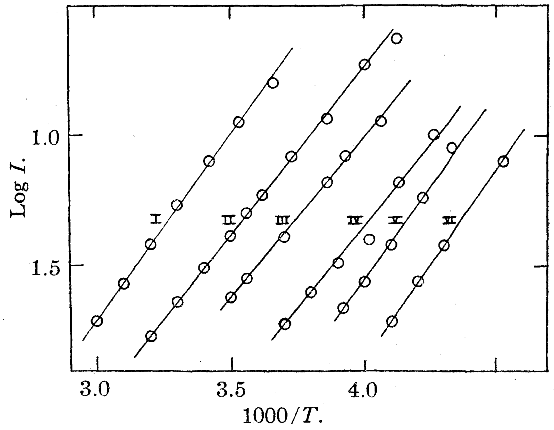

Fig. 2.—Plot of log I against $1/T$ for symmetrical tetramethoxyhexaphenylethanes. Curve I is plotted with respect to the horizontal scale given. Each succeeding curve is displaced two-tenths of a unit to the right with respect to this scale. The vertical scale is the same for all six curves: I, the 2,5-compound in toluene; II, the 2,5-compound in bromobenzene; III, the 3,4-compound in bromobenzene; IV, the 3,4-compound in toluene; V, the 2,4-compound in toluene; VI, the 2,4-compound in bromobenzene.

Since the color intensities of the toluene solutions (concentration 2 g. per 100 cc.) were determined by matching a 17-mm. column against a column of a standard solution of the same free radical in benzene (concentration 0.5 g. per 100 cc.) at room temperature (21–22°) and the diameters of the two tubes of the colorimeter were equal, the ratio K_t/K_b (K_t = the dissociation constant in toluene) at this temperature may be calculated from these data by using a simplified form of equation 5.

$$K_t/K_b \overset{=}{<} (N_t/N_b)(I_t/I_b)^2 \quad (6)$$

The simplification is possible because at the temperature in question $I_t < I_b$ so that $(I_0 - I_b)/(I_0 - I_t)$ is less than unity; consequently the simplified expression yields a *maximum* value for K_t/K_b at that temperature. The value of I_t/I_b is equivalent to the height of the benzene solution divided by four times the height of the toluene solution, since the latter contains four times as much solute as the former. At 22° the height of the benzene solution would be 30 mm.[10] so $K_t/K_b \overset{=}{<} 0.925$. If ΔH is independent of the nature of the solvent K_b/K_c will have the same value at 22° as at 6° and $K_t/K_c \overset{=}{<} 1.06 \pm 0.06$. The maximum variation in ΔH due to the nature of the solvent observed by Ziegler with hexaphenylethane was 1.5 kcal. Assuming that ΔH for the β-naphthyl compound in benzene exceeds by 1.5 kcal. the value in cyclohexane, the ratio K_b/K_c would become 1.32 ± 0.07 at 22° so it is reasonable to conclude that K_t/K_c does not exceed 1.30 at the latter temperature. The difference between this ratio and the value of unit previously assumed is negligible for the purpose of calculating ΔH since it changes the result by less than 0.1 kcal. Therefore, as far as uncertainties in the value of I_0 are concerned ΔH for the β-naphthyl compound probably lies between the limits 12.3 and 12.9 and, making allowance for experimental error, it may be taken as 12.9 ± 1.[11]

The Heats of Dissociation of Tetramethoxyhexaphenylethanes.—Similar colorimetric measurements have been made by Gomberg and Forrester[12] with three symmetrically substituted tetramethoxyhexaphenylethanes. A plot of log I against $1/T$ appears in Fig. 2. The curves are nearly linear at the higher temperatures and the slopes correspond to the following *minimum* values of ΔH in kcal.: di-(2,5-dimethoxyphenyl)-tetraphenylethane in toluene 12.8, in bromobenzene 11.6; di-(3,4-dimethoxyphenyl)-tetraphenylethane in toluene 11.4, in bromobenzene 11.3; di-(2,4-dimethoxyphenyl)-tetraphenylethane in toluene 12.7, in bromobenzene 13.0. The measurements at the lower temperatures have been disregarded because when the color intensities are low the experimental errors produce larger deviations in the plot. The behavior of the 2,4-compound in bromobenzene is exceptional, the color intensities, for some unexplained reason, pass through a minimum at about 5° and rise rapidly

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(10) Obtained from the value 28 mm. at 20° by interpolation using the *experimentally* observed linear relation between log I and $1/T$.

(11) The temperature of the standard benzene solution was not given directly by Gomberg and Sullivan who stated that it was at "room temperature." In order to obtain the most probable value for the ratio K_t/K_b, the value 21–22° for the room temperature given elsewhere in the same paper has been used. However, it is practically certain that the temperature of the standard did not exceed 30°, the highest temperature employed in the measurements. Since at that temperature the height of the standard was 41 mm., $(K_t/K_b)_{303} \overset{=}{<} 1.73$, $(K_t/K_c)_{303} \overset{=}{<} 2.56$, $(K_t/K_c)_{293} \overset{=}{<} 2.78$ and $\Delta H \overset{=}{<} 13.3$, which is within the limits of error of the final value.

(12) Gomberg and Forrester, THIS JOURNAL, **47**, 2373 (1925).

at lower temperatures. Nevertheless, the measurements above 10° yield a linear plot and correspond to the same value of ΔH as those made in toluene where the color intensities do not exhibit a minimum. In any event, the discrepancies at low temperatures cannot be ascribed to the failure of the approximation involved in equation 4, because such effects would be most pronounced at the higher temperatures.

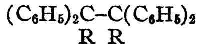
Discussion of Results

The averaged values of ΔH are collected in Table I together with the corresponding values ΔH^* estimated according to Conant's method by setting $\Delta S = 17$ E. U. in the expression[13]

$$\Delta H = \Delta F + T\Delta S \qquad (7)$$

TABLE I

HEATS OF DISSOCIATION OF HEXAARYLETHANES–TETRAPHENYL SERIES OF THE GENERAL FORMULA



$(C_6H_5)_2\underset{R}{C}-\underset{R}{C}(C_6H_5)_2$

R	ΔH, kcal.	ΔH^*, kcal.	ΔF, kcal.	ΔS, E. U.
β-Naphthyl	12.9	8.9	4.5	28
2,5-Dimethoxyphenyl	12.2	9.3	4.4	26
3,4-Dimethoxyphenyl	11.3	9.3	4.3	23
2,4-Dimethoxyphenyl	13.9	9.4	4.6	28

The values of ΔH^* are all low and the actual discrepancies for the methoxy compounds may be even greater, since values of I_0 sufficiently low to alter appreciably the values of ΔH based on equation 4, would correspond to *higher* values of ΔH and *lower* values of ΔF. The discrepancies may be due in part to errors inherent in the cryoscopic method of determining ΔF, but use of the value of ΔF for the β-naphthyl compound computed from Ziegler's photometric measurements reduces the difference between ΔH and ΔH^* by only 0.6 kcal. The value of $\Delta S = 17$ is approximately the mean value for hexaphenylethane; the extreme limits in the nine different solvents investigated by Ziegler, obtained by combining the highest ΔF with the lowest ΔH and *vice versa*, are 12.4 and 22.5. Since all of the values in Table I exceed the highest limit, it seems likely that the entropy of dissociation is not entirely independent of structural influences.

For the sake of completeness, a number of assumptions have been introduced in order to estimate the most probable value of ΔH for the β-naphthyl compound. However, the *minimum* values based on equation 4 are dependent on but two assumptions, namely, that the variations in color are due to a simple binary dissociation of colorless ethane molecules into colored free radicals (equation 1) and that I_0 is independent of the temperature. Of course, the conclusions drawn from these values are subject to the validity of these two assumptions, but, since the same two assumptions are involved in all of Conant's calculations, the minimum values of ΔH may properly be employed to test whether or not the results of Conant's method are entirely consistent with *all* the assumptions which he has made. Furthermore, Ziegler has shown that the absorption of the β-naphthyl compound is actually in quantitative agreement with the requirements of a binary dissociation over a dilution range of approximately 100–8850 liters in cyclohexane at 20°.

Pauling and Wheland's Theory.—Pauling and Wheland[3] have suggested that the low heats of dissociation of the hexaarylethanes are due entirely to a stabilization of the free radicals by resonance[14] and pointed out that the dissociation qualitatively paralleled the calculated resonance energy for a number of substituted ethanes as was to be expected if these ethanes had the same entropy of dissociation. It has just been shown that this condition may not be generally fulfilled.

They took 84 kcal. as the heat of dissociation of the normal C–C bond and gave the values 1.1078 α and 1.1715 α for the resonance energies of the triphenylmethyl and diphenyl-β-naphthylmethyl radicals, respectively. The symbol α represents the single exchange integrals involving adjacent atoms which are necessarily equal for the symmetrical benzene molecule and have been assumed equal in all other molecules. Using Ziegler's value of ΔH for hexaphenylethane in solution, Pauling and Wheland found $\alpha = -32.8$ kcal., in rough agreement with values of α from other sources. Since this experimental evidence[2] also presupposes the independence of T and I_0, it is a fair test to compare the value 7.0 kcal., calculated according to Pauling and Wheland's method for the β-naphthyl compound, with the experimental minimum value 12.3 kcal. This discrepancy certainly casts doubt on the significance of the rough agreement in the values of α noted above. As a matter of fact, Ziegler's studies on pentaphenylcyclopentadienyl[2] indicate that the varia-

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(13) The value of ΔH^* for the β-naphthyl compound is taken from Conant's paper and was based on ΔF as calculated from Gomberg and Sullivan's cryoscopic data in naphthalene solution. The other values have been calculated in the same manner from the cryoscopic data of Gomberg and Forrester in dichlorobenzene.

(14) See, however, Bent and co-workers [THIS JOURNAL, **57**, 1242 (1935); **58**, 165, 170 (1936)] for evidence regarding the importance of other factors than resonance.

tion of the absorption curve with the temperature is not sufficient to affect the values of ΔH by more than about 1 kcal. Accordingly, it seems very unlikely that the theory of Pauling and Wheland can be applied without modification to the calculation of heats of dissociation of hexaarylethanes in solution.

Summary

1. The heat of dissociation of di-β-naphthyltetraphenylethane and minimum values for the heats of dissociation of three other hexaarylethanes have been calculated from data available in the literature.

2. The results indicate that the entropy of dissociation of hexaarylethanes is not entirely independent of the nature of the aryl groups.

3. The heat of dissociation of di-β-naphthyltetraphenylethane in solution does not agree with the value calculated on the basis of Pauling and Wheland's resonance theory.

PROVIDENCE, R. I. RECEIVED MAY 5, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 55]

Preparation and Properties of Cobalt Nitrosyl Carbonyl and of Cobalt Carbonyl Hydride

BY GEORGE W. COLEMAN AND ARTHUR A. BLANCHARD

Blanchard and Windsor[1] in summarizing the properties of the volatile carbonyls, nitrosyl carbonyls and carbonyl hydrides of the metals, noted that in the volatile $CoNO(CO)_3$ the total of the atomic numbers is the same as in the volatile $Ni(CO)_4$; also that in the suspected volatile $HCo(CO)_4$ the same total of atomic numbers prevails.

In order to add further evidence of the similarity of the structure of $Ni(CO)_4$ and $CoNO(CO)_3$ the present study was undertaken to determine whether the action of bromine would liberate nitric oxide as well as carbon monoxide

$$Br_2 + Ni(CO)_4 \longrightarrow NiBr_2 + 4CO$$
$$Br_2 + CoNO(CO)_3 \longrightarrow CoBr_2 + NO + 3CO$$

Complete proof has been found that bromine does, in fact, give the expected reaction.

Incidentally, in preparing an additional supply of cobalt nitrosyl carbonyl, a greatly improved procedure has been worked out through adapting methods employed by Schubert[2] in studying the action of carbon monoxide with cysteine complexes of cobalt.

Also in the course of this procedure it has been possible to isolate the volatile hydride of cobalt carbonyl, $HCo(CO)_4$, in pure form and contribute to a knowledge of its properties.

Windsor and Blanchard[3] and Blanchard, Rafter and Adams[4] studied the formation of carbonyls when alkaline suspensions of nickel and cobalt sulfides and cyanides are treated with carbon monoxide. They did not attempt to identify intermediate complexes. Schubert, using cysteine compounds instead of sulfides or cyanides, isolated the intermediate stages, and defined the course of the reaction with cobalt salt with the equations, in which R = [$-CH_2CHNH_2COO-$]:

$$CoCl_2 + 2HSRH \cdot HCl + 6KOH \longrightarrow K_2Co(SR)_2 + 4KCl + 6H_2O$$
$$9K_2Co(SR)_2 + 8CO + 2H_2O \longrightarrow 6K_3Co(SR)_3 + 2HCo(CO)_4 + Co(OH)_2$$
$$K_3Co(SR)_3 + 6CO + 7KOH \longrightarrow HCo(CO)_4 + 2K_2CO_3 + 3K_2RS + 3H_2O$$

The present authors would make a summation of the above steps in the equation

$$2CoCl_2 + 12KOH + 11CO \longrightarrow 2KCo(CO)_4 + 3K_2CO_3 + 4KCl + 6H_2O \quad (1)$$

which shows a complete regeneration of the cysteine, a reduction of cobalt and a corresponding oxidation of carbon monoxide.

Schubert acidified the alkaline solution containing the complex $KCo(CO)_4$, and noted that a very bad odor was produced and that crystals separated which he identified as the dimeric cobalt tetracarbonyl $Co_2(CO)_8$. He was unable to detect either free hydrogen or any product to account for the hydrogen liberated from the postulated hydride $HCo(CO)_4$.

Experimental

Auxiliary Substances Promoting Absorption of Carbon Monoxide.—Several auxiliary substances other than

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[1] Blanchard and Windsor, THIS JOURNAL, **56**, 826 (1934).

[2] Schubert, *ibid.*, **55**, 4563 (1933).

[3] Windsor and Blanchard, *ibid.*, **55**, 1877 (1933).

[4] Blanchard, Rafter and Adams, *ibid.*, **56**, 16 (1934).

cyanides, sulfides and cysteine were tried, and the rate of absorption of carbon monoxide by an alkaline solution or suspension of cobaltous salt in the shaking apparatus[5] was measured. The results are shown in the tabulation. The shaking apparatus was filled with carbon monoxide, concentrated solutions of the various ingredients were run in, the volume was made up to 80 cc. and shaking was started with the cock open from the carbon monoxide reservoir. Concentrations are given in f. w. of the added substance per liter of the final volume of the mixture.

Cyanide, tartrate and cysteine produced the most notable absorption. Following the absorption of carbon monoxide, treatment of the alkaline cyanide solution with nitric oxide immediately produced brown vapors of cobalt nitrosyl carbonyl as already noted by Rafter and Adams, but similar treatment of the tartrate and cysteine solutions with nitric oxide was without effect.

Acidification of the cysteine solution following treatment with carbon monoxide and nitric oxide produced brown vapors which, when swept with carbon monoxide and nitric oxide through a tube filled with phosphorus pentoxide, and through a trap immersed in solid carbon dioxide and alcohol, condensed in the latter to a yellow solid which melted to a deep red liquid. When this liquid came to room temperature it very quickly changed to a dark colored crystalline mush. In this run the vapors blackened the connecting tubes and the phosphorus pentoxide tube through which they passed on the way to the trap. In the runs described later this blackening did not occur. Later experiments confirmed the conjecture that the dark red vapors contained both $Co(CO)_3NO$ and $HCo(CO)_4$.

$Co(NO_3)_2$	Auxiliary substance and concentration		KOH	Absorption of CO
0.5	$K_2C_2O_4$	2.0	6	None in 1 hour
.25	$K_2C_2O_4$	1.0	3	None in 2.5 hours
.5	$H_2C_4H_6O_6$	2.0	6	5 cc. in 1 hour
.5	$H_2C_4H_6O_6$	2.0	24	147 cc. in 5.25 hours
.5	$H_2C_4H_6O_6$	2.0	16	1700 cc. in 144 hours
.5	CH_2NH_2COOH	2.0	6	None in 0.5 hour
.5	CH_2NH_2COOH	2.0	12	3 cc. in 0.5 hour
.5	CH_2NH_2COOH	2.0	24	20 cc. in 2 hours
.5	CH_2NH_2COOH	2.0	3	10 cc. in 0.5 hour
.1	CH_2NH_2COOH	0.4	6	5 cc. in 0.5 hour
.5	CH_3CHNH_2	2.0	6	None in 0.5 hour
.5	KCNS	0.5	6	15 cc. in 2.5 hours
.5	$C_6H_4(OH)_2$	2.0	6	10 cc. in 2 hours
.5	KCN	0.5	2	355 cc. in 1.25 hours
.5	H_3BO_3	0.5	2	None in 1 hour
.5	C_6H_5COONa	2.0	6	5 cc. in 2 hours
.5	$HOOC.CH_2CH_2\cdot CHNH_2$ COOH	2.0	6	None in 2 hours
.5	$HSCH_2CHNH_2COOHHCl$	0.75	16	5465 cc. in 149 hours

Preparation of Cobalt Nitrosyl Carbonyl

First Run.—Sixty cc. of a solution 0.5 formal in cobalt nitrate, 0.75 formal in cysteine hydrochloride and 16 formal in potassium hydroxide absorbed carbon monoxide in the shaker at the rate of 160 cc. per hour at the start and the rate had diminished to 5 cc. per hour at the end of one hundred and forty-nine hours. In all, 5500 cc. of carbon monoxide was absorbed (4100 calculated according to equation (1)). One half of this solution was run into another tube for a later experiment (air being at all times excluded), and the half left in the shaking apparatus was treated with concentrated hydrochloric acid. Violent local effervescence took place at first, the carbon dioxide redissolving in the rest of the solution on shaking. Finally, the gas came off violently and one-half of the solution was lost by being blown out of the apparatus. The odor was so noxious that work had to be suspended until the laboratory was thoroughly ventilated.

After a slight excess of acid had been added to the one-half of the solution that was saved, the color was yellow and a black scum floated on top. Not more than a trace of solid had been collected in the trap during the acidification. A new trap was now introduced, and nitric oxide was run into the shaking apparatus which immediately became filled with reddish-brown vapors. The vapor was swept with nitric oxide through a phosphorus pentoxide tube into the trap cooled with dry ice, where a yellow solid collected. Thirty minutes later more reddish-brown vapors had collected which were again swept into the trap. The reddish-brown vapors continued to form for several days and were occasionally swept into the trap. In all 0.7 g. of yellow solid, melting sharply at approximately −11° to a deep red liquid, was collected. Thus a yield of $Co(NO)(CO)_3$ of about 54% based on the cobalt nitrate taken, was obtained.

Preparation of Cobalt Carbonyl Hydride

First Run.—The one-half of the solution reserved in the first part of the first run as above described was again introduced into the shaking apparatus without coming in contact with air. The train of phosphorus pentoxide tube and trap cooled with dry ice was again attached. Concentrated hydrochloric acid was added, this time with very great caution until an additional 1 cc. produced no more effervescence. After five minutes of shaking, a very pale yellow gas was noted, and this, swept with carbon monoxide into the trap, condensed to a pale yellow solid. Addition of more acid gave rise to more yellow gas. In all 11 cc. of normal hydrochloric acid was used before the yellow

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(5) Rafter, Thesis, Massachusetts Institute of Technology, 1932.

gas ceased to be produced (thus making the solution about 1 normal in free hydrochloric acid). The remaining solution was yellow with some black scum ($Co_2[CO]$) floating on top. The yellow solid collected in the trap melted sharply at −33° to a sulfur yellow liquid; after it was resolidified it was yellow; it became somewhat reddish after a few remeltings. At room temperature it showed effervescence and soon changed to a brown solid. This solid was then heated to 51° at which temperature it melted. Of the total gas evolved up to 51° a sample of 24.8 cc. was collected. Of this 10.3 cc. was absorbed by ammoniacal cuprous chloride, thus indicating 41.6% of carbon monoxide, and explosion with oxygen indicated 48.8% of hydrogen. The gas evolved on thus warming the hydride had a pale yellow color. Surrounding the upper part of the eudiometer with a cooling bath a thin deposit of yellow solid appeared at −23° and the remaining gas was colorless. This solid had completely revaporized when the bath temperature reached −11°. The volume decrease, due to the lowering of temperature of the upper one quarter of the gas tube and the condensation of the yellow constituent, was only 0.8 cc. Heating the tube to 250° caused no deposition of a cobalt mirror. This yellow constituent of the gas was not absorbed by concentrated potassium hydroxide nor by ferrous sulfate solution but it was removed by ammoniacal cuprous chloride solution.

The brown residue left after warming the hydride weighed 0.6605 g. It melted again at 51° and gave off gas freely at 60°; after it was heated to 250°, a brilliant black mirror covered the inside of the entire heated part of the tube; weight of mirror 0.2408 g. Calcd. for Co in $Co_2(CO_8)$, 0.2275. Volume of gas (all absorbed by ammoniacal CuCl) 385.5 cc. Calcd. for CO, 371 cc. Yield of $HCo(CO)_4$ = 26% based on $Co(NO_3)_2$ taken.

Second Run.—Fifty cc. of a solution 0.5 formal in cobalt nitrate; 0.3 formal in cysteine hydrochloride and 16 formal in potassium hydroxide absorbed a total of 4445 cc. of carbon monoxide [3400 calculated according to equation (1)]. Adding 12 normal hydrochloric acid until the solution was acid caused only a slight deposition of the hydride in the trap. On adding 20 cc. excess of 12 *N* hydrochloric acid and sweeping with carbon monoxide a yield of 0.4215 g. of the hydride was collected in the trap (10% yield). Again only a part of the gas from the decomposition of the hydride was collected and this proved to contain 50% hydrogen, and 50% carbon monoxide. This gas also contained the same yellow constituent as in the first run.

Third Run.—Fifty cc. of a solution 0.5 formal in cobalt nitrate; 2.0 formal in tartaric acid and 16 formal in potassium hydroxide absorbed 1700 cc. of carbon monoxide in one hundred and forty-four hours. The solution was a clear cherry red. Strong acidification and sweeping with carbon monoxide gave 0.2074 g. of the hydride or a 10% yield. The remaining solution was pink. The melting point and the odor of the hydride were identical with those of the product obtained in the first and second runs with cysteine. On letting the trap warm up to room temperature, 18.4 cc. of a light yellow gas was obtained. The light yellow constituent again condensed to a solid at −11°. Analysis gave 3.4 cc. of carbon monoxide and 12.8 cc. of hydrogen; calculated for 0.2074 g. of $HCo(CO)_4$ = 14.9 cc. H_2.

Treatment of Cobalt Nitrosyl Carbonyl with Bromine

Experiment 1.—0.0208 gram of $Co(NO)(CO)_3$, prepared by Adams by the cyanide method = 0.000122 f. w., dissolved in 5 cc. of carbon tetrachloride. Add 0.0750 g. Br_2 = 0.00041 f. w., dissolved in 15 cc. of carbon tetrachloride. Effervescence was noted. Found, 2.6 cc. NO; calculated for $Co(NO)(CO)_3$, 2.9 cc. Found 8.7 cc. CO; calcd., 8.7 cc.

Experiment 2.—0.0624 gram of $Co(NO)(CO)_3$, prepared by Adams by the cyanide method = 0.000361 f. w., dissolved in 15 cc. of CCl_4. Add 0.225 g. Br_2 = 0.0015 f. w. dissolved in 15 cc. of CCl_4. Found, 8.4 cc. NO; calcd. 8.7 cc. Found, 25.9 cc. CO; calcd. 26.2 cc.

Experiment 3.—0.2129 gram of $Co(NO)(CO)_3$, prepared by the cysteine method in first run above = 0.00123 f.w., dissolved in 15 cc. of CCl_4. Titrated with a solution of Br_2 in CCl_4 containing 0.01855 g. of Br_2 per cc. The end-point is the disappearance of the red color of the nitrosyl carbonyl followed by the appearance of the red color of bromine. It is difficult to observe because of the green precipitate of anhydrous $CoBr_2$. End-point at 10.65 cc. = 0.00123 f. w. Br_2; added 1 cc. more Br_2. Found, 26.0 cc. NO; calcd., 29.5 cc. Found, 88.4 cc. CO; calcd. 88.7 cc. Found, 0.260 g. $CoBr_2$; calcd., 0.268 g.

Experiment 4.—0.2163 gram = 0.00125 f. w. of $Co(NO)(CO)_3$, dissolved in 15 cc. of CCl_4. Add 0.2022 g. of Br_2, dissolved in 10.9 cc. of CCl_4 = 0.00126 f. w., which just gave end-point. Found, 29.9 cc. NO; calcd. 30.1 cc. Found, 89.3 cc. CO, calcd., 90.3 cc. Found, 0.2743 g. $CoBr_2$; calcd., 0.2735 g.

The above experiments show that nitric oxide and carbon monoxide are dislodged quantitatively by bromine both when the exact amount and when an excess of the latter is used. The same results were obtained with samples of cobalt nitrosyl carbonyl prepared by different methods.

Comments

The small amount of yellow gas admixed with the hydrogen obtained on warming $HCo(CO)_4$ to room temperature is very perplexing. Its melting point at above −23° is too high for it to be some undecomposed hydride. Since it does not give a cobalt mirror even at 250°, it is unlikely that it contains cobalt. One might surmise that it came from some side reaction of the cysteine, were it not for the fact that it is also obtained when tartaric acid instead of cysteine is used as the auxiliary substance. Its amount is small and its presence does not invalidate the main conclusion as to the formation of the volatile hydride and the decomposition of the latter into hydrogen and dimeric cobalt tetracarbonyl. Nevertheless its nature should be studied as soon as opportunity offers.

It appears that cobalt carbonyl hydride is a somewhat stronger acid than carbonic acid, for it is hardly displaced from its salt at all by carbonic acid, and it is not wholly driven from the solution until free hydrochloric acid in 1 N concentration is present.

The net result of the use of tartaric acid appears to be the same as that from the use of cysteine and can be represented by the same equation (1). Probably intermediate complexes of a similar nature are formed.

The metering of the carbon monoxide was only approximate. If in the first and second runs the excess of CO absorbed over that required by equation (1) is real, it is doubtless due to the formation of some potassium formate. Blanchard and Gilliland[6] noted the formation of a little nickel formate in the slow oxidation of nickel carbonyl by air where the principal reaction was

$$Ni(CO)_4 + {}^1/_2O_2 + H_2O \longrightarrow Ni(OH)_2 + 4CO$$

Summary

Bromine reacts quantitatively with cobalt nitrosyl carbonyl, displacing nitric oxide and carbon monoxide.

The absorption of carbon monoxide by alkaline cobalt salt solutions is promoted by the presence of cysteine, tartrate and several amino acids as well as the presence of cyanide and sulfide.

Acidification of the $KCo(CO)_4$ solution obtained by treating alkaline cobalt salt solution containing cysteine or tartrate with carbon monoxide sets free the very volatile hydride $HCo(CO)_4$. This hydride can be condensed to a light yellow crystalline solid which melts at −33° to a sulfur yellow liquid and decomposes at room temperature into the non-volatile dimeric cobalt tetracarbonyl and hydrogen. The hydride is distinctly an acid, its acid strength being markedly greater than that of carbonic acid.

Cobalt nitrosyl carbonyl is most advantageously prepared by the use of cysteine as above: after acidification, the hydride is allowed to decompose in the shaking apparatus, then treatment with nitric oxide yields the nitrosyl carbonyl.

CAMBRIDGE, MASS. RECEIVED JULY 28, 1936

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[6] Blanchard and Gilliland, THIS JOURNAL, **48**, 872 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Action of Bromine in Methyl Alcoholic Solution on Phenanthrene; a New Route to 9-Phenanthrol and 9-Phenanthrylamines[1]

BY L. F. FIESER, R. P. JACOBSEN[2] AND C. C. PRICE

In connection with a study of the reaction between phenanthrene and bromine in carbon tetrachloride solution,[3] a trial was made of the action on the hydrocarbon of a solution of bromine in methyl alcohol. Considering the ready formation of phenanthrene dibromide, and in analogy with known cases of the addition of methyl hypobromite to aliphatic and alicylic ethylenic linkages,[4] it seemed possible that the hydrocarbon might add the reagent in a similar fashion.

In the first experiments fine, colorless needles of a reaction product were observed to separate after mixing methyl alcoholic solutions of bromine and phenanthrene at room temperature, but the yield was poor. The results were somewhat improved by working at a lower temperature and by using a large excess of bromine, and it was found that the yield is increased very substantially by carrying out the reaction in the presence of sodium acetate to displace the bromine equilibrium in favor of the hypobromite. Eventually an easily reproducible procedure was developed by means of which a colorless product can be obtained in a quantity amounting to about one and one-third the weight of hydrocarbon employed. This material was granular and possibly different from that first observed. Purified by careful recrystallization, the substance melted at 107.5–108°, dec., and when stored in the cold room (5°) it remained apparently unaltered for about one day. At room temperature decomposition set in after a few hours. Although the analysis of the unstable substance presented difficulties, the results for carbon, hydrogen, bromine and methoxyl all point to the formula of a molecular compound composed of equivalent parts of phenanthrene

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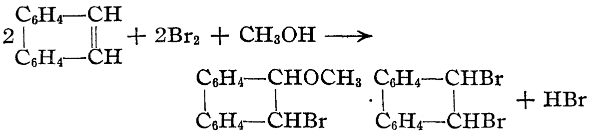
[1] The bromination reaction described in this paper was discovered in the course of other work by C. C. Price, who made a preliminary study of the formation of the product and of its conversion to 9-methoxyphenanthrene (Dissertation, 1936). A more detailed investigation of the formation, nature and preparative uses of the compound was subsequently made by R. P. Jacobsen, and these experiments form the basis of the present report.—L. F. F.

[2] Du Pont Research Fellow.

[3] Price, THIS JOURNAL, **58**, 1834 (1936).

[4] Conant and Jackson, *ibid.*, **46**, 1727 (1924); Jackson, *ibid.*, **48**, 2166 (1926); Jackson and Pasiut, *ibid.*, **49**, 2071 (1927); Meinel, *Ann.*, **510**, 129 (1934).

methoxybromide and phenanthrene dibromide, and the reaction thus appears to proceed as follows.



$$2\begin{array}{l}C_6H_4\text{—}CH\\ |\qquad\quad \|\\ C_6H_4\text{—}CH\end{array} + 2Br_2 + CH_3OH \longrightarrow \begin{array}{l}C_6H_4\text{—}CHOCH_3\\ |\qquad\quad |\\ C_6H_4\text{—}CHBr\end{array}\cdot\begin{array}{l}C_6H_4\text{—}CHBr\\ |\qquad\quad |\\ C_6H_4\text{—}CHBr\end{array} + HBr$$

This formulation is consistent with such observations as have been made of the properties of the substance. When warmed with a solution of potassium hydroxide and potassium acetate in methyl alcohol, it yielded a mixture of about equal parts of 9-methoxyphenanthrene and phenanthrene. The former substance presumably is produced by the elimination of hydrogen bromide from the methoxybromide component, while the latter evidently comes from the dibromide by loss of bromine When treated in the same way, pure phenanthrene dibromide afforded bromine-free phenanthrene in nearly quantitative yield. While the mixture of the ether and the hydrocarbon is not readily separated, pure 9-phenanthrol can be obtained very easily by short treatment of the crude mixture with hydrobromic–acetic acid followed by extraction with alkali, and the phenanthrene can be recovered in a satisfactory state of purity. Since the most satisfactory of the previous methods of preparing 9-phenanthrol (through phenanthrenequinone and dichlorophenanthrone[5]) leaves much to be desired, the new reaction series was studied with a view to the development of a better source of the hydroxy compound. It was found that all three reactions can be carried out rapidly with reasonably large amounts of material and that 9-phenanthrol can be obtained with regularity in a pure condition in over-all yields of 28–30%, based on the phenanthrene consumed. In its present state the process seems to have definite advantages over previous methods, and it is not impossible that further improvements can be made.

With 9-phenanthrol more readily available, the use of this material as a source of 9-phenanthrylamines was investigated. Such substances are of particular interest because of the structural relationship, in at least one important respect, to morphine. The conversion of 9-phenanthrol into 9-phenanthrylamine is described in the early literature, but the results were unsatisfactory (25% yield),[6] and methods of preparing the amine through 9-nitro-,[7] 9-nitro-10-bromo-,[8] or 9-acetylphenanthrene[9] all suffer from the fact that the starting materials are not easily available. Following the general procedure of Bucherer,[10] we obtained the amine from 9-phenanthrol in 90% yield. N-Alkylphenanthrylamines (methyl, ethyl, *n*-propyl and *n*-butyl) were obtained in about 70% yield by heating 9-phenanthrol with the appropriate primary amine and aqueous sodium bisulfite at 135–140° for about one day. N-(β-Hydroxyethyl)-9-phenanthrylamine was prepared from 9-phenanthrylamine and ethylene oxide, but only in poor yield.

The investigation of the bromination reaction is being continued and the preparation of further 9-amino derivatives more closely related to the alkaloids of the morphine group is in prospect.

Experimental Part[11]

Preparation of the Complex.—After a number of trials at different temperatures and varying the amounts of the reagents, the following procedure was adopted as the most satisfactory both as to yield and quality of the product. For efficient washing of the product, larger amounts are best handled in portions of the size indicated.

A solution of 50 g. of phenanthrene (m. p. 97.5–98°) and 15 g. of anhydrous sodium acetate in 900 cc. of warm methyl alcohol was cooled quickly to about 35–40° without allowing much phenanthrene to crystallize, and a solution of 25 g. of bromine in 100 cc. of cold methyl alcohol was added all at once. The mixture was cooled rapidly in a salt–ice bath and the temperature was brought to $-5°$. The complex began to separate from the red-brown solution during the cooling process, and after standing at $-5°$ for twenty to thirty minutes the yellow solid was collected and washed, after removing the filtrate, with three 100-cc. portions of a 5% solution of sodium acetate in 70% methyl alcohol. This removed the yellow color and left a nearly white solid. The original filtrate was treated with 75 cc. of 20% aqueous sodium acetate solution and an additional 15-cc. portion of bromine in 50 cc. of cold methyl alcohol, and cooled to $-10°$ for thirty minutes. A second crop of the complex separated, about equal in amount to the first, and it was washed as before. The total product weighed 63–65 g. (71–74%, calculated on the basis of the formula indicated) and melted at 105–107° with loss of hydrogen bromide. This crude product was employed in the next step without purification.

The material prepared in this way did not appear to undergo change when crystallized from ether–petroleum

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[5] Lachowicz, *J. prakt. Chem.*, **28**, 168 (1883); Schmidt and Lumpp, *Ber.*, **41**, 4215 (1908); Goldschmidt, Vogt and Bredig, *Ann.*, **445**, 135 (1925).

[6] Japp and Findlay, *J. Chem. Soc.*, **71**, 1115 (1897).

[7] Schmidt and Strobel, *Ber.*, **34**, 1461 (1901); **36**, 2508 (1903); Schmidt and Heinle, *ibid.*, **44**, 1488 (1911).

[8] Schmidt and Lodner, *ibid.*, **37**, 3575 (1904); Austin, *J. Chem. Soc.*, **93**, 1762 (1908).

[9] Bachmann and Boatner, THIS JOURNAL, **58**, 857 (1936).

[10] Bucherer, *J. prakt. Chem.*, **69**, 49 (1904).

[11] All melting points are corrected. Analyses by Mrs. G. M. Wellwood.

ether, using Norite for clarifying the solution and avoiding undue heating, and after several recrystallizations it was obtained as a colorless, granular solid, m. p. 107.5–108°, dec. One sample melted at this temperature without showing signs of decomposition. Samples dried in vacuum and kept at room temperature began to turn brown within a few hours, and the sample used for the following analyses was prepared the evening before it was used and stored at 5°. All of the analyses were made on the same sample, but this was recrystallized prior to the second methoxyl determination (the last of the series reported), although no darkening had been observed.

Anal. Calcd. for $C_{14}H_{10}Br_2 \cdot C_{14}H_{10}(OCH_3)Br$: C, 55.51; H, 3.70; Br, 38.24; OCH_3, 4.95. Found: C, 56.11, 56.23; H, 4.62, 4.97; Br, 38.06, 36.74; OCH_3, 4.96, 5.49.

The lack of concordance in the results may be connected with the difficulty in drying the sample completely at a low temperature, with its instability, or, particularly in the case of the carbon–hydrogen determinations, with a difficulty inherent in the combustion itself. The bromine content is about 10% higher than that calculated for the pure methoxybromide and this fact, and the definite methoxyl content found, provide convincing indications of the presence of the two components.

One sample, prepared at an earlier stage of the work, crystallized from ether in fine needles, m. p. 113–115°, uncorr., and the carbon value found in a single determination was about 5% higher than found above, but other analyses were not made and it is not known if this was the same or a different product.

In bromination experiments conducted at room temperature in methyl alcohol containing no sodium acetate the yields of the solid product which separated ranged from 20 to 30%. When the solution was cooled to 0° soon after mixing the reagents the yield was increased to 50%.

Debromination.—The crude, undried complex prepared in four lots from 200 g. of phenanthrene was suspended in 1 liter of methyl alcohol containing 40 g. of potassium hydroxide and 10 g. of potassium acetate. The mixture was heated with stirring at 50–55° for one hour, after which the temperature was raised to 60° for thirty minutes. The warm, deep yellow-red solution was decanted from precipitated potassium bromide, the latter being washed with methyl alcohol, and the solutions were combined and diluted with 200 cc. of water and cooled. The oil which separated soon solidified and the material was crystallized from methyl alcohol, using Norite. An additional quantity of material was obtained by further dilution of the mother liquor, and recrystallized. The total yield of material, consisting of a mixture of plates and needles and melting indefinitely at 60–80°, was 110 g. This was found from the subsequent treatment described below to be composed of nearly equal amounts of phenanthrene and 9-methoxyphenanthrene.

In two early experiments by different workers, both using sodium acetate in methyl alcoholic solution, 9-methoxyphenanthrene, m. p. 93–94° (calcd.: C, 86.50; H, 5.76. Found: C, 86.16; H, 5.76) was obtained as the sole product, but the results could not be repeated later. The starting materials were not fully analyzed and may have been different from that described above.

As the formation of phenanthrene from the dibromide component seemed surprising, a test experiment was made with the phenanthrene dibromide prepared by adding 5 g. of bromine to 5 g. of phenanthrene in 25 cc. of carbon tetrachloride solution and cooling. The crystalline product was washed well and heated for thirty minutes with a solution of 4 g. of potassium hydroxide and 0.5 g. of potassium acetate in 50 cc. of methyl alcohol. On decanting the solution and adding an equal volume of water, 4 g. of halogen-free phenanthrene separated as small leaflets. Once recrystallized it melted at 95.5–97° and gave no depression when mixed with authentic phenanthrene.

9-Phenanthrol.—The crystalline mixture (110 g.) obtained as described above was heated under reflux with 400 cc. of glacial acetic acid, and 60 cc. of 48% hydrobromic acid was added gradually. After boiling the mixture for two hours an equal volume of water was added and the precipitate was collected after cooling, washed, and the moist product was taken up in 300 cc. of ether. After thorough washing with water, the ethereal solution was extracted with three 50-cc. portions of 10% sodium hydroxide and the green alkaline extract, after one washing with ether, was acidified and extracted with 100 cc. of ether. The washed ethereal solution, after dilution with 25 cc. each of benzene and hexane, was dried over sodium sulfate and decolorized by filtration through a column of activated alumina. An impurity giving the solution an orange color was retained in a greenish band, and from the filtrate 48–50 g. of 9-phenanthrol was obtained in the form of faintly salmon-colored needles melting at 153–155°. From the washed ethereal solution remaining after extraction with alkali, 45 g. of crude phenanthrene was recovered, making the over-all yield of 9-phenanthrol 28–30%, based on material consumed. The crude phenanthrene after being distilled in vacuum and crystallized once from methyl alcohol was satisfactory for use in the bromination reaction.

9-Phenanthrylamine.—A mixture of 10 g. of 9-phenanthrol, 50 g. of 40–45% ammonium sulfite, and 50 cc. of concentrated ammonium hydroxide solution was heated in a sealed tube at 135–140° for twenty to twenty-five hours. The cooled mixture was extracted with ether and the solution, after being washed with dilute sodium hydroxide and with water, was dried over sodium sulfate, decolorized with Norite and concentrated somewhat. On adding hexane and cooling, there was obtained 9.1 g. (90%) of 9-phenanthrylamine, m. p. 135–136.8°. One recrystallization from ether–petroleum ether or benzene–hexane gave very faintly yellow needles, m. p. 137.5–138.5°.

In similar experiments conducted at 100° the yield of amine after heating for five hours was 20%, after twenty to twenty-five hours it rose to about 50%.

N-Alkyl-9-phenanthrylamines.—For the preparation of these substances a mixture of 2 g. of 9-phenanthrol, 10 g. of sodium bisulfite and either 10 cc. of water and 10 cc. of a 33% aqueous solution of the amine, or a mixture of 20 cc. of water and 5 cc. of the pure amine, was heated in a sealed tube at 135–140° for twenty to twenty-five hours. The reaction products, recovered as above, were obtained directly in a good condition and the melting point subsequently rose only 1–3° on further recrystallization. The first three substances were crystallized from benzene–ligroin or ether–petroleum ether, while 80% methyl alcohol was used in the case of the butyl compound. The amines all form heavy, pale yellow needles.

N-ALKYL-9-PHENANTHRYLAMINES

Alkyl group	Yield, %	M. p., °C.	% C Calcd.	% C Found	% H Calcd.	% H Found
Methyl	70	88.5– 89.5	86.91	86.85	6.33	6.27
Ethyl	70	97 – 98	86.87	86.96	6.84	7.11
n-Propyl	70	109.5–110.5	86.76	86.61	7.29	7.09
n-Butyl	62	102 –103	86.69	86.52	7.69	7.51

N-(β-Hydroxyethyl)-9-phenanthrylamine.—After heating a mixture of 2 g. of 9-phenanthrylamine, 5 cc. of benzene and 10 cc. of ethylene oxide in a sealed tube at 100° for seven hours, the excess ethylene oxide was expelled and the residue was extracted with ether. The solution was dried, decolorized and treated with petroleum ether, when 0.25 g. (10%) of a solid was obtained in the form of fine needles melting at 99.5–101°. The substance has a tendency to separate in a gelatinous condition. After two recrystallizations from ether–petroleum ether it was obtained as long, slender, colorless needles, m. p. 101–102°.

Anal. Calcd. for $C_{16}H_{15}ON$: C, 80.97; H, 6.38. Found: C, 81.22; H, 6.34.

When the reaction mixture was heated at 100° for only five hours considerable 9-phenanthrylamine was recovered along with some of the β-ethanol derivative. On conducting the reaction at 135–140° for either ten or twenty hours the ethereal extract of the product yielded only a resinous residue on evaporation. This distilled without apparent decomposition at about 250° (2 mm.) but the viscous, pale yellow distillate set to a glass and did not crystallize.

Summary

Treated with bromine in methyl alcoholic solution, phenanthrene is converted in about 70% yield into a very unstable substance which appears to be a complex containing one molecule each of phenanthrene methoxybromide and phenanthrene dibromide. The complex yields 9-methoxyphenanthrene and phenanthrene when warmed with alcoholic potassium hydroxide–acetate, and 9-phenanthrol is easily obtained from the mixture in a sufficiently satisfactory over-all yield to make this a useful preparative method. 9-Phenanthrylamine and typical N-alkyl derivatives can be obtained in good yield from 9-phenanthrol by the Bucherer reaction.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS. RECEIVED AUGUST 17, 1936

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Acylation and Alkylation of Beta Diketones and Beta Sulfonyl Ketones

BY E. P. KOHLER AND H. A. POTTER

In a recent paper,[1] in which we described the action of benzoyl chloride on the magnesium derivatives of a series of monoketones, we showed that there is a conspicuous difference in the behavior of phenyl and mesitylenic ketones, the former being converted into diketones and the latter largely into benzoates. We have now extended the comparison to the corresponding β-diketones and, as these diketones form copper derivatives which can be purified by crystallization, we were able to compare the behavior of phenyl and mesitylenic ketones when they are benzoylated by means of metallic derivatives that are very different from the magnesium compounds in their activity.

We also included in the comparison the corresponding β-sulfonyl ketones—tosyl acetophenone and tosyl acetomesitylene. These compounds are of special interest because the sulfonyl group increases the acidity of the hydrogen on an adjoining carbon atom but is incapable of participating in any process akin to enolization.

The nature of the products and the yields in which they were obtained are shown in the following table. In many cases the primary benzoylation products deprived some of the initial metallic derivatives of their metal and thus prevented complete acylation; the proportion of C-benzoyl to O-benzoyl derivatives is therefore more significant than the total yield. In the case of the copper compounds the great differences in solubility introduce an additional complication because in the very slow reactions a part of the initial material is lost through halogenation by the mechanism recently established by Michael and Carlson.[2] An attempt to obviate this difficulty by substituting benzoyl bromide for the chloride—in the cases marked with an asterisk—was unsuccessful because, while the bromide reacts far more rapidly than the chloride, the resulting cupric bromide is also a much better halogenating agent than the chloride.

An examination of this table shows that the difference in the mode of benzoylation of phenyl

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(1) Kohler, Tishler and Potter, THIS JOURNAL, **57**, 2517 (1935).

(2) Michael and Carlson, *ibid.*, **58**, 353 (1936).

TABLE I

Substance	Product	C-Acylation Per cent.	Product	O-Acylation Per cent.
$[(C_6H_5CO)_2CH]MgX$	$(C_6H_5CO)_3CH$	80.5	....	0
$[(C_6H_5CO)_2CH]_2Cu$	$(C_6H_5CO)_3CH$	80	....	0
$[(C_6H_5CO)_2CH]_2Cu^*$	$(C_6H_5CO)_3CH$	60	$(C_6H_5\underset{OCOC_6H_5}{\underset{\vert}{C}}{=}CHCOC_6H_5$ (I)	22
$\left[\begin{matrix}C_6H_5CO\\(CH_3)_3C_6H_2CO\end{matrix}{>}CH\right]MgX$	$(C_6H_5CO)_2CHCOC_6H_2(CH_3)_3$	65	$\left[\begin{matrix}C_6H_5CO\\(CH_3)_3C_6H_2CO\end{matrix}{>}CH\right]COC_6H_5$ (II)	18
$\left[\begin{matrix}C_6H_5CO\\(CH_3)_3C_6H_2CO\end{matrix}{>}CH\right]_2Cu$	$(C_6H_5CO)_2CHCOC_6H_2(CH_3)_3$	60	$\left[\begin{matrix}C_6H_5CO\\(CH_3)_3C_6H_2CO\end{matrix}{>}CH\right]COC_6H_5$ (II)	30
$\left[\begin{matrix}C_6H_5CO\\(CH_3)_3C_6H_2CO\end{matrix}{>}CH\right]_2Cu^*$	$(C_6H_5CO)_2CHCOC_6H_2(CH_3)_3$	45	$\left[\begin{matrix}C_6H_5CO\\(CH_3)_3C_6H_2CO\end{matrix}{>}CH\right]COC_6H_5$ (II)	30
$\left[\begin{matrix}(CH_3)_3C_6H_2CO\\(CH_3)_3C_6H_2CO\end{matrix}{>}CH\right]MgX$	....	0	$(CH_3)_3C_6H_2\underset{OCOC_6H_5}{\underset{\vert}{C}}{=}CHCOC_6H_2(CH_3)_3$ (III)	96
$\left[\begin{matrix}(CH_3)_3C_6H_2CO\\(CH_3)_3C_6H_2CO\end{matrix}{>}CH\right]_2Cu$	....	0	$(CH_3)_3C_6H_2\underset{OCOC_6H_5}{\underset{\vert}{C}}{=}CHCOC_6H_2(CH_3)_3$ (III)	49
$\left[\begin{matrix}C_7H_7SO_2\\C_6H_5CO\end{matrix}{>}CH\right]MgX$	$C_7H_7SO_2CH(COC_6H_5)_2$ (IV)	81	....	0
$\left[\begin{matrix}C_7H_7SO_2\\(CH_3)_3C_6H_2CO\end{matrix}{>}CH\right]MgX$	$C_7H_7SO_2\underset{COC_6H_5}{\underset{\vert}{CH}}COC_6H_2(CH_3)_3$ (V)	16	$C_7H_7SO_2CH{=}\underset{OCOC_6H_5}{\underset{\vert}{C}}C_6H_2(CH_3)_3$	64
$[(C_7H_7SO_2)_2CH]\ MgX$	$(C_7H_7SO_2)_2CHCOC_6H_5$	80	....	0
$\left[\begin{matrix}C_7H_7SO_2\\C_6H_5CO\\C_6H_5CO\end{matrix}{>}C\right]MgX$	....	0	$C_7H_7SO_2\underset{C_6H_5CO}{\underset{\vert}{C}}{=}\underset{OCOC_6H_5}{\underset{\vert}{C}}—C_6H_5$ (VII)	96
$\left[\begin{matrix}C_7H_7SO_2\\C_7H_7SO_2\\C_6H_5CO\end{matrix}{>}C\right]MgX$	....	0	$(C_7H_7SO_2)_2C{=}\underset{OCOC_6H_5}{\underset{\vert}{C}}—C_6H_5$ (VIII)	
$\left[\begin{matrix}C_6H_5SO_2\\C_6H_5SO_2\end{matrix}{>}CH\right]MgX$	$(C_6H_5SO_2)_2CHCOC_6H_2(CH_3)_3$ (IX)	80	....	0

and mesitylenic ketones is just as marked in the β-diketones and the β-sulfonyl ketones as it is in the monoketones. It shows also that the course of the benzoylation of the metallic derivatives of these compounds is not greatly affected by the nature of the metal; it depends almost entirely on the character of the hydrocarbon residues and the mesityl group effectively promotes O-benzoylation.

For reasons stated earlier, the β-sulfonyl ketones are especially interesting. As they behaved toward benzoylating agents essentially like the polyketones, we also examined the behavior of tosyl acetomesitylene in reactions involving alkylation. In alcohol the sodium compound reacted rapidly with methyl iodide and the sole product of the reaction was the C-alkyl derivative. We were unable to induce either the magnesium or the sodium compound to react with methyl iodide in ether or benzene but both reacted with dimethyl sulfate in these non-polar solvents and formed O-methyl derivatives exclusively. Mesitylenic ketones, therefore, differ from phenyl ketones also in their tendency to form O-alkyl derivatives.

These β-sulfonyl ketones also provided a means of examining the view that sulfonyl groups do not promote the enolization of a carbonyl group in the β-position because they cannot serve as partners in conjugation. In support of this view Arndt and Martius[3] described the behavior of a series of mono- and disulfonyl compounds toward alcoholic ferric chloride. The behavior of our series of sulfonyl compounds in solutions of ferric chloride in methyl alcohol—or better in freshly prepared solutions in acetone—was as follows: with $C_7H_7SO_2CH_2COC_6H_5$, $C_7H_7SO_2CH_2COC_6H_2(CH_3)_3$ and $(C_7H_7SO_2)_2CHCOC_6H_5$ the tests were negative; $C_7H_7SO_2CH(COC_6H_5)_2$ slowly developed a red color which was feeble in alcohol, stronger in acetone; both $C_7H_7SO_2CH(COC_6H_5)COC_6H_2(CH_3)_3$ and $(C_6H_5SO_2)_2CHCOC_6H_2(CH_3)_3$ rapidly developed deep red colors in both solvents.

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(3) Arndt and Martius, *Ann.*, **499**, 244 (1932).

The view that sulfonyl groups cannot promote enolization is manifestly no longer tenable because the difference between acetomesitylene which does not respond to any tests for enolization and disulfonyl derivative which enolizes must be due to the two phenylsulfonyl groups. It is doubtless true that the sulfonyl group is far less effective than the carbonyl group in promoting enolization; the introduction of another benzoyl group into the completely enolic dibenzoylmethane merely stabilizes the ketonic form while the introduction of a tosyl group completely inhibits enolization. But when the same group is introduced into benzoyl acetomesitylene, the product still enolizes in solution—an indication that the tendency to enolize is much more pronounced in mesitylenic than in phenyl ketones.

From the foregoing account and the facts presented in the earlier paper it is evident that all types of ketones which contain the group $CH-COC_6H_2(CH_3)_3$ differ from those which have the group $CH-COC_6H_5$ in that they have a greater tendency to enolize and to form acyl and alkyl derivatives of the enolic modification. The reason for this peculiarity is not clear but it appears probable that the predominant O-acylation and O-alkylation is associated with the tendency to enolize.

Experimental Part

I. Preparation of Materials

The diketones and their copper derivatives which were known were prepared by conventional methods but the copper derivative of dibenzoylmethane was recrystallized before use by solution in pyridine and reprecipitation with ether. Tosyl acetophenone was made by Arndt and Martius[3] (p. 281) by treating chloroacetophenone with sodium toluene sulfinate. In order to secure the intermediates, we undertook to prepare it by means of a series of reactions which can be represented as follows

$$C_7H_7SNa + ClCH_2COC_6H_5 \longrightarrow C_7H_7SCH_2COC_6H_5 \longrightarrow C_7H_7SOCH_2COC_6H_5 \longrightarrow C_7H_7SO_2CH_2COC_6H_5$$

We found, however, that, owing to oxidation and reduction in the alkaline solution, the principal products of the first step were the sulfoxide and acetophenone. The procedure was as follows.

A solution of 172 g. of chloroacetophenone in boiling methyl alcohol was treated with an equivalent quantity of sodium *p*-thiocresolate. The mixture was boiled for several hours, then freed from most of the methyl alcohol by distillation. An ethereal extract of the residue, distilled under diminished pressure, gave 50 g. of acetophenone and 168 g. of the sulfoxide. The sulfoxide melts at 46° and boils at 182–184° (5 mm.). It is oxidized to the sulfone by hydrogen peroxide.

Anal. Calcd. for $C_{15}H_{14}O_2S$: C, 69.7; H, 5.6. Found: C, 69.6; H, 6.0.

Tosyl Acetomesitylene: $C_7H_7SO_2CH_2COC_6H_2(CH_3)_3$.—Sodium toluene sulfinate reacts much less readily with chloroacetomesitylene than with chloroacetophenone. The best results were obtained by heating equivalent quantities of the reactants and a small quantity of alcohol (about one-third of the volume of the solids) in sealed tubes for seventy-five hours at 100°. The contents of the tubes were acidified with dilute acid and extracted with benzene. The benzene solution, in turn, was extracted with bicarbonate to remove sulfinic acid and finally with normal aqueous sodium hydroxide. From the yellow alkaline solution acids precipitated the sulfonyl ketone. It crystallized from methyl alcohol in needles and it melted at 180°. The yield was about 50%.

Anal. Calcd. for $C_{18}H_{20}O_3S$: C, 68.4; H, 6.3. Found: C, 68.2; H, 6.3.

Tribenzoyl Methyl Chloride: $(C_6H_5CO)_3CCl$.—A slow stream of chlorine was passed through a suspension of tribenzoylmethane until all of the solid disappeared. The chloroform was evaporated and the residue was recrystallized from methyl alcohol. The product separated in needles melting at 122°.

Anal. Calcd. for $C_{22}H_{15}O_3Cl$: C, 72.8; H, 4.1. Found: C, 72.5; H, 4.2.

The chloride did not serve the purpose for which it was made because sodium toluene sulfinate reduced it rapidly and quantitatively to tribenzoylmethane and when it was treated with sodium thiocresolate in benzene it reacted in accordance with the equation

$$(C_6H_5CO)_3CCl + 2NaSC_7H_7 \longrightarrow NaCl + (C_6H_5CO)_3CNa + C_7H_7S{-}SC_7H_7$$

II. Benzoylation

In order to get significant results with the magnesium derivatives it was necessary to prepare and benzoylate them in ether at low temperatures because at higher temperatures both the magnesium derivatives themselves and their benzoylation products are cleaved in part into new magnesium derivatives which then undergo further benzoylation. Thus when the magnesium derivative of benzoyl acetomesitylene was benzoylated in boiling benzene the principal products were the magnesium derivatives of dibenzoyl and tribenzoyl methane.

For manifest reasons some diketone or sulfo ketone was regenerated in all cases in which one of the products was formed by C-benzoylation. In many of these cases also—especially in the benzoylation of the sulfonyl compounds—the primary product suffered further benzoylation. The final result, therefore, was a mixture which might contain diketone and one or more of its stereoisomeric benzoates, triketone and its benzoates, and the excess of acid chloride. And, in the case of the copper compounds, usually it also contained a halogen derivative of the diketone.

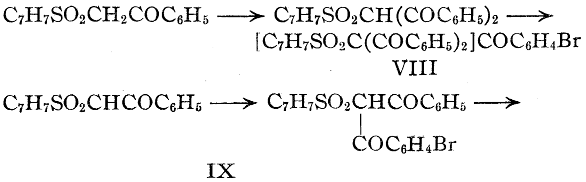
The separation of these mixtures, frequently troublesome, was in part chemical. In general ether, when present, was removed and replaced with benzene. The benzene solutions were boiled with water to decompose excess of chloride or bromide, then cooled and extracted with dilute bicarbonate until free from benzoic acid. The benzene layer was then shaken with sodium carbonate which converted a part of the triketone into the sparingly soluble ketonic modification and removed the remainder as a soluble sodium salt. Extraction with aqueous sodium hydroxide then removed both the regenerated diketone and its halogen compound and these substances were separated either by crystallization or when necessary by converting the diketone into its copper derivative. The benzene solution then contained only benzoates. The separation of the isomeric benzoates by crystallization was always troublesome and sometimes impossible but the nature of the products and the quantities in which they were present could always be established by hydrolysis with cold dilute methyl alcoholic sodium hydroxide. The important constants of the new products are recorded in the following table. The Roman numerals refer to structural formulas in Table I.

TABLE II

Formula	Crystal form	M. p., °C.	Composition, % Calcd. C	Calcd. H	Found C	Found H
$C_{22}H_{16}O_3$ (I)	(a) Yellow tables	108	80.5	4.8	80.3	4.9
	(b) Colorless cubes	125	80.5	4.8	80.2	4.8
$C_{25}H_{22}O_3$ (II)	Yellow prisms	91	81.1	6.0	81.0	6.3
$C_{28}H_{28}O_3$ (III)	Yellow plates	136	81.6	6.8	81.5	6.8
$C_{22}H_{18}O_4S$ (IV)	Thin needles	196	69.8	4.8	69.6	4.5
$C_{25}H_{24}O_4S$ (V)	Prisms	147	71.4	5.7	71.2	5.7
$C_{25}H_{24}O_4S$ (VI)	(a) Needles	120	71.4	5.7	71.4	5.8
	(b) Prisms	126	71.4	5.7	71.6	5.7
$C_{29}H_{22}O_5S$ (VII)	Needles	166	72.2	4.6	72.1	4.6
$C_{29}H_{21}O_5BrS$ (VIII)	Prisms	189	62.0	3.7	61.7	3.8
$C_{22}H_{17}O_4BrS$ (IX)	Needles	212	57.8	3.7	58.1	3.9
$C_{29}H_{21}O_5BrS$ (X)	(a) Needles	182	62.0	3.7	61.9	3.9
	(b) Prisms	201	62.0	3.7	61.8	4.0

III. Proof of Structure

In most cases the products formed by O-acylation were readily distinguished from the C-acyl derivatives by their lack of solubility in aqueous alkali. This test, however, was not applicable to those tosyl compounds which contained four acyl groups. There was little doubt concerning the structure of these compounds because they were readily formed also by benzoylation in pyridine but we nevertheless decided to establish with certainty the manner in which the fourth acyl group enters the molecule. To this end we employed *p*-bromobenzoyl chloride in accordance with the scheme

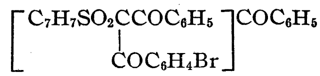


$$C_7H_7SO_2CH_2COC_6H_5 \longrightarrow C_7H_7SO_2CH(COC_6H_5)_2 \longrightarrow [C_7H_7SO_2C(COC_6H_5)_2]COC_6H_4Br$$

VIII

$$C_7H_7SO_2CHCOC_6H_5 \longrightarrow C_7H_7SO_2\underset{\substack{|\\COC_6H_4Br}}{C}HCOC_6H_5 \longrightarrow$$

IX



$$\left[C_7H_7SO_2\underset{\substack{|\\COC_6H_4Br}}{C}COC_6H_5\right]COC_6H_5$$

X

As the final products of the two series are different, the fourth group evidently enters as benzoate. The constants of these compounds have been included in Table II.

IV. Alkylation of Tosylacetomesitylene

Alkylation with Diazomethane: $C_7H_7SO_2CH{=}C(OCH_3)$-$C_6H_2(CH_3)_3$.—An excess of diazomethane was passed into a solution of the sulfonyl ketone in cold benzene. The solution evolved gas slowly but regularly. It was left to itself overnight, then diluted with petroleum ether. The product crystallized from benzene–petroleum ether in large prisms and it melted at 137°. The yield was 93%.

Anal. Calcd. for $C_{19}H_{22}O_3S$: C, 69.1; H, 6.7. Found: C, 69.2; H, 6.8.

This product is evidently an ether because it is insoluble in alkalies and regenerates the sulfonyl ketone when it is digested with hydrochloric acid. When it was heated for six hours to 130° in a vacuum it was transformed into an isomer which crystallized from methyl alcohol in sparkling cubes and melted at 147°. This isomer likewise is an ether; it also is insoluble in alkalies but is hydrolyzed by acids. Neither of these ethers was rearranged to the C-methyl derivative by prolonged boiling with alcoholic sodium methylate.

Anal. Calcd. for $C_{19}H_{22}O_3S$: C, 69.1; H, 6.7. Found: C, 69.0; H, 6.7.

Alkylation of the Magnesium Derivative.—A solution of 6.3 g. of the tosyl compound in benzene was added to a small excess of ethylmagnesium bromide and the solution was distilled until all of the excess ethyl bromide and the ether had been expelled. It was then treated cautiously with excess of dimethyl sulfate, boiled for seven hours and decomposed in the usual manner. The benzene layer contained 6.2 g. of the methyl ether melting at 147°—a yield of 94%.

Alkylation of the Sodium Derivative in Benzene.—A solution of 3.2 g. of the tosyl compound in benzene was treated with an equivalent quantity of sodium and left to itself until all of the metal had disappeared. Excess of dimethyl sulfate was added then and the mixture was boiled for four hours and decomposed in the usual manner. The benzene layer contained 3 g. of the methyl ether melting at 137°—a yield of 90%.

Alkylation with Methyl Iodide in Alcohol: $C_7H_7SO_2CH$-$(CH_3)COC_6H_2(CH_3)_3$.—A boiling methyl alcoholic solution of 3.2 g. of the tosyl compound and 3 g. of methyl iodide was treated gradually with two equivalents of sodium methylate and boiled for two hours. The solution remained clear until it was diluted with ice water. It then deposited a very sparingly soluble product which was recrystallized from acetone–methyl alcohol. It separated in lustrous needles melting at 171°. The yield was 96%.

Anal. Calcd. for $C_{19}H_{22}O_3S$: C, 69.1; H, 6.7. Found: C, 69.2; H, 6.9.

The methyl derivative is extracted from its ethereal solution by aqueous sodium hydroxide and although very slightly soluble in methyl alcohol it dissolves freely in methyl alcoholic sodium hydroxide. The crude product contained no material that was not extracted from ether by aqueous sodium hydroxide; it therefore contained neither ethers nor dimethyl derivatives.

Summary

This paper contains an account of the results obtained in a study of the acylation and alkylation of a series of β-diketones and β-sulfonyl ketones.

CAMBRIDGE, MASS. RECEIVED AUGUST 1, 1936

[CONTRIBUTION NO. 32 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Reduction of Nitroguanidine. VII. Preparation of Aminoguanidine by Catalytic Hydrogenation

BY EUGENE LIEBER AND G. B. L. SMITH

The catalytic hydrogenation of nitroguanidine to nitrosoguanidine with nickel and platinum catalysts in neutral media has been reported.[1] The further reduction to aminoguanidine has not been studied extensively.[2] Recently McGill[3] has suggested the manufacture of aminoguanidine by catalytic hydrogenation with a catalyst of nickel dispersed on kieselguhr (all of the ordinary hydrogenating catalysts are also claimed) at temperatures between 25 and 125° (the preferred temperature is 80°) in the *absence* of any substantial amounts of acid. However, it has been found that the optimum conversion to aminoguanidine is obtained in media of relatively high acid concentration. McGill,[3] in the examples cited in the patent, gives no yields but claims that for nickel catalyst the use of elevated pressure is essential for increased yields. We have found that the yields for a nickel catalyst are conditioned not solely by pressure but by the type of solvent used.

The molar ratio of hydrogen to hydrogen acceptor obtained in the catalytic hydrogenation of nitroguanidine depends upon the environmental conditions of the solvent. For the first molar proportion of hydrogen the reduction proceeds as follows.

Media	Principal product	Ratio, H_2 : Acceptor
Neutral	Nitrosoguanidine	1:1
Basic	Nitrosoguanidine	1:1
Acid	Aminoguanidine	3:1

In acid media of such a concentration that the molar ratio of nitroguanidine to acid is one or higher the reduction proceeds without the formation of nitrosoguanidine. This is a new observation and is of significant importance for the preparation of aminoguanidine by catalytic hydrogenation. If the molar ratio of acid to nitroguanidine be below one then the distribution of reduction products depends upon the acid concentration. At ratios of acid above one, the hydrazino formation was found to be linear with hydrogen absorption.

Raney nickel catalyst can be used in both neutral and alkaline media. The Adams platinum oxide catalyst can be used in neutral and acid media but is completely poisoned in alkaline media of even low concentrations. The reduction in neutral aqueous media at atmospheric pressure and room temperature gives low yields of aminoguanidine, the principal products appearing to be ammonia and guanidine. At higher hydrogen pressures superior yields of aminoguanidine are obtained with platinum oxide in 15% aqueous acetic acid as compared with Raney nickel in neutral solvents. With increasing temperatures to 125° the yields of aminoguanidine with Raney nickel fall off more rapidly than with platninum oxide as shown by Fig. 1. This also illustrates the effect of type of solvent, especially at 75°.[3]

Experimental

Method.—The Adams platinum oxide and Raney nickel catalysts were prepared in the usual manner. The apparatus employed has been described previously,[1] while the high pressure equipment was of the Adkins type.

The experimental technique and procedures devised for the recovery of the aminoguanidine with minimum loss will be made clear by the description of typical reductions obtained with platinum and nickel catalysts.

Reduction in Acid Media with Platinum Oxide Catalyst.—20.8 g. of nitroguanidine and 1 g. of platinum oxide are suspended in 125 ml. of 15% aqueous acetic acid. The reduction is carried out at 125 atm. and room temperature

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[1] Lieber and Smith, THIS JOURNAL, **57**, 2479 (1935).

[2] Audrieth and Schmidt, University of Illinois, private communication, used Raney nickel in ethyl alcohol and identified the aminoguanidine through the melting point of the benzalazine obtained by hydrolysis of the reduction mixture.

[3] McGill, U. S. Patent 2,033,203, March 10, 1936.

and is allowed to continue until no further hydrogen is absorbed. Slightly more than 3 molar quantities of hydrogen is usually taken up. A small amount of Norit is added and the solution filtered from catalyst into a 500-ml. volumetric flask. After washing the filter paper the volume is adjusted and a 2-ml. portion is titrated with 0.1 *N* potassium iodate solution.[4] From the titer required the titration yield of aminoguanidine was found to be 81.8%. From these data the amount of sulfuric acid required for the formation of aminoguanidinium sulfate is calculated (the addition of too large an excess of sulfuric acid causes the formation of the less easily crystallizable primary salt) and is added after concentrating the solution of the acetate under 10 mm. pressure on a water-bath maintained at 50–60°. The sulfate should be reconcentrated until crystallization of the salt takes place in the warm solution. An equal volume of ethyl alcohol is added and after cooling the white crystals are filtered on a Büchner funnel, pressed dry and washed with a small amount of cold absolute alcohol, dried in a vacuum desiccator and then at 100° for three hours to remove the water of crystallization; yield 16.8 g. or 68.3%; m. p. (Dennis bar) 206°. *Anal.* Calcd. for $(CH_6N_4)_2H_2SO_4$: H_2SO_4, 39.84; N_2H_4, 26.02. Found: H_2SO_4, 39.77; N_2H_4, 26.11, 26.07.

Benzal-aminoguanidine.—$C_6H_5CH{=}NNHC(NH)NH_2$; m. p., found, 177–78°, reported 178°.[5] *Anal.* Calcd. for $C_8H_{10}N_4$: C, 59.26; H, 6.17; N_2H_4, 19.75. Found: C, 59.60; H, 6.79; N_2H_4, 20.16, 20.02.

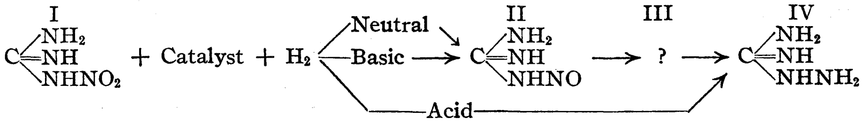
Reduction in Absolute Methyl Alcohol with Raney Nickel.—20.8 g. of nitroguanidine and 10 g. of Raney nickel are suspended in 125 ml. of methyl alcohol and reduced at 125 atm. and room temperature. The reduction mixture is treated with Norit and filtered. The solution is saturated with carbon dioxide for several hours and the voluminous white precipitate which forms is filtered and washed with alcohol and ether; yield 15 g. or 55.2%. *Anal.* Calcd. for $CH_6N_4H_2CO_3$: N_2H_4, 23.53. Found: N_2H_4, 22.78.

Distribution of Reduction Products with Acid Concentration.—Ten grams of nitroguanidine and 0.5 g. of platinum oxide are suspended in 100 ml. of water, 0.1 and 1 *N* hydrochloric acid, respectively, and reduced at 1 atm. until 1 molar proportion of hydrogen has been absorbed (2300 ml.). The reduction mixture was examined for nitrosoguanidine, aminoguanidine and unreacted nitroguanidine. The results obtained were:

Molar ratio HCl/nitroguanidine	0	0.1	1.0
Acid concentration, *N*	0	.1	1
Reduction products:			
% Nitrosoguanidine	59	17.5	Absent
% Aminoguanidine	None	Present	46.2
% Nitroguanidine recovered	None	11.5	61.5

Discussion

The catalytic hydrogenation of nitroguanidine may be summarized as follows



$$\underset{\text{I}}{\text{C}\begin{smallmatrix}\text{NH}_2\\=\text{NH}\\\text{NHNO}_2\end{smallmatrix}} + \text{Catalyst} + \text{H}_2 \xrightarrow[\text{Basic}]{\text{Neutral}} \underset{\text{II}}{\text{C}\begin{smallmatrix}\text{NH}_2\\=\text{NH}\\\text{NHNO}\end{smallmatrix}} \longrightarrow \underset{\text{III}}{?} \longrightarrow \underset{\text{IV}}{\text{C}\begin{smallmatrix}\text{NH}_2\\=\text{NH}\\\text{NHNH}_2\end{smallmatrix}}; \quad \text{I} \xrightarrow{\text{Acid}} \text{IV}$$

In neutral and basic media, nitrosoguanidine is the first product of reduction and may be readily isolated in good yield,[1] while in acid media the reduction proceeds directly to aminoguanidine. Of the substances I and II, nitrosoguanidine is the least stable and it is therefore reasonable that route I to IV by way of II should yield less of IV, than its direct formation in acid media in which II does not appear as an intermediate reduction product. The increased yields of IV with Raney nickel using alcohol as a solvent may be explained on the basis that II is less subject to dearrangement in alcohol than it is in water. The products obtained in the reduction of II with *one* molar proportion of hydrogen (II ⟶ III) have never been studied and we are at present engaged upon that phase of this investigation. Preliminary experiments have yielded small quantities of unknown reduction products of nitroguanidine including a reddish-orange substance having dye and indicator properties.

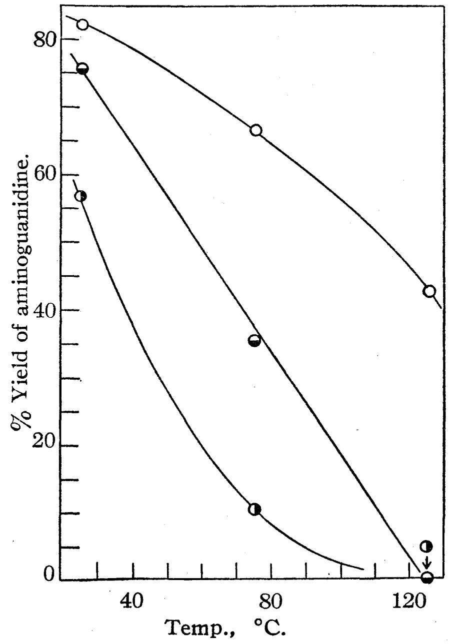


Fig. 1.—Hydrogenation of nitroguanidine at 125 atm.: ○, Pt in 15% acetic acid; ◑, Raney Ni in water; ◒, Raney Ni in CH_3OH.

Summary

The catalytic hydrogenation of nitroguanidine in neutral, acid and basic media to aminoguani-

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[4] Jamieson, "Volumetric Iodate Methods," Chemical Catalog Co., New York, N. Y., 1926, p. 36.

[5] Thiele, *Ann.*, **270**, 35 (1892).

dine has been studied and optimum conditions for the preparation of aminoguanidine with satisfactory yields by that method are described.

BROOKLYN, NEW YORK RECEIVED AUGUST 1, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 147]

The Condensation of Certain Aromatic Methyl Ketones

BY DANIEL B. CLAPP AND AVERY A. MORTON

Bernhauer, Müller and Neiser[1] have studied recently the condensation of aromatic methyl ketones by means of potassium pyrosulfate and sulfuric acid. They were successful by this method, in obtaining 1,3,5-tri-*p*-diphenylbenzene from *p*-acetyldiphenyl, but failed in an attempt to prepare 1,3,5-tri-α-naphthylbenzene and 1,3,5-tri-β-naphthylbenzene from α- and β-acetylnaphthalene, respectively. In the course of other work we have prepared the above three compounds by the method of Reddelien,[2] which involves the use of aniline and aniline hydrochloride. This method is more suitable for the preparation of 1,3,5-tri-*p*-diphenylbenzene than that with potassium pyrosulfate, since in the former case purification involves only a few recrystallizations of the crude product.

Experimental

1,3,5-Tri-*p*-diphenylbenzene.—*p*-Acetyldiphenyl (120 g., 0.61 mole), aniline hydrochloride (6.4 g.), and freshly distilled aniline (86 g.) were heated together at 175° under a carbon dioxide atmosphere for three hours. The aniline was removed by distillation, and the residue was poured, while still hot, into a pan, where it quickly set to a brittle, red-brown resin. On grinding the resin in a mortar with ether, and filtering, 43.5 g. of crude product was obtained. Three recrystallizations from toluene gave 25 g. of pure 1,3,5-tri-*p*-diphenylbenzene; yield 23%; white needles; m. p. 230.5–231°; gives no color with cold concentrated sulfuric acid; almost insoluble in ether, alcohol and acetone; slightly soluble in glacial acetic acid; soluble in benzene and toluene.

Anal. Calcd. for $C_{42}H_{30}$: C, 94.34; H, 5.66; mol. wt., 534. Found: C, 94.50, 94.31; H, 5.71, 5.68; mol. wt. (Rast), 536, 538.

1,3,5 - Tri - α - naphthylbenzene.—α - Acetylnaphthalene[3] (26 g., 0.153 mole), aniline (21.4 g.) and aniline hydrochloride (1.6 g.) were heated for one and one-half hours under carbon dioxide at 175°. The aniline was then removed by distillation under atmospheric pressure, and the remaining tar refluxed with 100 cc. of glacial acetic acid for one hour. On cooling, 4 g. of solid separated, which gave 2.8 g. of pure material after four recrystallizations from a mixture of equal parts of glacial acetic acid and acetic anhydride; yield 18%. In preparations in which impure α-acetylnaphthalene (contaminated with the β-isomer) was used, only tars separated from the acetic acid solution on cooling. However, it was found that an attempt to purify the acetic acid solution by boiling with decolorizing carbon caused the adsorption of the 1,3,5-tri-α-naphthylbenzene on the carbon, from which it could be recovered in a relatively pure condition by extraction with a glacial acetic acid–acetic anhydride mixture. The substance crystallizes in white, flat needles with rounded ends; m. p. 190.5–191°; it gives no color with concentrated sulfuric acid.

Anal. Calcd. for $C_{36}H_{24}$: C, 94.69; H, 5.31; mol. wt., 456. Found: C, 94.61; H, 5.40; mol. wt. (Rast), 466, 450.

1,3,5 - Tri - β - naphthylbenzene.—β - Acetylnaphthalene (Eastman Kodak Co.) (19.2 g., 0.113 mole), aniline (15.6 g.) and aniline hydrochloride (1.2 g.) were heated for four and one-half hours under carbon dioxide at 175°. After the reaction mixture had stood in the ice box for one day, 5.5 g. of crystalline material had separated. Three recrystallizations from toluene gave 3.4 g. of pure substance; yield 20%; white needles; m. p. 234–235°; gives no color with cold concentrated sulfuric acid; less soluble than tri-α-naphthylbenzene in common solvents.

Anal. Calcd. for $C_{36}H_{24}$: C, 94.69; H, 5.31; mol. wt., 456. Found: C, 94.58; H, 5.38; mol. wt. (Rast), 462, 468.

Summary

1,3,5-Tri-*p*-diphenylbenzene, 1,3,5-tri-α-naphthylbenzene and 1,3,5-tri-β-naphthylbenzene have been prepared from *p*-acetyldiphenyl, α-acetylnaphthalene and β-acetylnaphthalene, respectively, by the action of aniline and aniline hydrochloride.

CAMBRIDGE, MASS. RECEIVED AUGUST 8, 1936

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(1) Bernhauer, Müller and Neiser, *J. prakt. Chem.*, **145**, 301 (1936).

(2) Reddelien, *Ann.*, **388**, 194 (1912); *cf.* Vörlander, Fischer and Wille, *Ber.*, **62**, 2836 (1929).

(3) Fröschl, *Monatsh.*, **59**, 275 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HARVARD MEDICAL SCHOOL]

Studies in the Physical Chemistry of Amino Acids, Peptides and Related Substances. VII. A Comparison of the Solubility of Amino Acids, Peptides and their Derivatives

BY THOMAS L. MCMEEKIN, EDWIN J. COHN AND JOHN H. WEARE

I. Introduction

The solubilities of α-amino acids[1] and certain of their derivatives[2] in water and ethyl alcohol have been reported previously. Although the solubility measurements themselves suggest certain generalizations, such as that solubility in water increases with the dipole moment, and diminishes with the length of the paraffin chain, the exceptional behavior of certain molecules has been noted and associated with differences in crystal lattice energy. If the ratio of solubility in two solvents be compared, this disturbing factor is eliminated and more precise rules may be deduced. One of these states that the ratio of the solubility in alcohol to that in water is increased threefold for each CH_2 group in hydrocarbon chains terminating in methyl groups. This rule holds not only for amino acids but for other sufficiently insoluble compounds such as the formyl amino acids, hydantoins and hydantoic acids.[2] In terms of mole fraction of solute in water, N_0, and ethanol, N_A, it may be written

$$\log N_0/N_A = K_2 + 0.49\ (CH_2)_n \qquad (1)$$

where n is the number of CH_2 groups and K_2 a constant depending upon the nature of the polar groups.

A further rule is implicit in the above equation, for it suggests that changes in the logarithm of the solubility ratio are additive not only for non-polar but for polar groups. Thus the change in the ratio of solubility from water to alcohol, tentatively ascribed to dipolar ionization, has been estimated by a comparison of α-amino acids and their hydantoic acids. Subtracting the logarithm of the solubility ratio of the uncharged hydantoic acids ($N\mu_A/N\mu_0$) from that of α-amino acids (N_{zA}/N_{z0}), we obtained

$$\log f_e = \log N_{zA}/N_{z0} - \log N\mu_A/N\mu_0 = 3.85 - 1.12 = 2.73 \qquad (2)$$

This calculation neglects the influence of the amide linkage and also the movement of the proton which results in the dipolar ion structure of amino acids and peptides. The amide group and the peptide linkage, which generally decrease solubility, are further considered in the present investigation, in which the above rules are extended to both solvents and solutes of different dipole moments. On the one hand, we have extended equation (1) to a variety of solvents, including higher alcohols, acetone and a solvent more polar than water, namely, formamide. On the other, we have extended the applicability of equation (2) to amino acids and peptides of long dipole moments.

II. Methods and Materials

The same methods of determining solubility were employed as have been described previously.[1,2] The concentrations of the hydantoic acids were usually determined by direct titration, advantage being taken of their acidic properties. The concentrations of the amino acids and peptides were determined by dry weight, or by Kjeldahl nitrogen analysis. In cases where the solubilities were very small, the concentrations were determined by digestion followed by direct Nesslerization. The solubility of amino acids in formamide was determined by precipitating the amino acids with one volume of alcohol and four volumes of ether. After standing for twenty-four hours, and washing, the insoluble amino acids were weighed. Nitrogen analyses and melting point determinations on the precipitates from formamide demonstrated that they were pure amino acids.

Solvents.—Density or boiling point determinations were always used to verify the purity of the solvents employed. In all cases the appropriate blank determination was made on the solvent. The butanol was redistilled and the fraction used boiled at 117–118°. The formamide prepared by crystallization at $-5°$ was neutral in reaction, free from ammonium salts, melted from -3 to $-1°$ and had a specific conductivity of 4×10^{-5}.

Substances.—The purification of the α-amino acids and the preparation of hydantoic acid, methylhydantoic acid, formylglycine and formylaminobutyric acid have been described previously.[1,2] The same method sufficed for all the hydantoic acids, save those of peptides. In the case of peptide hydantoic acids the reaction was carried out at room temperature for two hours before acidification. For convenience in comparing amino acids with their corresponding uramido acid derivatives, the uramido acid is designated as a hydantoic acid of the amino acid. The more accurate chemical names are given in parentheses in the description of preparations.

β-Alanine Hydantoic Acid (β-Uramidopropionic Acid).—There was a slight variation in the solubility of this compound, indicating decomposition during the solubility determination, or an impure product. The preparation

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(1) Cohn, McMeekin, Edsall and Weare, THIS JOURNAL, **56**, 2270 (1934).

(2) McMeekin, Cohn and Weare, *ibid.*, **57**, 626 (1935).

TABLE I

SOLUBILITY OF AMINO ACIDS AND PEPTIDES IN DIFFERENT SOLVENTS

Solvent	Density of satd. soln., ρ	Soly. moles per liter, C	Log soly. mole fraction, N	Density of satd. soln., ρ	Soly. moles per liter, C	Log soly. mole fraction, N
	Glycine			*dl*-α-Aminocaproic acid		
Water	1.0831	2.886	−1.247	0.9991	0.0866	−2.801
Formamide	1.13306	0.0838	−2.476	1.13089	.0173	−3.161
Methanol	0.78696	.00426	−3.762	0.78730	.00854	−3.458
Ethanol	.7851	.00039	−4.638	.7851	.00104	−4.215
Butanol	.80674	.0000959	−5.055	.80674	.000336	−4.512
Acetone	.78566	.0000305	−5.648	.78566	.0000793	−5.233
	β-Alanine			ϵ-Aminocaproic acid		
Water	1.1581	6.123	−0.816	1.0895	3.848	−0.975
5% Ethanol	1.1509	5.827	− .836	1.0834	3.733	− .983
10% Ethanol	1.1416	5.620	− .848	1.0794	3.625	− .991
20% Ethanol	1.1361	5.180	− .876	1.0662	3.439	− .998
40% Ethanol	1.0520	3.531	−1.011	1.0326	2.852	−1.050
60% Ethanol	0.9596	1.687	−1.283	0.9707	1.909	−1.185
70% Ethanol	.9086	0.814	−1.561			
80% Ethanol	.8638	.242	−2.033	.8742	0.485	−1.719
90% Ethanol	.8271	.0382	−2.759	.8304	.0713	−2.487
95% Ethanol				.80848	.0139	−3.134
Ethanol	.7856	.00189	−3.955	.7851	.00194	−3.947
	Triglycine					
Water	1.0229	0.309	−2.241			
80% Ethanol	0.8554	.000608	−4.636			
90% Ethanol	.8249	.0000381	−5.672			
Ethanol	.7851	.00000106	−7.206			

was repeated a number of times, always giving a product of the same properties, and melting between 168–169°.

Anal. Calcd. for $C_4H_8O_3N_2$: N, 21.2; eq. wt., 132.07. Found: N, 21.1; eq. wt., 132.1.

α-Aminocaproic Hydantoic Acid (α-Uramidocaproic Acid).—The pure substance melted at 169–170°.

Anal. Calcd. for $C_7H_{14}O_3N_2$: N, 16.08; eq. wt., 174.1. Found: N, 16.0; eq. wt., 174.2.

ϵ-Aminocaproic Hydantoic Acid (ϵ-Uramidocaproic Acid).—The pure substance melted at 179–180°.

Anal. Calcd. for $C_7H_{14}O_3N_2$: N, 16.08; eq. wt., 174.1. Found: N, 16.1; eq. wt., 174.6.

δ-Aminovaleric Hydantoic Acid (δ-Uramidovaleric Acid).—The pure substance melted at 179–180°.

Anal. Calcd. for $C_6H_{12}O_3N_2$: N, 17.49; eq. wt., 160.1. Found: N, 17.4; eq. wt., 160.8.

Diglycine Hydantoic Acid (Carbamidoglycylglycine).—The substance melted at 194–195°.

Anal. Calcd. for $C_5H_9O_4N_3$: N, 24.0; eq. wt., 175.09. Found: N, 23.9; eq. wt., 175.0.

Triglycine Hydantoic Acid (Carbamidodiglycylglycine). The substance melted at 204–205°.

Anal. Calcd. for $C_7H_{12}O_5N_4$: N, 24.1; eq. wt., 232.08. Found: N, 24.0; eq. wt., 231.9.

β-Alanine was prepared by a modification of the method of Mulder.[3] β-Bromopropionic acid was allowed to stand for seven days with a large excess of ammonia. The ammonia was removed and the substance purified by crystallization. After three crystallizations from alcohol–water mixtures the pure substance melted at 197–198°. Nitrogen: found, 15.5; calcd., 15.7.

ϵ-Aminocaproic acid was prepared by the method of Wallach.[4] Later samples were obtained from the University of Illinois. After three crystallizations, the substance melted at 201–202°. Nitrogen: found, 10.56; calcd., 10.69.

Triglycine was prepared by the method of E. Fischer.[5] Nitrogen: found, 22.1; calcd., 22.2.

III. Experimental Results

The solubility measurements upon amino acids and peptides are recorded in Table I and those upon their derivatives in Table II. Apparent molal volumes, calculated from the densities of many of the solutions studied, are recorded in Table III. The values previously ascribed to the CH_2, CONH, COOH and NH_2 groups[6] yield satisfactory estimates of the apparent molal volumes, Φ, of the hydantoic acids.

The observed apparent molal volumes of the amino acids and peptides are smaller than those calculated, as a result of the electrostriction of solvent molecules due to the charged groups of dipolar ions.[6]

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(3) Mulder, *Ber.*, **9**, 1903 (1876).

(4) Wallach, *Ann.*, **312**, 171 (1900).

(5) Fischer, *Ber.*, **36**, 2982 (1903).

(6) Cohn, McMeekin, Edsall and Blanchard, THIS JOURNAL, **56**, 784 (1934).

TABLE II

SOLUBILITY OF HYDANTOIC ACIDS AND FORMYL COMPOUNDS IN DIFFERENT SOLVENTS

Solvent	Density of satd. soln., ρ	Soly. moles per liter, C	Log soly. mole fraction, N	Density of satd. soln., ρ	Soly. moles per liter, C	Log soly. mole fraction, N
	Formylglycine			Formyl-α-aminobutyric acid		
Water	1.0570	1.849	−1.432	1.0043	0.256	−2.325
Methanol	0.8280	0.710	−1.533	0.8222	.646	−1.539
Ethanol	.8023	.295	−1.762	.8018	.355	−1.674
Heptanol	.82412	.0347	−2.311	.82473	.0500	−2.152
	Hydantoic acid			α-Aminocaproic hydantoic acid		
Water	1.0112	0.329	−2.217	0.99727	0.00690	−3.903
Formamide	1.15405	.837	−1.462	1.13141	.165	−2.175
Methanol	0.79178	.0797	−2.488	0.79390	.1123	−2.335
80% Ethanol				.85947	.0867	−2.472
90% Ethanol	.82887	.0710	−2.485	.82920	.0803	−2.427
Ethanol	.7865	.0242	−2.851	.78885	.0477	−2.551
Butanol	.80674	.00643	−3.228	.80739	.01786	−2.785
Acetone	.78566	.00248	−3.737	.78588	.00463	−3.466
	α-Alanine hydantoic acid (Methylhydantoic acid)			β-Alanine hydantoic acid		
Water	1.00454	0.193	−2.451	1.00287	0.158	−2.539
Ethanol	0.7877	.0440	−2.590	0.78692	.0170	−3.002
	δ-Aminovaleric hydantoic acid			ε-Aminocaproic hydantoic acid		
Water	0.99763	0.0174	−3.502	0.99725	0.00690	−3.903
80% Ethanol				.85690	.0322	−2.910
90% Ethanol				.82619	.0228	−2.979
Ethanol	.78622	.00762	−3.350	.78639	.00756	−3.354
Butanol				.80643	.00278	−3.593
	Diglycine hydantoic acid			Triglycine hydantoic acid		
Water	1.0050	0.126	−2.638	1.0011	0.0446	−3.092
80% Ethanol	0.85695	.0220	−3.075			
90% Ethanol	.82564	.00851	−3.410			
Ethanol	.7857	.00115	−4.171	0.7851	.000077	−5.345

TABLE III

Solute	CH_2 groups, cc.	CONH groups, cc.	NH_2 + COOH groups, cc.	Apparent molal volume, cc. Calcd.	Obsd.
Hydantoic acid	16.3	20.0	40.7	77.0	77.6
α-Alanine hydantoic acid	32.6	20.0	40.7	93.3	94.2
β-Alanine hydantoic acid	32.6	20.0	40.7	93.3	95.8
α-Aminocaproic hydantoic acid	81.5	20.0	40.7	142.2	146.4
ε-Aminocaproic hydantoic acid	81.5	20.0	40.7	142.2	146.4
Diglycine hydantoic acid	32.6	40.0	40.7	113.3	112.4
Triglycine hydantoic acid	48.9	60.0	40.7	149.6	149.5

The aminocaproic hydantoic acids are so insoluble in water that no great confidence can be placed on the values of Φ estimated for this solvent. The apparent molal volumes of those molecules, sufficiently soluble to be studied in more than one solvent, vary to a small extent in the different solvents employed (Table IV).

Solubility in Alcohol–Water Mixtures.—Our previous communications have been concerned largely with α-amino acids and their derivatives. Two series of molecules, in which the ammonium groups are at a greater distance from the dissociated carboxyl groups, are here reported. In the one only non-polar CH_2 groups intervene between the charged groups, in the other (peptide) series, there is an alternation of CH_2 and CONH groups. Solubility in the first series appears to increase with increase in the dipole moment. Peptides of glycine on the other hand are less soluble the larger the number of glycine residues in the chain. This would appear to depend, at least in part, on close packing in the crystal lattice since peptides containing side chains of unequal lengths are often more soluble than those of glycine.[7] The hydantoic acids of both series

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(7) Fischer, "Untersuchungen über Aminosäuren, Polypeptide und Proteine," Julius Springer, Berlin, 1906, Vol. I, p. 333.

have been prepared and are far less soluble in water than the dipolar ions from which they were derived.

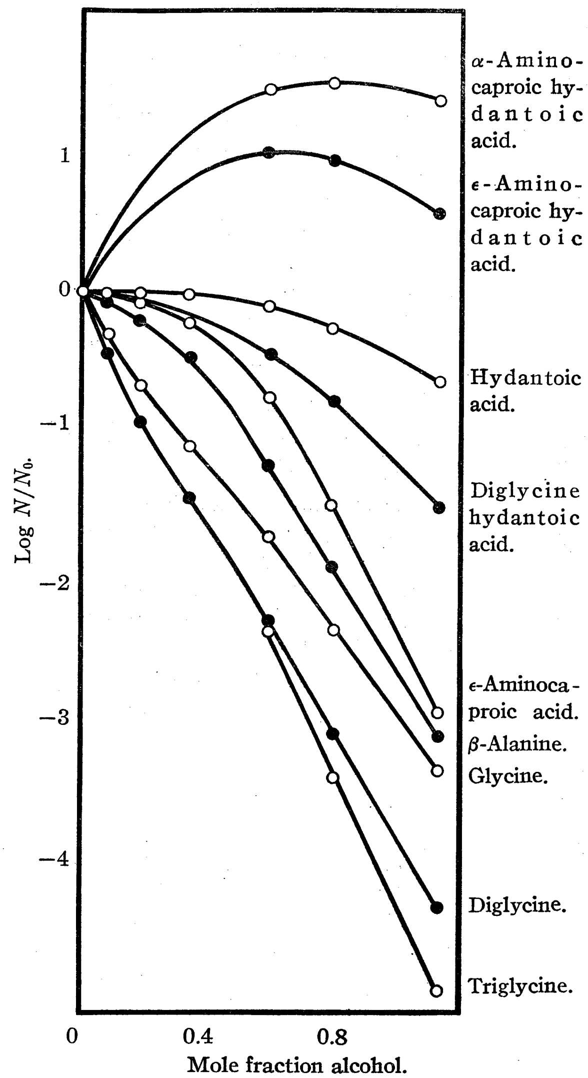

Fig. 1.

The ratio of the solubility, N, of these three classes of molecules in alcohol–water mixtures, to that in water, N_0, is plotted in Fig. 1 against mole fraction alcohol. The shapes of the glycine, diglycine and triglycine curves are very similar. All have steep segments at low mole fractions of alcohol, with comparable points of inflection in the range in which the solvent molecules are approximately equal in number. In systems containing larger amounts of ethanol the logarithm of the solubility may as a first approximation be considered to vary inversely as the mole fraction of alcohol. Straight lines have been drawn through these segments of the curves of glycine and its peptides.

TABLE IV

APPARENT MOLAL VOLUMES OF HYDANTOIC ACIDS AT 25°

Solvent	Concentration, moles per liter	Molal volume, cc.
	Hydantoic acid	
Formamide	0.837	79.8
Water	.250	77.6
Methanol	.0797	68.2
80% Ethanol	.1256	75.7
90% Ethanol	.071	76.1
Ethanol	.0242	(63.2)[a]
	α-Aminocaproic hydantoic acid	
Formamide	0.165	150.6
Water	.0069	(146.4)[a]
Methanol	.1123	139.2
80% Ethanol	.0867	144.8
90% Ethanol	.0803	146.7
Ethanol	.0477	138.5

[a] Concentration too low for accurate measurements of molal volume.

The curves describing the behavior of hydantoic acids in alcohol–water mixtures also form a family though their shape is quite different from that of the amino acids and peptides from which they were derived. The additional peptide linkage in the hydantoic acid of diglycine, as compared with hydantoic acid, is reflected in decreased solubility; and the additional CH_2 groups of α-aminocaproic hydantoic acid in increased solubility in systems rich in alcohol. The curve of the latter substance is very similar to that of formylleucine or benzamide. The isomer, ε-aminocaproic hydantoic acid, in which the CH_2 groups all lie between polar groups, behaves far more like formyl-α-aminobutyric acid, that is to say, like a molecule with two less CH_2 groups. Its solubility in 80% ethanol is approximately tenfold that in water and threefold that in ethanol, a type of behavior characteristic of a class of proteins, the prolamines.

The measurements on β-alanine and ε-aminocaproic acid cannot be considered as accurate as those upon the other substances studied, in part because their large dipole moments render difficult their purification, in part because the great solubility which results from these moments renders difficult accurate solubility measurements.

The curves for β-alanine and ε-aminocaproic acid clearly belong to a third family. In systems rich in alcohol these curves approach the straight lines characteristic of glycine and its peptides. Small amounts of ethanol, however, have but very slight precipitating action on these amino acids of long dipole moment, presumably because of their very great solubility and, therefore, the very high dielectric constants of their saturated solutions in water. Assuming that the dielectric constant increments of these two substances remain the same in concentrated as in dilute solution,[8] the dielectric constants of a saturated aqueous β-alanine solution would be 300 and of ϵ-aminocaproic acid 370, or more than four times that of water. A comparable calculation yields an estimate of 72 for the dielectric constant of 80% ethanol saturated with ϵ-aminocaproic acid. Only at alcohol concentrations higher than these do the compositions of the solutions containing these amino acids approach those of the pure solvents. The shapes of these curves in solutions containing small amounts of alcohol appear to depend in large part upon the high dielectric constants of the solutions.

Solubility in Pure Solvents.—The conditions that obtain in pure solvents are simpler than those in alcohol–water mixtures. Water is by far the best solvent for the amino acids. Their solubility in alcohols is smaller the longer the hydrocarbon chain of the latter, but is smaller in acetone than in butanol, although the former has a higher dielectric constant. The solubilities of the amino acids are also smaller in formamide than in water, despite its higher dielectric constant.

Certain of the less polar derivatives of the amino acids are more soluble in other solvents than in water. Thus hydantoic acid is more soluble in formamide than in water, as is the hydantoic acid of α-aminocaproic acid which is moreover more soluble in all of the alcohols than in water. The influence of the hydrocarbon chain of the solute in increasing solubility in a solvent with a hydrocarbon chain of somewhat the same length is also reflected by the measurements upon formyl α-aminobutyric acid.

Influence of the Hydrocarbon Chain.—The influence of the hydrocarbon chain is more readily examined, as we have previously shown[1,2] if we consider the solubility ratio. Values of log N/N_0 are plotted against the number of CH_2 groups, in the molecule $n\mathrm{CH_2}$ in Fig. 2. The values for glycine, alanine, diglycine and hydantoic acid are from Studies II and III of this series.[1,2] Straight lines are drawn connecting the experimental values even when only two members of the series have been studied, since no exception has been found to the rule that provided CH_2 groups are in hydrocarbon chains terminating in methyl groups, the increase in log N/N_0 for each additional CH_2 group is, within the limits of error, identical, whether we are comparing amino acids or their derivatives (Table V). This influence of the CH_2 group is smaller for formamide than for methanol, and for methanol than for ethanol. There is no significant difference between the previously published coefficient for CH_2 groups between water and ethanol, 0.49,[1] and that for acetone. The coefficient for the higher alcohols is slightly greater. The value of 0.53 appears to be reached with butanol, and is not increased by further increase in the CH_2 groups of the solvent. It is probable that still greater influences of the CH_2 groups of the solvent might, however, be observed were we to study solutes of longer hydrocarbon chains.

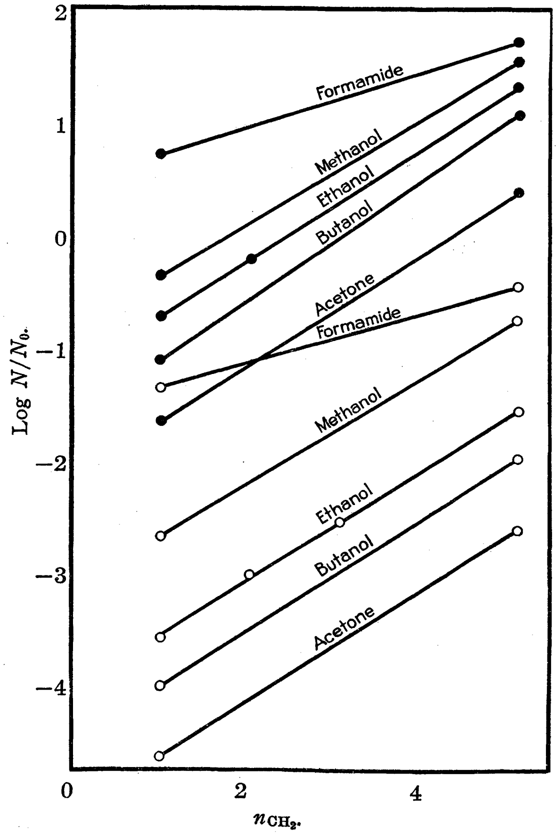

Fig. 2.—Solubility ratios of amino acids ○, and hydantoic acids prepared from them ●, in different solvents.

The influence of the CH_2 groups would appear to increase inversely as the dielectric constant of the solvent (Table IX), were we considering only the alcohols and acetone. Formamide, however,

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(8) Wyman and McMeekin, THIS JOURNAL, **55**, 908 (1933).

TABLE V

INFLUENCE OF THE CH_2 GROUPS OF THE SOLUTE UPON SOLUBILITY RATIO IN DIFFERENT SOLVENTS

Solute	Number of CH_2 groups, n_{CH_2}	Log. of soly. ratio, $\log N/N_0$	$\frac{\Delta \log N/N_0}{\Delta n_{CH_2}}$
Formamide			
Glycine	1	−1.229	
α-Aminocaproic acid	5	−0.360	0.217
Hydantoic acid	1	+ .755	
α-Aminocaproic hydantoic acid	5	+1.728	.243
Methanol			
Glycine	1	−2.515	
α-Aminocaproic acid	5	−0.657	0.464
Formylglycine	1	− .101	
Formyl α-aminobutyric acid	3	+ .786	.444
Hydantoic acid	1	− .271	
α-Aminocaproic hydantoic acid	5	+1.568	.460
Ethanol			
Formylglycine	1	−0.330	
Formyl α-aminobutyric acid	3	+ .651	0.491
Hydantoic acid	1	− .630	.491
α-Alanine hydantoic acid	2	− .139	.496
α-Aminocaproic hydantoic acid	5	+1.352	.497
Acetone			
Glycine	1	−4.401	
α-Aminocaproic acid	5	−2.432	0.492
Hydantoic acid	1	−1.520	
α-Aminocaproic hydantoic acid	5	+0.437	.489
Butanol			
Glycine	1	−3.808	
α-Aminocaproic acid	5	−1.711	0.524
Hydantoic acid	1	−1.011	
α-Aminocaproic hydantoic acid	5	+1.118	.532
Heptanol			
Formylglycine	1	−0.880	
Formyl α-aminobutyric acid	3	+0.173	0.527

has a higher dielectric constant than water, and we must therefore conclude that its behavior in these studies is determined, at least in part, by factors other than the dielectric constant.

Influence of Dipolar Ion Structure.—The same solubility ratios may be employed in estimating the influence of dipolar ion structure, by means of equation (2). This calculation is carried out in Table VI, which in conjunction with Table V demonstrates the additivity of the influence of the paraffin chain and of dipolar ionization. The value of 2.73, derived from the previous comparison[1] of all α-amino acids (corrected for the influence of the CH_2 group) with hydantoic and methyl hydantoic acid, holds also for the measurements in Table VI.

The comparison of the peptides of glycine with their hydantoic acids reveals no difference in the free energy change from water to ethanol with change in the dipole moment. This is contrary to what was expected on the basis of theoretical calculations, which suggested that this quantity would increase with increase in the dipole moment[1] (p. 2275).[9,10] The influence of dipolar ionization does not appear to be greater in the case of triglycine than of diglycine, or of diglycine than of glycine.

Influence of the Amide Group.—Hydantoic acids terminate in an amide group not present in the amino acids or peptides from which they are derived. In this, as in previous calculations, we have considered that the terminal $CONH_2$ group has but very small influence. This notion was deduced from a comparison of the solubility in water and ethanol of glycine with glutamine and asparagine. The measurements upon asparagine

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(9) Scatchard and Kirkwood, *Physik. Z.*, **33**, 297 (1932).

(10) Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

TABLE VI

INFLUENCE OF DIPOLAR IONIZATION UPON THE SOLUBILITY RATIO IN DIFFERENT SOLVENTS

Substance	Log of soly. ratio log N/N_0	Influence of dipolar ionization
Formamide		
Glycine	−1.229	
Hydantoic acid	+0.755	−1.98
α-Aminocaproic acid	− .360	
α-Aminocaproic hydantoic acid	+1.728	−2.09
Methanol		
Glycine	−2.515	
Hydantoic acid	−0.271	−2.24
α-Aminocaproic acid	− .657	
α-Aminocaproic hydantoic acid	+1.568	−2.23
Ethanol		
Glycine	−3.391	
Hydantoic acid	−0.630	−2.76
α-Alanine	−2.856	
α-Alanine hydantoic acid	−0.139	−2.72
β-Alanine	−3.139	
β-Alanine hydantoic acid	−0.463	−2.68
α-Aminocaproic acid	−1.414	
α-Aminocaproic hydantoic acid	+1.352	−2.77
Diglycine	−4.367	
Diglycine hydantoic acid	−1.533	−2.83
Triglycine	−4.965	
Triglycine hydantoic acid	−2.253	−2.71
Butanol		
Glycine	−3.808	
Hydantoic acid	−1.011	−2.80
α-Aminocaproic acid	−1.711	
α-Aminocaproic hydantoic acid	+1.118	−2.83
Acetone		
Glycine	−4.401	
Hydantoic acid	−1.520	−2.88
α-Aminocaproic acid	−2.432	
α-Aminocaproic hydantoic acid	+0.437	−2.87

TABLE VII

SOLUBILITY RATIOS OF DIPOLAR IONS IN WATER AND ETHANOL

	Log N_A/N_0	Δ Log N_A/N_0
Glycine	−3.391	
Asparagine	−3.402	−0.011
Glutamine	−3.466	− .064
Diglycine	−4.367	− .976
Triglycine	−4.965	−1.574

are perhaps the more accurate and the difference between its solubility ratio and that of glycine must be considered within the errors of experiment. The influence of the amide group was, therefore, considered negligible.

If we assume the influence of dipolar ion structure on the solubility ratio to be that estimated in Table VI, we may subdivide the influence of the amide group into two parts. Thus, subtracting 2.73 from the value for glycine should yield −0.66 for its hypothetical uncharged isomer; a value not very different from that determined for glycol amide, which has the same composition though a different structure. The value for formylglycine is −0.33. The difference +0.33 might be considered to yield the effect of the carbonyl group. Comparable calculations could be made by comparing the other formyl compounds that have been studied with the corresponding amino acids.

Formylglycine and hydantoic acid differ by an NH group. The change in their solubility ratios is given below:

	Log N_A/N_0	Δ Log N_A/N_0
Formylglycine	−0.33	
Hydantoic acid	− .63	−0.30

According to this calculation the influences of the CO and NH groups are opposite in sign, as might have been expected from the small apparent influence of terminal amide groups on the solubility ratios reported.

Influence of the Peptide Linkage.—Quite different is the influence of the peptide linkage. Glycylglycine and asparagine are isomers. The comparison of glycine and its peptides with their hydantoic acids (Table VI) indicates that variation in the dipole moment of the molecule has no measurable influence on the change in free energy in passing from water to ethanol. The great difference in Δ log N_A/N_0 between glycine and its peptides (Table VII) would therefore appear to be due to the CONH group between polar groups. The negative value of log N_A/N_0 for diglycine is larger than that for glycine by −0.976. The comparable value for triglycine, −1.574, is only −0.598 larger. The smaller influence of the second peptide linkage presumably is related to the greater distance of CH_2 and CONH groups in the larger molecule from the polar terminal groups.

Influence of CH_2 Groups between Polar Groups.—That CH_2 groups situated between polar groups have but slight influence on the solubility ratio has previously been demonstrated by comparison of aspartic with glutamic acid, and of asparagine with glutamine. Since there is no appreciable change in the solubility ratio, when instead of one CH_2 group two are present between polar groups, we assumed that the first also behaved as though it was not subject to the rule valid for CH_2 groups in the paraffin chain. With increase in the number of groups between polar groups intermediate behavior should obtain. This phenomenon has been investigated by studying the hydantoic acids of α, β, δ, and ε-amino acids. It will be observed that the larger the number of CH_2 groups between polar groups the greater the influence of each upon the solubility ratio (Table VIII). The coefficient per CH_2 group between the hydantoic acid of an α- and β-amino acid is but 0.167, whereas that between comparable δ- and ε-compounds is more than twice as great, namely 0.397, approaching that characteristic of the paraffin chain.

TABLE VIII

INFLUENCE OF THE POSITION OF GROUPS UPON THE SOLUBILITY RATIO IN ETHANOL AND WATER

	Number of CH_2 groups, n	Log of soly. ratio, $\log N/N_0$	$\frac{\Delta \log N/N_0}{\Delta n_{CH_2}}$
Hydantoic acid	1	−0.630	0.167
β-Alanine hydantoic acid	2	− .463	.308
δ-Aminovaleric hydantoic acid	4	+ .152	.397
ε-Aminocaproic hydantoic acid	5	+ .549	.495
α-Aminocaproic hydantoic acid	5	+1.352	

Comparison of the solubility ratio of ε-aminocaproic acid in water and ethanol with that of its hydantoic acid constitutes the one exception noted thus far to the rule deduced in Table VI, and suggests that CH_2 groups between the charged groups of a dipolar ion have a smaller influence than those between other polar groups at this distance from each other. This is not unexpected since the moment of the former is more than ten times that of the widely separated polar groups of this hydantoic acid.

	$\log N_A/N_0$	$\Delta \log N_A/N_0$
ε-Aminocaproic acid	−2.972	
ε-Aminocaproic hydantoic acid	+0.549	−3.521

Discussion.—The influence of the polar and non-polar groups of molecules upon solubility has been stressed previously.[11–13] "A comparison of various insoluble substances has proved that the spreading tendency depends upon the presence of certain active groups of radicles in the organic molecule, these being the groups which tend to increase the solubility of organic substances in water. For example, pentane, C_5H_{12}, is practically insoluble in water, but amyl alcohol, $C_5H_{11}OH$, is relatively soluble. Thus the hydroxyl groups in organic molecules exert strong attractive forces on the hydroxyl groups in the water molecules and these manifest themselves by an increase in solubility. Similarly the carboxyl group, COOH, tends to make the lower fatty acids much more soluble in water than the corresponding hydrocarbons"[13] (p. 161).

"Traube found that with molecules of aliphatic compounds having different lengths of hydrocarbon chains" the decrease in the surface tension of the pure liquid, divided by the osmotic pressure of the dissolved substance in the underlying solution, "for dilute solutions increases about threefold for each CH_2"[13] (p. 164). Our investigations confirm the applicability of Traube's rule[14] to the ratio of solubility in water and organic solvents.

The accuracy with which the above rule appears to hold even when solubility is not very low was, however, not foreseen. Thus in all the solvents studied there was no appreciable difference between the coefficient for the CH_2 group calculated from glycine and α-aminocaproic acid and from the far less soluble hydantoic acids (Table V), despite the high solubility of glycine and the high dielectric constant of its aqueous solution. This result may mean that the logarithm of the activity coefficient of glycine in saturated aqueous solution is not very large. Scatchard[15] estimates this quantity to be about −0.15 from freezing point determinations.

The CH_2 rule appears to hold for monoamino monocarboxylic α-amino acids as well as for their derivatives, but not for dicarboxylic acids, where the hydrocarbon chain terminates in a carboxyl group. The study of the hydantoic acids of β-, δ- and ε-amino acids suggests that interaction between the carboxyl, amide and CH_2 groups extends to the neighboring CH_2 groups, but not very much farther. The term interaction is used since the present studies yield no evidence as to whether polar groups are masking the effect of non-polar groups, or non-polar those of polar groups.

This interaction appears to extend to a greater distance, in the case of CH_2 groups between the charged groups of a dipolar ion. None the less, the fields of force set up must be restricted largely to the intervening atoms and cannot extend very far beyond them. Otherwise, the simple CH_2 rule would not apply to α-amino acids, for the co-

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(11) Freundlich, *Ergebnisse exakt. Naturwissenschaften*, **12**, 82 (1933).

(12) Hildebrand, "Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, N. Y., 2 ed., 1936.

(13) Langmuir, *Chem. Rev.*, **13**, 147 (1933).

(14) Traube, *Ann.*, **265**, 27 (1891).

(15) Scatchard and Prentiss, THIS JOURNAL, **56**, 1486 (1934).

efficient relating glycine and alanine would be different from that relating norvaline and norleucine.

Finally the results reported as solubility ratios may be transformed into calories and compared with the studies of Butler and his co-workers,[16] who have considered the free energy change, ΔF, from the gaseous state to aqueous solution. Our results recalculated (Table IX) suggest that the free energy increment for the CH_2 group in aqueous solutions referred to alcohols, ranges from 600 to 700 calories. Butler estimates the free energy in aqueous solution referred to the gaseous state as 200 calories per CH_2 group. Butler further estimates a change in free energy of about 6000 calories if NH_2 be substituted and 7400 calories if COOH be substituted in the paraffin chain.

The free energy in aqueous solution referred to alcohols due to dipolar ionization we estimate at -3000 to -4000 calories. This estimate is based on the comparison of the amino acids and the hydantoic acids and includes, as has previously been pointed out, effects due to the amide group and to the movement of the proton from the carboxyl to the ammonium group.

TABLE IX

Solvent	Dielectric constant[a]	Influence of CH_2 groups $\Delta \log N/N_0$	ΔF, cal.	Influence of dipolar ionization $\Delta \log N/N_0$	ΔF, cal.
Formamide	>84	+0.23	314	−2.03	−2768
Methanol	32.71	+ .44	600	−2.24	−3054
Ethanol	24.28	+ .49	668	−2.73	−3722
Acetone	20.83	+ .49	668	−2.87	−3913
Butanol	17.51	+ .53	723	−2.82	−3845
Heptanol	9.33	+ .53	723	....	....

[a] We are indebted to Dr. Wyman for measuring the dielectric constants of the solvents employed. The value for formamide is taken from "Int. Critical Tables," Vol. VI, p. 83.

These quantities define all the solubility measurements reported. They reveal no exceptional behavior such as was expected, due either to interaction between dipolar ions in concentrated aqueous solution, or to the changing ratio of dipolar ions and uncharged molecules in solvents of low dielectric constant. Moreover they do not reveal change in $\Delta \log N/N_0$ or of ΔF with change in the reciprocal of the dielectric constant, such as would be expected. The relations that obtain, however, appear to be far simpler than could have been predicted.

Summary

1. The solubilities of amino acids and peptides of different dipole moments have been studied in various solvents at 25°.

2. The logarithm of the ratio of solubility in any solvent, N, to that in water, N_0, is increased by a constant amount for each CH_2 group in hydrocarbon chains terminating in methyl groups. This amount is 0.53 for butanol and heptanol, 0.49 for acetone and ethanol, 0.44 for methanol and 0.23 for the most polar solvent studied, formamide.

3. When only one or two CH_2 groups are situated between polar groups the solubility ratio is but little affected. The larger the number of CH_2 groups situated between polar groups the more nearly the solubility is influenced, as in hydrocarbon chains ending in methyl groups.

4. CH_2 groups situated between the charges of a dipolar ion influence the solubility ratio far less than those between other polar groups. The electric moments of dipolar ions are generally more than fivefold as great as the moments of the carboxyl, hydroxyl, amine or amide groups.

5. Solutions of dipolar ions such as β-alanine and ϵ-aminocaproic acid are so concentrated and have such high dielectric constants that conditions existing in them must be considered different from those in the pure solvent.

6. The peptides of glycine are all less soluble than glycine and so are other α-amino acids and the hydantoic acids derived from them. Comparison of the solubility ratios of these dipolar ions with their hydantoic acids yields, as estimates of the influence of dipolar ionization upon the logarithm of the solubility ratio, -2.03 from water to formamide, -2.24 to methanol, -2.73 to ethanol, -2.82 to butanol and -2.87 to acetone.

7. The comparison of the peptides of glycine with their hydantoic acids has revealed no change in solubility ratio with change in the dipole moment of the peptide.

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[16] Butler, Ramchandani and Thomson, *J. Chem. Soc.*, 280 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Acid Catalysis in Sulfuric Acid–Acetic Acid Solutions. The Rate of Bromination of *m*-Nitroacetophenone[1]

BY MARTIN A. PAUL AND LOUIS P. HAMMETT

Previous papers have given applications of indicator measurements to the study of acid catalysis in solutions containing water.[2-4] Over wide ranges of composition, direct proportionality was found between the acidity of the medium as measured by simple basic indicators[2] and the speeds of certain reactions. These results led us to make a similar investigation in a solvent, glacial acetic acid, which is of great utility as a medium for organic reactions and in which the pioneer work of Hall and Conant[5] on super-acid solutions was carried out.

The reaction studied was the bromination of *m*-nitroacetophenone, which proceeds at a rate suitable for measurement in dilute solutions of sulfuric acid in acetic acid. It is a case of the frequently studied acid-catalyzed ketone halogenation.[6] It is characteristic of this type of reaction that the rate is independent of the halogen concentration, but is proportional to the concentration of ketone. The reaction in dilute aqueous solutions exhibits the phenomena of general acid catalysis in the Brönsted sense and is also subject to a pronounced catalysis by bases.

With this ketone and under the conditions of low ketone concentration necessary to keep the rate within reasonable limits at the high acidities encountered, the method used by previous investigators,[6] namely, dilution of a sample of the reaction mixture with water containing a small excess of potassium iodide and some sodium acetate and titration with thiosulfate of the liberated iodine, was entirely unsatisfactory. The difficulty arises from the fact that the monobrominated acetophenone derivative halogenates further in the diluted aqueous solution at a rate which seriously affects the titers obtained. The same phenomenon exists with ω-bromoacetophenone as with its nitro derivative, but the magnitude of the effect is smaller. In the original sulfuric–acetic acid mixtures, the rate of bromination of these brominated ketones is small relative to that of the unbrominated compounds while the latter use up iodine at a negligibly small speed in the solutions diluted with water. Apparently bromine substitution in the methyl group of these compounds shifts the catalytic minimum (the acid concentration separating the region of predominantly acid catalysis from that in which basic catalysis is most important) to quite high acidities, especially for the ketone brominating more slowly. This is in accord with the trend noted by Watson and Yates[6l] for the brominated acetones. An aqueous acetate buffer acts therefore as a powerful basic catalyst for the halogenation of ω-bromo-*m*-nitroacetophenone. Applied to Watson's data[6m,n] on halogenation in an acetic acid, water, hydrochloric acid mixture, our observations indicate that, for the ketone *m*-nitroacetophenone, toward the end of a run the rate of disappearance of iodine from the solutions diluted for titration may have been nearly as great as the rate of disappearance of bromine from the undiluted reaction mixture. Unless only initial titers were used in computing rate constants, his value for this ketone may therefore be high.

A colorimetric method of the sort used by Bartlett and Vincent[7] in the study of the iodination of menthone proved entirely satisfactory and was therefore used throughout this work.

Experimental

Apparatus.—The colorimeter was the Bausch and Lomb instrument used in previous work.[8] The mirror was replaced by an illuminator similar to that described by Beaver.[9] The scales were calibrated and had no error exceeding ±0.1 mm. For indicator measurements in acetic acid solutions, a closed cell with plane parallel ends, described by Hammett and Deyrup,[2] was employed.

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[1] From part of a thesis submitted by Martin A. Paul in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

[2] Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[3] Hammett and Paul, *ibid.*, **56**, 830 (1934).

[4] Hammett, *Chem. Rev.*, **16**, 67 (1935).

[5] Hall and Conant, THIS JOURNAL, **49**, 3047 (1927); Conant and Hall, *ibid.*, **49**, 3062 (1927).

[6] (a) Lapworth, *J. Chem. Soc.*, **85**, 30 (1904); (b) Dawson with Leslie, *ibid.*, **95**, 1860 (1909); (c) with Wheatley, **97**, 2048 (1910); (d) with Ark, **99**, 1740 (1911); (e) with Carter, 2282 (1926); (f) with Dean, 2872 (1926); (g) with Hoskins, 3166 (1926); 213, 458, 756, 1146, 1290 (1927); (h) *Trans. Faraday Soc.*, **24**, 640 (1928); (i) Hughes and Watson, *J. Chem. Soc.*, 1945 (1929); (j) Watson, *Chem. Rev.*, **7**, 173 (1930); (k) Hughes, Watson and Yates, *J. Chem. Soc.*, 3318 (1931); (l) Watson and Yates, *ibid.*, 1207 (1932); (m) Nathan and Watson, *ibid.*, 217 (1933); (n) Evans, Morgan and Watson, *ibid.*, 1167 (1935); (o) Morgan and Watson, *ibid.*, 1173 (1935).

[7] Bartlett and Vincent, THIS JOURNAL, **55**, 4992 (1933).

[8] Hammett and Paul, *ibid.*, **56**, 827 (1934).

[9] Beaver, *J. Opt. Soc. Am.*, **18**, 41 (1929).

For the rate measurements, one cup of the colorimeter was fitted with a jacket having a bottom made of optically clear glass (Fig. 1). Water from a thermostat was circulated through it by means of an air-lift pump and, with suitable insulation, the contents of the cup could be kept at 25.00 ± 0.01°. This precision was quite adequate for our purpose, estimating the temperature coefficient of the bromination of acetophenone derivatives in solution to be about 20% per degree.[6n]

To reduce evaporation of bromine, each cup had a closely fitting glass cap with a hole bored through of diameter slightly larger than that of the plungers. Loss of bromine from the cups so equipped was less than 2% per hour, negligible since no runs lasted longer than an hour.

Method: Indicator Measurements.—Indicator measurements were made essentially according to the method of Hammett and Deyrup.[2] The reference solution was acetic acid containing enough sodium acetate (about 0.5 molar) to completely convert the bases to their colored uncharged forms. Absorption of water from the atmosphere by this solution during a set of observations was found to be too small to affect readings.

Method: Rate Measurements.—As a reproducible color standard for measuring the concentration of bromine in acetic acid solutions, bromine water prepared freshly as needed from a standard potassium bromate solution by addition of potassium bromide (100% excess) and sulfuric acid (final concentration about 0.5 molar) was adopted. The specific color intensities of bromine in the two media are different due, no doubt, to a shift in the absorption spectrum, but the yellow colors nevertheless may be matched without difficulty.[10] Accordingly, solutions of bromine in acetic acid were made up and their concentrations determined by titration. The apparent concentrations of 0.00500 and 0.00250 molar bromine water were determined against each of these by colorimetric comparison. These experiments tested the constancy of the concentration–color intensity ratio (Beer's law) for bromine dissolved in acetic acid. For six concentrations of bromine covering the range 0.006–0.001 molar, the concentration c_S of bromine in glacial acetic acid colorimetrically equivalent to 0.00500 molar bromine water was 0.00381 ± 0.00004 molar and to 0.00250 molar bromine water, 0.00191 ± 0.00003 molar. Deviation from Beer's law in the range examined is thus within the precision of matching (2–5%). The 0.00500 molar bromine water was found to be equivalent to 0.00415 molar bromine in the mixed solvent acetic acid–water in the mole ratio 1–1.

The precedure was to make up a solution of ketone, sulfuric acid and acetic acid by weight in a 25-ml. glass-stoppered volumetric flask and to bring to mark with acetic acid at 25°. The flask was then kept in the thermostat for at least fifteen minutes while water was circulated through the jacket of the reaction cup. Standard bromine water was prepared and introduced into the other cup of the colorimeter. A drop of bromine was then added to the flask, a stop watch (calibrated by telephone time) started, the solution thoroughly shaken and a sample poured into the jacketed cup. The latter was immediately racked to a convenient height, r, and left there during the run. Readings of the length, h, of the standard solution required to balance colorimetrically the "unknown" were taken at times, t, read to the nearest one-tenth minute. The first reading could be made within one and one-half to two minutes after addition of the bromine, while mixing and transfer of the solution took about one-half minute. The initial ketone concentration, c^0_K, was between 0.005 and 0.05 molar and was always so chosen as to have the run last between twenty and sixty minutes.

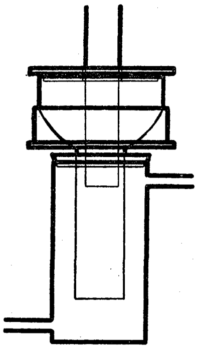

Fig. 1.—Diagram of colorimetric reaction cup.

Rate Calculations.—Previous investigators have used ketone concentrations so much larger than the bromine concentration that the reaction rate, which is independent of the latter concentration, is essentially constant throughout the run. This procedure would give rates at the higher acidities much too large to be measured, but its abandonment requires some variations in the usual calculation of the rate constant. The fundamental equation is

$$-\frac{dc_K}{dt} = -\frac{dc_{Br_2}}{dt} = kc_K \qquad (1)$$

where c_K is ketone concentration and c_{Br_2} is bromine concentration. Using superscript zero to denote initial concentrations at time zero we have

$$-dc_{Br_2}/dt = kc_K = k\ \{c^0_K - (c^0_{Br_2} - c_{Br_2})\} \qquad (2)$$

The integrated equation is

$$\ln\left(1 - \frac{c^0_{Br_2} - c_{Br_2}}{c^0_K}\right) = -kt \qquad (3)$$

Experimentally the bromine concentration is given by

$$c_{Br_2} = c_S(h/r) \qquad (4)$$

where h and r are the previously defined colorimeter readings. Substituting in (3) we obtain

$$\ln\ \{1 - (h_0 - h)\ (c_S/rc^0_K)\} = -kt \qquad (5)$$

For the initial readings ($h_0 - h$ small) this reduces to

$$(h_0 - h)\ (c_S/rc^0_K) = kt \qquad (6)$$

In calculating the constant for a run, equation 6 was applied to the initial experimental points and the value of h_0 thus obtained was used in equation 5 to obtain the value of k, all experimental points being used. Both calculations were made by the method of least squares. In no case did the mean error in k from a single run exceed 5%. Figure 2, in which h and the quantity $c \equiv -\log\ \{1 - c_S\ (h_0 - h)/rc^0_K\}$ are plotted against t, is a graphical representation of the re-

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(10) Flexser, Hammett and Dingwall, THIS JOURNAL, **57**, 2111 (1935).

sults of a typical experiment. Conformity of the data with equation (5) for different initial ketone and bromine concentrations establishes the validity of the assumptions that the rate of reaction is independent of the latter and proportional to the former. That ω-bromo-*m*-nitroacetophenone is the product was proven by obtaining this compound on dilution with water when a run was tried using a relatively high concentration of *m*-nitroacetophenone. In the range of acidity studied, the rate of bromination of this product is negligibly small at the concentrations at which it was present, but at higher acidities, it is great enough to make independent measurements of the rate for the unbrominated ketone impossible. Lower acidities were not tried for fear of auto-catalysis by hydrobromic acid.

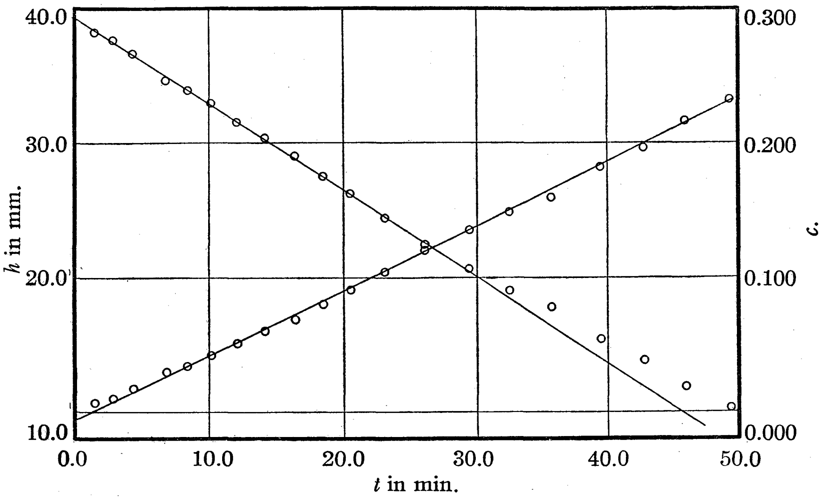

Fig. 2.—Graphical representation of typical bromination experiment: $c°_K$ = 0.01015 mole/liter; $c_{H_2SO_4}$ = 0.0609 mole/liter.

Materials.—Acetic acid was prepared from commercial 99.5% reagent by the method of Orton and Bradfield.[11] Samples reacting with bromine were rejected. The water content, estimated by the freezing-point method, was between 0.3 and 0.1%. No extraordinary precautions other than rapid manipulation were taken to keep out water from the atmosphere during experiments. No effect on the measurements from this source could be detected. In fact, many of the runs were made with just sufficient acetic anhydride (prepared by fractional distillations of the commercial C. P. reagent) added to react with the quantity of water present. Orton and Jones[12] have shown that this reaction is very rapid in acetic acid in the presence of a small concentration of sulfuric acid. No significant difference could be detected between rates of bromination in this medium and in 99.8% glacial acetic acid. Of course, measurements were impossible on very humid days.

Sulfuric acid was prepared by distillation of 50% fuming acid into C. P. concentrated reagent and dilution with more of the latter to maximum freezing point.

m-Nitroacetophenone was recrystallized to constant melting point, 77.3° from ethyl alcohol and water.

Bromine was of analytical reagent grade.

Potassium bromate was recrystallized twice from water and dried at 180°. Its equivalent weight was within 0.1% of the theoretical value when checked with that of potassium iodate purified in the same way. The latter was used as primary standard for calibration of thiosulfate solutions. Potassium bromide was recrystallized from water and was bromate free.

Results

Table I contains the results of indicator measurements in sulfuric acid–acetic acid solutions. *M* is molality of sulfuric acid, c_{BH^+} and c_B are concentrations of indicator acid and base, and H_0 is the acidity function. The pK' of −0.17 for *o*-nitroaniline is from previous work.[8] The difference in basic strength of the two indicators employed is the same within experimental error as for aqueous solutions of strong acids.[2,3] Data for solutions containing sodium bisulfate (prepared by mixing an acetic acid solution of sodium acetate with excess of a solution of sulfuric acid in acetic acid) and for solutions of sulfuric acid in the mixed solvent, acetic acid–water in mole ratio 1–1, are included. Table II gives mole fractions of sulfuric acid required to produce the same simple basic indicator acidity in the three media, water, acetic acid and their equimolar mixture.

Table III summarizes the results of measurements of the rate of bromination of the ketone *m*-nitroacetophenone in sulfuric acid–acetic acid solutions. The unimolecular velocity constants, *k*, are expressed in natural logarithms and minutes. Measurements in solutions containing the salt sodium bisulfate and in solutions of sulfuric acid in mole-to-mole acetic acid–water are also given. In Fig. 3, log *k* is plotted against H_0 of the medium. We have measured the reaction rate in the medium used by Evans, Morgan and Watson,[6n] 0.5 molar hydrochloric acid in 75% acetic acid–water by volume and our value for *m*-nitro-

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[11] Orton and Bradfield, *J. Chem. Soc.*, 983 (1927).

[12] Orton and Jones, *ibid.*, **101**, 1708 (1912).

TABLE I

IONIZATION OF INDICATORS IN H_2SO_4–CH_3COOH SOLUTIONS

o-Nitroaniline ($pK' = -0.17$)

m	Log *m*	Log (c_{BH^+}/c_B)	H_0
0.0195	−1.71	+0.71	−0.88
.0262	−1.58	.85	−1.02
.0290	−1.54	.89	−1.06
.0412	−1.38	.98	−1.15
.0506	−1.30	1.16	−1.33
.0591	−1.23	1.20	−1.37
.0680	−1.17	1.26	−1.43
.0837	−1.08	1.34	−1.51
.0901	−1.05	1.37	−1.54
.1132	−0.95	1.44	−1.61
.1273	− .90	1.48	−1.65

p-Chloro-*o*-nitroaniline ($pK' = -0.91$)

m	Log *m*	Log (c_{BH^+}/c_B)	H_0
0.0721	−1.14	+0.52	−1.43
.1036	−0.98	.64	−1.55
.1197	− .92	.77	−1.68
.1429	− .84	.88	−1.79
.1705	− .77	.94	−1.85
.1981	− .70	1.06	−1.97
.247	− .61	1.15	−2.06
.283	− .55	1.26	−2.17
.348	− .46	1.34	−2.25
.496	− .30	1.58	−2.49
.641	− .19	1.66	−2.57
.756	− .12	1.83	−2.74
.932	− .03	1.95	−2.86
1.110	+ .05	2.05	−2.96
1.332	+ .12	2.18	−3.09
1.593	+ .20	2.27	−3.18

EFFECT OF $NaHSO_4$ ON H_0; INDICATOR–*o*-NITROANILINE

Mole/liter of solution at 25° H_2SO_4	$NaHSO_4$	Log (c_{BH^+}/c_B)	H_0
0.0266	0.0000		−0.99 (interpolated)
.0266	.0266	+0.86	−1.03
.0266	.0797	+1.05	−1.22

IONIZATION OF *o*-NITROANILINE IN SOLUTIONS OF H_2SO_4 IN THE SOLVENT CH_3COOH–H_2O, MOLE RATIO 1–1

Moles of H_2SO_4 per 1000 g. of solvent	Log (c_{BH^+}/c_B)	H_0
1.707	+1.09	−1.26
1.912	1.26	−1.43
2.790	1.78	−1.95
2.998	2.00	−2.17

TABLE II

EFFECT OF COMPOSITION OF MEDIUM ON H_0 OF H_2SO_4–H_2O–CH_3COOH SOLUTIONS

	Mole fraction of H_2SO_4 in		
H_0	H_2O	CH_3COOH–H_2O Mole ratio 1–1	CH_3COOH
−1.26	0.059	0.063	0.0028
−1.43	.067	.070	.0042
−1.95	.094	.098	.0118
−2.17	.104	.105	.0169

acetophenone is about 20% lower than theirs, a result possibly due to failure of dilution to arrest the reaction in the latter stages of their runs.

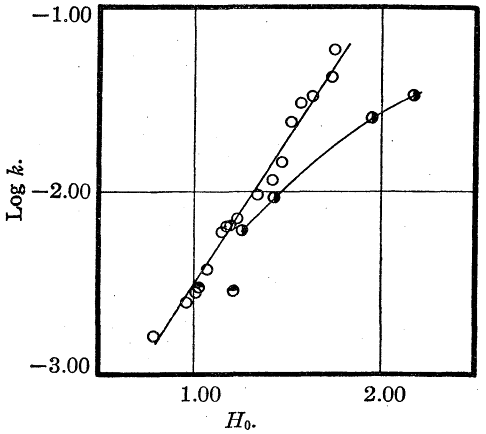

Fig. 3.—Relations between H_0 and log *k* in bromination of *m*-nitroacetophenone: ○, H_2SO_4 in CH_3COOH, $M = 0.0161$–0.146; ◑, H_2SO_4 in $CH_3COOH + H_2O$, molar ratio 1–1; ◓, H_2SO_4 in $CH_3COOH + NaHSO_4$ (data taken from Table III).

TABLE III

RATE OF BROMINATION OF *m*-NITROACETOPHENONE IN H_2SO_4–CH_3COOH SOLUTIONS

Concentration of H_2SO_4 in mole/liter	*k*	Log *k*
0.0161	0.00160	−2.80
.0251	.00244	−2.61
	.00246	−2.61
.0282	.00268	−2.57
	.00296	−2.53
.0322	.00372	−2.43
.0392	.00567	−2.25
	.00643	−2.19
.0405	.00622	−2.21
	.00666	−2.18
.0434	.00606	−2.22
	.00645	−2.19
	.00682	−2.16
.0484	.00709	−2.15
.0609	.00848	−2.07
	.01089	−1.96
.0731	.0105	−1.98
	.0116	−1.93
	.0120	−1.92
.0786	.0151	−1.82
.0810	.0146	−1.84
.0914	.0237	−1.62
.1032	.0288	−1.54
	.0319	−1.50
.1196	.0297	−1.53
	.0352	−1.45
.1454	.0409	−1.39
	.0421	−1.37
.1462	.0594	−1.23

TABLE III (*Concluded*)

EFFECT OF $NaHSO_4$ ON RATE OF BROMINATION OF *m*-NITROACETOPHENONE IN H_2SO_4–CH_3COOH SOLUTIONS

Mole/liter H_2SO_4	$NaHSO_4$	*k*	Log *k*
0.0266	0.0000	0.00260	−2.58[a]
.0266	.0266	.00284	−2.55
		.00294	−2.53
.0266	.0797	.00278	−2.56
		.00286	−2.54

[a] Interpolated.

RATE OF BROMINATION OF *m*-NITROACETOPHENONE IN SOLUTIONS OF H_2SO_4 IN THE SOLVENT CH_3COOH–H_2O, MOLE RATIO 1–1

Concn. of H_2SO_4 in mole/liter	*k*	log *k*
1.68	0.00622	−2.21
	.00617	−2.21
1.88	.00868	−2.06
	.01002	−2.00
2.52	.0264	−1.58
	.0243	−1.61
2.82	.0341	−1.47
	.0332	−1.48

RATE OF BROMINATION OF *m*-NITROACETOPHENONE IN 0.5 MOLAR HCl IN THE MEDIUM 75% ACETIC ACID IN WATER BY VOLUME

$$k = 0.000396 \pm 0.000005$$
$$.000395 \pm .000007$$

In terms of "fall of 0.02 *N* thiosulfate titer per minute per 20 cc. of solution containing 0.1 molar ketone concentration," this constant would have the value 0.079. Evans Morgan and Watson[6n] have reported 0.099.

Discussion

As was to be expected and has been reported by Hall and Spengeman[13] on the basis of more extensive data than ours, a solution of sulfuric acid in glacial acetic acid is much more acid than one of the same sulfuric acid concentration in water. Our measurements on solutions in the equimolar mixture of the two solvents show that this medium resembles water much more nearly than it does acetic acid. This is true no matter what concentration scale is used, but is especially true, as Table II shows, on the basis of mole fractions. The mole fraction of sulfuric acid necessary to produce a given value of H_0 in the mixed solvent is nearly identical with that required to produce the same acidity in water alone, whereas a much smaller mole fraction of the strong acid is required in glacial acetic acid.

Qualitatively the behavior of the reaction rates is parallel. The concentration of sulfuric acid required to produce a given rate is much higher in the mixed solvent than in glacial acetic acid, and in either solvent an increase in H_0 is accompanied by an increase in rate. The kind of simple quantitative correlation between reaction rate and indicator acidity which we have previously found in mixtures of strong acids with water is however lacking. In the first place, we note that two solutions, one in glacial acetic acid, the other in the equimolar acetic acid–water mixture, which possess the same value of H_0, do not necessarily give rise to equal reaction rates. Obviously we have to deal with specific effects of the solvent upon the rate.

Furthermore, the plot (Fig. 3) of log *k* against H_0 for the experiments in glacial acetic acid, while satisfactorily linear, possesses a slope considerably greater than unity (about 1.6), a phenomenon not susceptible to any simple interpretation. Barring specific solvent effects, a reaction of ketone with solvated hydrogen ion would lead to unit slope in this plot, and unit slope has, indeed, been found for a number of reactions in mixtures of strong acids with water.[2–4] Although the data are too scanty for assurance, our few measurements in the mixed acetic acid–water solvent are not inconsistent with unit slope in this medium also. That the effect is due to catalysis by molecular sulfuric acid seems improbable for two reasons. In the first place, the activity of molecular sulfuric acid in the solvent acetic acid is known from the measurements of Hutchison and Chandlee,[14] and is fairly closely proportional to the molality of the sulfuric acid in dilute solutions. Our reaction rates, on the other hand, increase considerably more rapidly than the first power of the sulfuric acid molality. Furthermore, the magnitude of a catalysis by molecular acid should be increased by the addition of sodium bisulfate, and our results show that the salt has relatively little effect upon the rate.

It follows that specific effects are present in these acetic–sulfuric acid solutions which were absent in the aqueous solutions in which we have found simple proportionality between rate and acidity.[2–4] Further work will be necessary in order to determine the region within which these simple relations apply and to account for the existence of the specific effects.

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(13) Hall and Spengeman, reported at the Kansas City meeting of the American Chemical Society, April, 1936.

(14) Hutchison and Chandlee, THIS JOURNAL, **53**, 2881 (1931). See also La Mer and Eichelberger, *ibid.*, **54**, 2763 (1932).

Summary

By a colorimetric method the rate of bromination of the ketone *m*-nitroacetophenone has been measured in solutions of sulfuric acid in acetic acid of concentration varying from 0.016 to 0.15 molal. Measurements to establish the effect of sodium bisulfate upon the rate of the reaction in these solutions and a limited series of measurements in solutions in a mixed acetic acid–water solvent have also been made.

It has been found that in the acetic acid solution the rate of reaction increases with increasing sulfuric acid concentration more rapidly than does either the acidity function H_0, the stoichiometric concentration of sulfuric acid, or the activity of sulfuric acid.

NEW YORK, N. Y. RECEIVED JULY 23, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Energy Levels in Electrochemistry. II

BY WILDER D. BANCROFT AND JAMES E. MAGOFFIN

In aqueous solutions sulfuric acid can only be reduced electrolytically when the concentration is very high. Raising the temperature is equivalent to increasing the concentration. Sodium sulfate and ammonium sulfate solutions cannot be reduced electrolytically at any concentrations and temperatures that can be reached in open vessels.

On the other hand sulfurous acid and sodium sulfite can easily be oxidized electrolytically to sulfuric acid and sodium sulfite. A sulfite–sulfate electrode is therefore a one-way electrode, the reaction being irreversible electrolytically.[1] It was shown in our previous paper[2] that at constant temperature and constant *p*H, the potential difference at a sulfite–sulfate electrode should be a function of the concentration of the sulfite and independent of the concentration of the sulfate as an oxidation product. Lewis, Randall and Bichowsky[3] found that at constant temperature and constant *p*H the change of electromotive force with change of concentration of sulfurous acid was described very well by the theoretical formula. They did not find that sulfate concentration had no effect because they varied the *p*H at the same time. This gap was filled by Noyes and Steinour[4] who showed that, "provided the hydrogen-ion concentration is nearly the same, hydrochloric acid and sulfuric acid produce (in association with sulfurous acid) substantially the same electromotive force."

Schaum[5] and von der Linde[6] found that the electromotive force of a sodium sulfite electrode varies with the concentration as it should, and that it makes no difference whether one dilutes with water or with sodium sulfate. The addition of a drop of benzyl alcohol was found to shorten the time necessary to reach equilibrium. We have not been able to confirm this effect of benzyl alcohol; but our experiments were made with smooth platinum electrodes and not with platinized electrodes.

The case of the cysteine–cystine electrode is more striking, because the same general results have been obtained by all workers. Dixon and Quastel[7] found that the electromotive force of this electrode at constant temperature and constant *p*H is a function of the concentration of cysteine and is independent of the concentration of cystine. This is the more interesting because cystine can be reduced to cysteine with tin and hydrochloric acid. The discrepancy between the potential difference generated by cysteine and that necessary to reduce cystine to cysteine is therefore not very large; but it is sufficient to change the electrode from the reversible to the irreversible class. Dixon thought that cysteine was a stronger reducing agent at a mercury electrode by about 200 mv. than at a gold electrode. He ascribed this, apparently erroneously, to the high hydrogen over-voltage which can be observed at a mercury electrode.

Dixon found that glutathione behaved like cysteine. Michaelis and Flexner[8] have confirmed Dixon on the important points; but they offer a different and apparently better explanation for

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(1) Conant, *Chem. Rev.*, **3**, 4 (1926).

(2) Bancroft and Magoffin, THIS JOURNAL, **57**, 2561 (1935).

(3) Lewis, Randall and Bichowsky, *ibid.*, **40**, 356 (1918).

(4) Noyes and Steinour, *ibid.*, **51**, 1418 (1929).

(5) Schaum, *Z. Elektrochem.*, **7**, 483 (1901).

(6) Von der Linde, Inaugural Dissertation, Marburg, 1902.

(7) Dixon and Quastel, *J. Chem. Soc.*, **123**, 2943 (1923); Dixon, *Proc. Roy. Soc.* (London), **B101**, 57 (1927).

(8) Michaelis and Flexner, *J. Biol. Chem.*, **79**, 689 (1928).

the behavior of a mercury electrode. They report, p. 721, that "a solution of cysteine in absence of oxygen establishes a definite potential at an indifferent electrode. This potential is independent of the concentration of cystine and depends logarithmically on the concentration of cysteine [over the range from 0.1 to 0.002 M at a pH of 4.6] and of hydrogen ions. The potential is identical at electrodes of blank platinum, gold-plated platinum, and mercury, and reproducible to within 5 mv. Slight traces of oxygen displace the potential to the positive side. Mercury is much less sensitive to oxygen than platinum or gold-plated platinum and has the advantage of yielding final values in a relatively short time."

If the explanation offered by Michaelis and Flexner for the behavior of mercury electrodes is right, it should be general and should apply to all reducing agents. This is the more important because many measurements of the electromotive forces of reducing agents are made in the presence of air. The measurements given in our previous paper in Table II were repeated, using mercury electrodes instead of smooth platinum ones. The results are given in Table I.

TABLE I

Pt | M Na_2SO_3 + A | Calomel electrode: A = concentration of other salt; B = E_c with smooth platinum electrode; C = E_c with mercury electrode. The calomel electrode is always cathode

A	B	C
Zero	0.146	0.313
M/10 Na_2SO_4	.153	.320
M $NaSO_4$	.149	.310
M NaCl	.182	.323
M NaBr	.188	.341
M NaCNS	.228	.347
M NaOH	.271	.278
M NaI	.302	.499

The electromotive forces obtained with the mercury electrodes, with the exception of the cell containing sodium hydroxide, are 120–200 mv. higher than the corresponding ones with platinum electrodes. This agrees with the results of Dixon and of Michaelis. The constant values are reached much more quickly with mercury than with platinum, so that a mercury electrode is more convenient to use than a platinum one. Mercury electrodes should be tried in measurements of photographic developers.

It seemed desirable to know something about the temperatures at which sodium sulfate and some other salts could be reduced by so energetic a reducing agent as metallic sodium. A small oven was constructed of asbestos board and a glow-coil heater installed. The dry salts were mixed with approximately an equal weight of metallic sodium and placed in a hard-glass test-tube which was lowered into the oven through a small aperture in the roof. The mixture was stirred thoroughly throughout the heating, and the temperature was measured by inserting the bulb of a thermometer into the salt–sodium mixture. No correction was made for emergent stem and the temperatures given are only first approximations. After heating, the apparatus was allowed to cool and the mixture was then poured into water to decompose any excess sodium. The resulting solution was made acid with nitric acid and tested for reduction products. In the case of the sulfates and sulfites the test was made for sulfides, while chlorides were tested for in the case of chlorates and perchlorates. Reduction of potassium chlorate was also attempted with a 0.7% sodium amalgam at temperatures below the melting point of sodium. The data are given in Table II.

TABLE II

APPROXIMATE REDUCTION TEMPERATURE WITH SODIUM

Salt	Temp., °C.
Sodium sulfate	370
Sodium sulfite	300
Potassium perchlorate	280
Potassium chlorate	100 (70)

The temperatures of reduction given in Table II show that sulfites are reduced more readily than sulfates and chlorates than perchlorates. This was to be expected, because chlorates break down when heated at a lower temperature than perchlorates and because sulfates seem to go direct to sulfides when heated. It would be possible to do decomposition-voltage measurements for sodium sulfate in the presence of fused caustic soda; but this delightful task was left for somebody else. It was hoped to determine the approximate temperature at which hydrogen reduces platinized sodium sulfate; but the time at our disposal did not permit of this.

Potassium chlorate can be reduced by sodium amalgam at temperatures below the melting point of sodium; but the reduction is very slow, only traces of chloride being formed on heating for three hours at 70°. At 100° sodium amalgam reduces potassium chlorate quantitatively in a few minutes.

In the light of what we now know, Quastel, Stephenson and Whetham[9] were very close to the truth a dozen years ago. "It was found [by Quastel and Whetham[10]] that in the presence of resting bacteria succinic acid donates hydrogen to methylene blue with the production of fumaric acid. It was also found that in the presence of the bacteria fumaric acid oxidizes leucomethylene blue, so that finally an equilibrium is established between succinic acid, fumaric acid, methylene blue and leucomethylene blue."

Bernheim and Dixon[11] made use of the same concept in their study of the reduction of nitrates to nitrites in animal tissues. "If it is assumed that the nitrate invariably requires activation before it can be reduced in the tissues, it is clear that the catalyst responsible must be associated in a very special way with the particular oxidase systems in the cell. . . .

"Nitrates differ from methylene blue in giving no oxidation potential at a platinum electrode, in this respect resembling the aromatic nitro-compounds. The latter are nevertheless easily reduced, both *in vitro*, for example by –SH compounds (cysteine, glutathione, etc.) and also by the dehydrases. Nitrates are not reduced by cysteine unless a nitrate-activating catalyst is present (Quastel, Stephenson and Whetham)."

The colloid chemist—and still more the physical chemist—is not yet accustomed to considering "resting" bacteria, of which he has never before heard, as acting as catalytic agents to succinic acid in something the same way that platinum does to hydrogen. It is evident, however, that some day there will be an extensive study of the catalytic action of "resting" bacteria.

From our point of view the formulation of all oxidation–reduction systems is very simple. If a substance does not pass through a more strongly reducing stage while being oxidized, it will give an electromotive force with an inert electrode quite apart from any catalytic action of the electrode or of the solution. If the substance does pass through a more strongly reducing stage while being oxidized, it will not act electromotively as a reducing electrode unless the electrode metal or the solution is a sufficiently powerful catalytic agent to eliminate the effect of the energy hump. The converse is also true. If a substance does not pass through a more strongly oxidizing stage while being reduced, it will give an electromotive force with an inert electrode quite apart from any catalytic action of the electrode or of the solution. If the substance does pass through a more strongly oxidizing stage while being reduced, it will not act electromotively as an oxidizing electrode unless the electrode metal or the solution is a sufficiently powerful catalytic agent to eliminate the effect of the energy hump.

Any given oxidation–reduction system may be reversible both ways as with the ferrous–ferric electrode; it may be reversible one way as with the cysteine–cystine electrode; or it may be irreversible both ways as with the chloride–chlorate or chlorate–perchlorate electrode.

This accounts for potassium nitrate, nitrobenzene and acetic acid not giving oxidation potentials, and for ammonia, aniline, and alcohol not giving reduction potentials. On the other hand, phenylhydroxylamine and nitrosobenzene is a completely reversible system and so is hydroquinone and quinone.[12]

Summary

The general results of this paper are:

1. Since the reduction of cystine to cysteine is not strictly reversible, the electromotive force of a cysteine–cystine electrode is theoretically a function of the temperature, the *p*H and the concentration of cysteine but not a function of the concentration of cystine.

2. If an electron transfer between an inert metal and an oxidizable or reducible substance involves passing through an energy hump under the conditions of the experiment, a reducing potential or oxidizing potential characteristic of that substance will not be set up; otherwise, it will.

3. "Resting" bacteria are catalytic agents for some systems and we shall some day have a bacterial chemistry based on this property.

ITHACA, N. Y. RECEIVED JUNE 30, 1936

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[9] Quastel, Stephenson and Whetham, *Biochem. J.*, **19**, 305 (1925).

[10] Quastel and Whetham, *ibid.*, **18**, 519 (1924).

[11] Bernheim and Dixon, *ibid.*, **22**, 132 (1928).

[12] Gladstone and Hickling, "Electrolytic Oxidation and Reduction," 1936, p. 159.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY AND MIAMI UNIVERSITY]

The Effect of Halogen Substituents on the Rearrangement of Allyl Aryl Ethers. II. Ethers which Behave Abnormally

BY CHARLES D. HURD AND CARL N. WEBB

The previous paper[1] of this series dealt with three halogen-substituted allyl aryl ethers which rearranged normally into allylphenols. Eleven related compounds, nine ethers and two phenols, are taken up in this paper. The list is given in Table I.

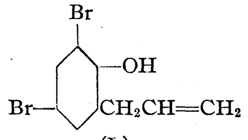
TABLE I

COMPOUNDS STUDIED

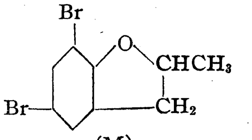
Symbol	Name	Formula
A	Allyl 2,4,6-tribromophenyl ether	$CH_2{=}CHCH_2{-}O{-}C_6H_2Br_3$
B	Allyl 2-methyl-4,6-dibromophenyl ether	$CH_2{=}CHCH_2{-}O{-}C_6H_2MeBr_2$
C	Allyl 2,6-dibromophenyl ether	$CH_2{=}CHCH_2{-}O{-}C_6H_3Br_2$
D	Allyl 2-methyl-6-bromophenyl ether	$CH_2{=}CHCH_2{-}O{-}C_6H_3MeBr$
E	β-Chloroallyl phenyl ether	$CH_2{=}CCl{-}CH_2{-}O{-}C_6H_5$
F	β-Bromoallyl phenyl ether	$CH_2{=}CBr{-}CH_2{-}O{-}C_6H_5$
G	γ-Chloroallyl phenyl ether	$CHCl{=}CHCH_2{-}O{-}C_6H_5$
H	γ-Chloroallyl *p*-tolyl ether	$CHCl{=}CHCH_2{-}O{-}C_6H_4CH_3$
I	γ-Bromoallyl phenyl ether	$CHBr{=}CHCH_2{-}O{-}C_6H_5$
J	*o*-(β-Chloroallyl)-phenol	$HO{-}C_6H_4{-}CH_2CCl{=}CH_2$
K	*o*-(γ-Chloroallyl)-phenol	$HO{-}C_6H_4{-}CH_2CH{=}CHCl$

The results show that none of the nine ethers rearranges in the normal fashion. All give greater or less amounts of hydrogen halide and polymeric products. No C_3- or C_6-hydrocarbons were liberated, a matter of some significance[2] with A and B. Differing from the three ethers mentioned in the previous paper, none of the ethers A-D possessed unsubstituted ortho positions but C and D possessed available para positions. Therefore, they might be expected to give normal rearrangement products. Actually D did rearrange in part to 2-methyl-4-allyl-6-bromophenol. In the case of C, the phenolic mixture which was obtained seemed to be a mixture of 4-allyl-2,6-dibromophenol[3] and 2-allyl-6-bromophenol but it could not be separated satisfactorily.

That the ortho bromine may be replaced by the incoming allyl group was definitely established with the tribromo ether (A) since 2-allyl-4,6-dibromophenol (L) was a reaction product. An isomeric product, probably 2-methyl-5,7-dibromocumarane (M), was also isolated. It will be recalled that none of it was formed from allyl 2,4-dibromophenyl ether during pyrolysis[1] in spite of the large yield of L, but in this case hydrogen bromide was absent. With hydrogen bromide present the change, in part, of L into M would be anticipated.[4] The rearrangement of L into M by hydrogen bromide was confirmed by experiment. The transformation of A into L involves a dehydrogenation of the solvent or reactant: (A) + 2H ⟶ (L) + HBr.

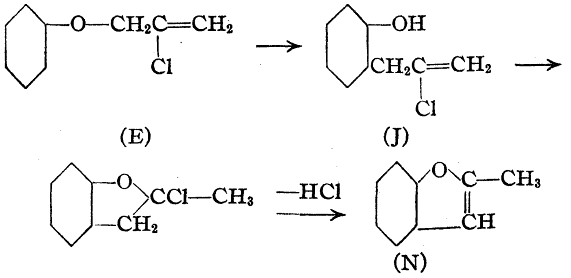


(L)



(M)

The haloallyl aryl ethers (E-I) apparently underwent rearrangement as an initial effect but only with E was the isomeric phenol (J) isolable. In this case also much of it isomerized to 2-methylcumarone (N). Part of the N polymerized but the fact that some of it was isolable was due to its comparative dilution, since when pure



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(1) Hurd and Webb, THIS JOURNAL, **58**, 941 (1936).

(2) Claisen and Tietze, *Ann.*, **449**, 81 (1926), reported such hydrocarbons from an allyl 2,4,6-trialkylphenyl ether.

(3) Raiford and Howland, THIS JOURNAL, **53**, 1051 (1931), reported non-rearrangement of (C) but they included no details.

(4) For similar ring-closures, see Claisen and Tietze, *Ber.*, **58**, 280 (1925).

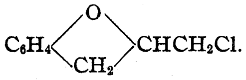
TABLE II

PROPERTIES OF THE ETHERS

Ether	B. p.			Analyses, %			Moles of HX envolved per mole of ether
	°C.	mm.	n^{20}_D	Halogen	Calcd.	Found	
A	—	—	(a)	Br	64.67	64.72	0.74
B	137–141	4	(b)	Br	52.26	52.40	.58
C	112–113	2	1.5830	Br	—	—	.62
D	81–85	0.5	1.5451	Br	35.22	35.68	.15
E	89–91	12	1.5329	Cl	21.04	21.28	.54
F	83–88	7	1.5557	Br	—	—	.39
G	122–127	27	1.5421	Cl	21.04	21.15	.24
H	101–106	7	1.5360	Cl	19.42	19.41	.44
I	101–103	7	1.5620	Br	37.52	37.68	.03

[a] M. p. 76–77°. [b] M. p. 34–37°.

J was pyrolyzed only the polymers were found. Considerable search was made for *o*-(β-bromoallyl)-phenol from F but none was found, contrary to von Braun.[5] Complex phenols were found in 18–29% yields and also neutral polymers but phenol itself was the only phenol actually isolable. The N formed from G contained a persistent chlorine-containing impurity. It was formed normally *via* *o*-(α-chloroallyl)-phenol, and not *via* K. On heating, the chief reaction of K was isomerization to 2-(chloromethyl)-cumarane,



Significant amounts of phenol and 1,3-dibromopropene were formed from (I), evidently by reaction of the liberated hydrogen bromide on the unused ether: $C_6H_5OCH_2CH{=}CHBr + HBr \longrightarrow C_6H_5OH + BrCH_2CH{=}CHBr$.

Experimental Part

Eastman 2,3-dibromopropene and tribromophenol were used in this work. The 2-methyl-6-bromophenol[6] was generously supplied by Dr. R. C. Huston of Michigan State College. It was redistilled before use: b. p. 204–207° (742 mm.). The 1,3-dibromopropene,[7] 2,6-dibromophenol[8] and 2-methyl-4,6-dibromophenol[8] were prepared by methods described in the literature; the percentage yields, respectively, were 23, 35 and 82.

2,3-Dichloropropene.—Although this is not new, there are no satisfactory directions for its preparation. It was found that the excellent directions for 2,3-dibromopropene[9] were adaptable. The following procedure, out of several tried, gave the best results. A mixture of 144 g. of trichloropropane, 13 g. of water and 90 g. of crushed (not powdered) sodium hydroxide was placed in a 500-cc. round-bottomed flask under a 3-ball Snyder floating-ball column. The mixture was heated with a smoky flame at such a rate that slow distillation took place. The distillate was washed with water, dried and fractionated through the column. That portion which was collected at 92.5–97° weighed 86 g. (80% yield). Redistillation gave these constants: b. p. 93–96°, n^{21}_D 1.4600.

Trichloropropane.—Several modifications of the directions of Pfeffer and Fittig[10] were used. Distilled glycerol dichlorohydrin (b. p. 170–176°) was used instead of the crude material. After treatment of this with phosphorus pentachloride most of the phosphorus oxychloride was distilled off before washing the product with water. From 170 g. of dichlorohydrin, 110 g. of trichloropropane (57% yield) was obtained; b. p. 153–158°.

1,3-Dichloropropene.—This was made by the method of Hill and Fischer[11] but in much lower yields. The best yield obtained was 34% for material boiling at 106–109°, or 39% for material boiling at 106–112°. Much larger amounts of trichloropropane and recovered glycerol dichlorohydrin were obtained than Hill and Fischer reported. Also, there was 60–65 g. of a high-boiling residue from 330 g. of dichlorohydrin.

Preparation of the Ethers

The ethers were prepared as before.[1] In the case of the chloroallyl and bromoallyl ethers, the limiting factor for yield was the dihalopropene rather than the phenol. In these cases 1.1 moles of the phenol was used for each mole of halide. Slight modification was necessary in the case of (A). It, being a solid and insoluble in ether, was worked up by solution in chloroform, and was recrystallized therefrom for purification.

In the synthesis of B, dibromo-*o*-cresol acted peculiarly. When the potassium carbonate was added to it in acetone solution, the mixture warmed, a gas was evolved and a sticky, brown precipitate formed. After the subsequent nine hours of refluxing with allyl bromide, much of the latter was unused. The yield of ether was very low and there was much tar.

Ethers A,[12] C,[3] F,[5] G[13] and H[13] have been made previously and analyzed. Ether A was prepared in a 0.7-mole run, and E in a 1.0-mole run. The other runs were 0.2–0.5 molar. The percentage yields, respectively, for the various ethers (A to I) were: 91, 11, 91, 77, 60, 85, 72, 65, 77. The constants and analytical data are summarized in Table II.

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(5) Von Braun, Kuhn and Weismantel, *Ann.*, **449**, 264 (1926).

(6) Huston and Neeley, THIS JOURNAL, **57**, 2177 (1935).

(7) Von Braun and Kuhn, *Ber.*, **58**, 2170 (1925).

(8) Zincke and Hedenström, *Ann.*, **350**, 273 (1906).

(9) Lespieau and Bourguel, *Organic Syntheses*, **5**, 49 (1925).

(10) Pfeffer and Fittig, *Ann.*, **135**, 359 (1865).

(11) Hill and Fischer, THIS JOURNAL, **44**, 2582 (1922).

(12) Varda, *Gazz. chim. ital.*, [2] **23**, 495 (1893); Raiford and Birosel, THIS JOURNAL, **51**, 1776 (1929).

(13) Bert, *Compt. rend.*, **192**, 1565 (1931).

Pyrolyses

The apparatus and procedure were the same as described in the previous paper.[1] Experiments were performed at 200–220°, usually for two hours. Ethers E and H were heated without solvents, ethers A, F, G, I both with and without solvents (tetralin, decalin, fluorene), and ethers B, C, D only with solvents. The HX evolved was absorbed in 0.5 *N* alkali. Solvents, in the case of A, F, G, I, did not affect the quantity of hydrogen halide evolved (see Table II). An exothermic reaction was noticed only in the case of A, but the other allyl ethers (B, C, D) might have behaved similarly had no solvent been present. The maximum temperature attained on a 25-g. sample of A, heated by a bath at 202–223°, was 270°. The inside temperature of the chloro- or bromoallyl ethers (E-I) always lagged below the bath temperature.

In all the runs, phenolic and neutral tars were produced. Also, from A, C, and D a liquid product was formed in traces which appeared to be allyl bromide. A similar product, namely, 1,3-dibromopropene, was formed in greater quantity from (I). Results with the various ethers will be listed.

Allyl 2,4,6-Tribromophenyl Ether.—A 25-g. portion of the ether was heated for two hours at 197–211° in 63 g. of tetralin. The principal phenolic product distilled at 125–130° (2 mm.); 13.5 g., 68% yield. It was essentially 2-allyl-4,6-dibromophenol. When treated with chloroacetic acid it gave 2-allyl-4,6-dibromophenoxyacetic acid,[1] m. p. 114–116°.

The neutral fraction weighed 6.6 g., about half of which was 2-methyl-5,7-dibromocumarane, b. p. 130–135° (1 mm.). This was synthesized for comparison. When (A) was heated without a solvent, the only identifiable product was a small amount of tribromophenol.

2-Methyl-5,7-dibromocumarane.—A sample of 2-allyl-4,6-dibromophenol was boiled for two hours with an aqueous acetic acid solution of hydrogen bromide according to Claisen's general method.[4] The cumarane (M) was collected in 47% yield at 129–134° (1 mm.); $n^{20}\text{D}$ 1.6075.

Anal. Calcd. for $C_9H_8OBr_2$: Br, 54.77. Found: Br, 54.75.

Allyl 2-Methyl-4,6-dibromophenyl Ether.—Sixteen grams of (B), mixed with 24 g. of tetralin and heated for two hours, yielded 5.5 g. of phenolic products and 8.1 g. of neutral material. No pure products were isolable from the fractions.

Allyl 2,6-Dibromophenyl Ether.—From 47 g. of (C), heated with 66 g. of tetralin, there was isolated 17.2 g. of crude phenolic material. Distillation at 2 mm. gave these fractions (°C., g., $n^{20}\text{D}$, % Br): 96–98, 2.9, 1.5784, 39.97; 98–104, 6.2, 1.5842, (no anal.); 107–112, 2.4, 1.5953, 44.61; 112–117, 2.3, 1.6057, 46.14; residue, 3 g. The lowest fraction appeared to be chiefly 2-allyl-6-bromophenol (calcd. Br, 37.54), and the highest fraction chiefly 4-allyl-2,6-dibromophenol (calcd. Br, 54.77).

Distillation of the neutral products at 1–2 mm. yielded 3 g. of naphthalene (formed by dehydrogenation of the tetralin), and 7.4 g. of the recovered ether, b. p. 102–112°.

Allyl 2-Methyl-6-bromophenyl Ether.—Thirty-three grams of (D), mixed with 33 g. of tetralin, yielded 7.7 g. (23%) of 2-methyl-4-allyl-6-bromophenol; b. p. 101–110° (1.5 mm.), $n^{20}\text{D}$ 1.5711.

Anal. Calcd. for $C_{10}H_{11}OBr$: Br, 35.2: Found: Br, 35.3.

Evidence was obtained for about 1 g. of 2-methyl-6-bromophenol but there was no evidence for 2-methyl-6-allylphenol, which would be anticipated if there were replacement of the bromine in (D) as in (A). No pure products were isolated from the 14.2 g. of crude neutral material.

β-Chloroallyl Phenyl Ether.—When heated for two hours at 216–223°, this ether (52 g.) yielded a colorless phenolic oil (12.4 g.) which boiled at 130–134° (12 mm.); $n^{20}\text{D}$ 1.5778. Analysis showed this to have the composition of *o*-(β-chloroallyl)-phenol. When allowed to stand, this material gradually became viscous and finally changed to a solid.

From the neutral material, 8 g. of 2-methylcumarone was isolated; b. p. 190–193°, b. p. 56–57° (8 mm.), $n^{20}\text{D}$ 1.5590.

Anal. Calcd. for C_9H_8O: C, 81.8; H, 6.06. Found: C, 81.4; H, 6.21.

This material reacted with bromine in carbon disulfide to give an oil; b. p. 116–119° (15 mm.); $n^{20}\text{D}$ 1.5873. 2-Methylcumarone (b. p. 190–193°, $n^{25}\text{D}$ 1.5552) and its bromination product (b. p. 114–118° (15 mm.); $n^{20}\text{D}$ 1.5875) were prepared for comparison by the method of Adams and Rindfusz.[14]

β-Bromoallyl Phenyl Ether.—When this ether was heated without a solvent, only a tar resulted. When 15 g. of (F) was heated with 3 g. of decalin or 5 g. of fluorene, 2–3 g. of a bromine-containing, infusible solid resembling carbon accumulated on the sides of the flask. Considerable phenolic substances (18–29%) were extracted from the reaction mixture. Distillation gave rise to a trace of phenol, identified as tribromophenol. Nothing distilled at 135° (14 mm.), the b. p. of *o*-(β-bromoallyl)-phenol. The residue was a tar.

Less than 1 g. of (F) was recovered on attempted distillation of the neutral material. The thick tarry residue weighed 3.5 g.

γ-Chloroallyl Phenyl Ether.—Fourteen different runs were carried out with (G). Practically no phenolic products were obtained except in the runs with fluorene as solvent. Thus, from 31–33 g. of G (in 11–14 g. of fluorene), heated for forty, ninety and four hundred forty minutes, there was formed 0.5, 1.2 and 2.3 g. of phenols. The 0.5 and 1.2-g. portions were thick, dark oils which gave good chlorine tests. The 2.3-g. portion yielded 0.53 g. of phenol (identified as tribromophenol) on steam distillation.

The principal product from (G) was a neutral material of lower b. p. It could not be separated completely from unchanged G either by vacuum distillation or by chemical means. On distillation at atmospheric pressure, it polymerized. Data from two runs will be listed, with and without a solvent.

Without Solvent.—In this run, 30.8 g. of G, $n^{21}\text{D}$ 1.5424, was heated for three hours at 215–225°, then distilled at 27 mm. (°C., g., $n^{21}\text{D}$): 103–112, 0.5, 1.5606; 112–115, 3.5, 1.5598; 115–118, 3, 1.5573; 118–120, 4, 1.5493; dark residue, 17 g. The 3.5-g. fraction (112–115°) possessed a

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(14) Adams and Rindfusz, THIS JOURNAL, **41**, 648 (1919). See also Claisen, *Ann.*, **418**, 84 (1919); *Ber.*, **53**, 322 (1920).

refractive index 0.0174 higher than G. Analysis (Cl, 12.8%) indicated 39.4% of chlorine-free material.

With Solvent.—In this run, 30.8 g. of G, n^{23}D 1.5392, admixed with 11.5 g. of fluorene, was heated at 250–255° for forty minutes. From it there was collected at 9 mm. about 23 g. of distillates (°C., g., n^{23}D). 68–74, 1.9, 1.5718; 74–77, 3.3, 1.5657; 78–82, 5.0, 1.5572; 83–85, 8.7, 1.5468; 85–88, 4.8, 1.5437. The residue, nearly colorless, was chiefly fluorene. None of the fractions, in common with G, possessed activity toward alcoholic or ammoniacal silver nitrate. This and other evidence suggests that the chlorine-containing impurity in the fractions is (G). The 1.9-g. fraction (68–74°) possessed a refractive index 0.0326 higher than the original ether. Analysis (Cl, 7.72%) indicated 63.3% of chlorine-free material.

γ-Chloroallyl *p*-Tolyl Ether.—From 25 g., only 0.3 g. of phenolic material was found. In the neutral portion, 10.4 g. of (H) was recovered. There was 10.8 g. of a black residue the mol. wt. of which, determined cryoscopically in benzene, was 424. This suggests a trimer of 2,5-dimethylcumarone (mol. wt., 438).

γ-Bromoallyl Phenyl Ether.—From 18.9 g. of (I), the most interesting neutral material was 1.41 g. of liquid, b. p. 157°, which was satisfactory for 1,3-dibromopropene. About 27% of (I) was recovered. The neutral tar weighed 2 g. The only recognizable phenolic product from this ether was phenol itself, formed in 9–18% yields.

The *o*-Chloroallylphenols

o-(β-Chloroallyl)-phenol (J), b. p. 95–100° (1 mm.), 130–134° (12 mm.), was a product of pyrolysis of β-chloroallyl phenyl ether (E).

Anal. Calcd. for C_9H_9OCl: Cl, 21.04. Found: Cl, 21.02.

o-(γ-Chloroallyl)-phenol (K) was prepared in 17% yield by reaction of 47 g. of phenol, 11.5 g. of fine sodium, 250 cc. of dry benzene and 56 g. of 1,3-dichloropropene for seventeen hours. The first half of the reaction was performed at room temperature, the last half at refluxing temperature. On working up the products (alkali-extraction and vacuum distillation), 14.5 g. of (K) was obtained; b. p. 151–156° (31 mm.), n^{23}D 1.5638. Concurrently, 4.5 g. of the isomeric ether (G) was obtained from the alkali-insoluble portion. The phenol (K) was analyzed.

Anal. Calcd. for C_9H_9OCl: Cl, 21.04. Found: Cl, 21.05.

Pyrolyses.—Phenols J and K were heated without solvents in the manner described above for the ethers. The hydrogen chloride evolved from J was 0.73 mole (per mole of J) during ninety minutes, whereas that from K was only 0.023 mole during two hundred minutes.

Approximately equal amounts of molasses-like phenolic and neutral products were formed from J. The phenolic material gradually became quite hard and resinous. There was 54% recovery of K. From a 6-g. run, the principal product was 1.03 g. of a neutral, halogen-containing material; b. p. 106–108° (9 mm.), n^{23}D 1.5595. Analysis and comparison with synthetic material showed it to be 2-(chloromethyl)-cumarane.

Anal. Calcd. for C_9H_9OCl: Cl, 21.04. Found: Cl, 20.15.

Synthetic 2-(Chloromethyl)-cumarane.—Five grams of K, mixed with 20 cc. of acetic acid and 10 cc. of 48% hydrobromic acid, was heated for two hours. This is Claisen's method[4] of ring-closure. There was 2.3 g. of K recovered. From the neutral material, 1.5 g. of the desired cumarane was collected between 140–155° (28 mm.), two-thirds of which was collected at 145–155°. This fraction, n^{24}D 1.5615, was analyzed.

Anal. Calcd. for C_9H_9OCl: Cl, 21.04. Found: Cl, 20.94.

Summary

Allyl aryl ethers were prepared wherein the aryl groups were 2-methyl-6-bromophenyl, 2,4-dibromophenyl, 2-methyl-4,6-dibromophenyl and 2,4,6-tribromophenyl. Also, "allyl" phenyl ethers were synthesized wherein the "allyl" group represented β- and γ-chloroallyl, β- and γ-bromoallyl. γ-Chloroallyl *p*-tolyl ether was also studied. All nine of these ethers evolved hydrogen halide on heating and gave rise to a complex mixture of products. The only cases which rearranged into isolable phenolic isomers were allyl 2-methyl-6-bromophenyl ether, β-chloroallyl phenyl ether and possibly allyl 2,6-dibromophenyl ether. Other phenolic products and neutral materials were formed. Cyclization was encountered in many cases and tarry polymeric products invariably were formed.

The chief organic products formed during the pyrolysis of allyl tribromophenyl ether were 2-allyl-4,6-dibromophenol and 2-methyl-5,7-dibromocumarane.

For purposes of comparison, study was also made of the pyrolysis of *o*-(β-chloroallyl)-phenol and *o*-(γ-chloroallyl)-phenol.

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RECEIVED JUNE 1, 1936

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Phenanthrene Derivatives. VI. The Preparation of 1-, 2- and 3-Phenanthryl Halides

BY W. E. BACHMANN AND CHARLOTTE H. BOATNER[1]

During the sixty-four years that have elapsed since the discovery of phenanthrene only one mono-halogen derivative, other than the 9-phenanthryl halides, has been prepared. This is not due to lack of effort, for numerous attempts have been made to obtain these compounds. An extensive study of the halogenation of phenanthrene and of phenanthrene derivatives was undertaken by Sandqvist[2] who succeeded in obtaining 3-chlorophenanthrene from 3-phenanthrenesulfonic acid. The attempts at the total synthesis of the phenanthryl halides met with no more success. Pschorr[3] applied his method of synthesis to the preparation of 1- and 3-bromophenanthrene but the attempt failed in the last step of the process. Berger[4] likewise was unable to prepare 2-bromophenanthrene by a similar procedure. Nylen,[5] somewhat more successful, obtained a small amount of 3-chlorophenanthrene by the Pschorr synthesis.

The idea of preparing the phenanthryl halides through the diazo reaction was first conceived by Schmidt[6] but he abandoned the investigation because of the difficulty of obtaining the phenanthryl amines. Werner and Kunz[7] reported that 3-aminophenanthrene could not be diazotized. Although Schmidt[8] reported the successful diazotization of this amine, he did not state the yield of the coupling product obtained with β-naphthol, and his method of diazotization is laborious. In view of these results no attempt was made in the present investigation to use the ordinary methods of diazotization. Instead, we resorted to the method of de Milt and van Zandt[9] which was developed recently for the diazotization of weakly basic and insoluble amines. Using their procedure we were able to diazotize 1-, 2- and 3-amino-phenanthrenes successfully.

Although the iodophenanthrenes were obtained by treating the phenanthrene diazonium sulfates with potassium iodide, the Sandmeyer reaction proved to be unsatisfactory for the preparation of the chloro- and bromophenanthrenes. These halides were obtained by using the procedure of Schwechten,[10] which involves the intermediate formation and subsequent decomposition of a complex formed by interaction of the diazonium compound and mercuric halide and potassium halide. In Table I are presented the yields and properties of the phenanthryl halides that were prepared. By heating the aqueous solutions of the diazonium salts the corresponding 1-, 2- and 3-phenanthrols were obtained. We are now engaged in the preparation of the 4-phenanthryl halides and are also investigating other methods of preparation.

Experimental Part

Preparation of Chlorophenanthrenes and Bromophenanthrenes.—The 1-, 2- and 3-aminophenanthrenes[11] were all diazotized in exactly the same manner. One and five-tenths grams of sodium nitrite was added with stirring to a cold mixture of 7.5 cc. of water and 15 cc. of concentrated sulfuric acid. The mixture was then heated with stirring on a steam-bath until a clear solution of nitrosylsulfuric acid was obtained. This solution was cooled to 0° and stirred mechanically as a solution of 1.93 g. (0.01 mole) of aminophenanthrene (1-, 2- or 3-isomer) in 10 cc. of pyridine was added drop by drop in the course of an hour. After addition was complete the mixture was stirred for one hour longer; it was then diluted to a volume of 200 cc. by addition of ice and water and treated with a solution of 1 g. of urea in 25 cc. of water in order to destroy the excess of nitrous acid. After the solution had been stirred at 0° for another hour, the diazonium salt solution was ready for reaction.

To the yellow solution of the phenanthrene diazonium sulfate from 1.93 g. of aminophenanthrene was added a solution of 11 g. of mercuric chloride and 11 g. of potassium chloride in 50 cc. of water. The mixture was allowed to stand in the cold for an hour in order that the deeply colored (yellow, orange or orange-red) precipitate of the double salt which formed could coagulate. The precipitate was filtered off, washed with water and air-dried for twelve to twenty hours. The dry double salt (6 g.) was intimately mixed with 12 g. of potassium chloride and the mixture was heated cautiously in a 50-cc. distilling flask with a free flame, keeping the temperature just high

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(1) From part of the Ph.D. dissertation of Charlotte H. Boatner.

(2) Sandqvist, *Ann.*, **369**, 104 (1909).

(3) Pschorr, *Ber.*, **39**, 3106 (1906).

(4) Berger, *J. prakt. Chem.*, **133**, 331 (1932).

(5) Nylen, *Ber.*, **53**, 198 (1920).

(6) Schmidt, *ibid.*, **12**, 1153 (1879).

(7) Werner and Kunz, *ibid.*, **34**, 2524 (1901).

(8) Schmidt, *ibid.*, **34**, 3531 (1901).

(9) De Milt and van Zandt, THIS JOURNAL, **58**, 2044 (1936). In a private communication, Professor de Milt informed us that she had secured quantitative diazotization of some 3-aminophenanthrene which we had sent her.

(10) Schwechten, *Ber.*, **65**, 1605 (1932).

(11) Bachmann and Boatner, THIS JOURNAL, **58**, 2097 (1936).

TABLE I

PHENANTHRYL HALIDES

All of the compounds were obtained as colorless crystals by recrystallization from alcohol.

Compound	Cryst. form	M. p., °C.	Yield, %	Formula	Analyses, % Calcd.	Found
1-Chlorophenanthrene	Plates	120–120.5	41	$C_{14}H_9Cl$	Cl 16.7	16.7
2-Chlorophenanthrene	Plates	85.5–86	42			16.7
3-Chlorophenanthrene	Needles	80.5–81.5[a]	48			16.9
1-Bromophenanthrene	Needles[b]	109.5–110	72	$C_{14}H_9Br$	Br 31.1	30.6
2-Bromophenanthrene	Plates	95–96	70			31.2
3-Bromophenanthrene	Needles	83–84	70			31.1
1-Iodophenanthrene	Fine needles	112.5–113	53	$C_{14}H_9I$	I 41.8	41.0
2-Iodophenanthrene	Prisms	116–116.5	47			40.9
3-Iodophenanthrene	Stout needles	83.5–84	47			41.8

[a] Nylen[5] reported a melting point of 80–81° for the product obtained by the Pschorr synthesis. Sandqvist[2] reported the two values, 70.5–71 and 81°, for the product prepared by interaction of 3-phenanthrenesulfonyl chloride and phosphorus pentachloride. [b] The compound also crystallizes in the form of plates.

enough for evolution of nitrogen to take place. When no more nitrogen was evolved, the chlorophenanthrene was distilled from the mixture under reduced pressure (4 mm.). The distillate was extracted with benzene in order to remove inorganic salts, the benzene solution was boiled with charcoal, filtered and evaporated and the residue of chlorophenanthrene was then recrystallized from alcohol. All of the halides are readily soluble in benzene and in acetone but only slightly soluble in cold alcohol.

The bromophenanthrenes were prepared in a similar manner. For larger runs the procedure was modified somewhat. Thus, the double salt (63 g.), which was obtained by addition of a solution of 55 g. of mercuric bromide and 55 g. of potassium bromide in 200 cc. of water to the diazonium salt solution from 9.65 g. of 2-aminophenanthrene, was mixed with twice its weight of potassium bromide, and the mixture was then heated cautiously in an evaporating dish on a sand-bath until evolution of nitrogen had ceased. The reaction product was digested with hot water, the residue was taken up in benzene, the filtered benzene solution was evaporated and the residue of 2-bromophenanthrene was purified by distillation, b. p. 185° (4 mm.), followed by recrystallization from alcohol; yield 9.0 g.

Preparation of Iodophenanthrenes.—A pale yellow precipitate was formed on addition of 10 g. of potassium iodide in 25 cc. of water to the diazonium salt solution from 9.65 g. of 3-aminophenanthrene (or its 1- or 2-isomer). After standing overnight at room temperature the reaction mixture was heated at 100° until no more nitrogen was evolved. The precipitate which had formed was filtered from the cooled solution and dissolved in benzene; the benzene solution was washed with a solution of sodium bisulfite and with water and then evaporated to dryness. The residue of 3-iodophenanthrene was purified by distillation, b. p. 190° (4 mm.), followed by recrystallization from alcohol; yield 7.2 g. By using the procedure involving the intermediate formation and subsequent decomposition of a double salt with mercury iodide and potassium iodide a 31% yield of 3-iodophenanthrene was obtained.

Preparation of Phenanthrols.—The phenanthrene diazonium sulfate solution from 1.93 g. of aminophenanthrene was diluted to a volume of 400 cc. and heated at 100° until decomposition was complete. The precipitate of phenanthrol was filtered off and purified through its water-soluble potassium salt. The yields were: 1-phenanthrol, 11%; 2-phenanthrol, 40%; 3-phenanthrol, 39%. The properties of the compounds agreed with those described in the literature.

Summary

By means of the diazo reaction 1-, 2- and 3-chlorophenanthrene, 1-, 2- and 3-bromophenanthrene, 1-, 2- and 3-iodophenanthrene and 1-, 2- and 3-phenanthrol have been prepared.

ANN ARBOR, MICHIGAN RECEIVED SEPTEMBER 8, 1936

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Heats of Adsorption at −183°. Carbon Monoxide on Copper

BY RALPH A. BEEBE, GEORGE W. LOW, JR., AND SEYMORE GOLDWASSER

Recent investigation[1] has shown that the reaction $H_2 + D_2 = 2HD$ is catalyzed by chromium oxide and supported nickel at temperatures as low as −183°, giving evidence for an activated as well as a van der Waals adsorption even at this low temperature. Because in general the magnitude of the heat effect is approximately one order higher for activated adsorption than for van der Waals, experimental data on heats of adsorption have been considered important in deciding which type is predominant in any given case. However, Gould, Bleakney and Taylor,[1] by indirect reasoning from their results on the catalytic activity of chromium oxide at low temperatures, have suggested that the heat of activated adsorption of hydrogen on this catalyst is very small at −183° and therefore of the magnitude commonly believed to attend van der Waals adsorption. For a more complete understanding of the phenomena at −183° it is apparent that experimental data on the heats of adsorption are needed. These are often calculated by application of the Clapeyron–Clausius equation to pressure data at two temperatures; however, this procedure cannot be used if the residual pressure is too small to measure as is often the case especially for the initial portions of the surface covered. The authors have therefore considered it important to develop a direct calorimetric method for measuring the heat values at low temperatures.

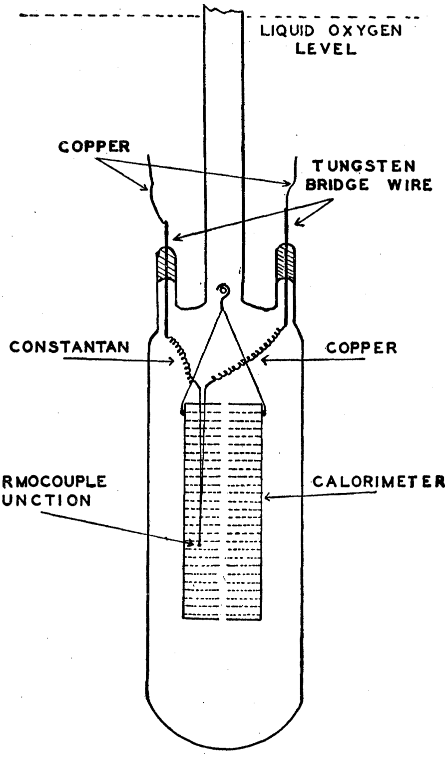

Fig. 1.

Because the problems attendant upon the heat measurements at 0° have been studied carefully by one of us[2] for carbon monoxide on copper, this case has been chosen as a point of attack in developing a method at −183°.

Experimental

Apparatus.—The apparatus was identical with that of Beebe and Wildner[2b] except for the method of leading in the thermocouple wires. In one method (Fig. 1) tungsten wire bridges were substituted for the "Picein" seals which had been satisfactory at 0° but would not hold the vacuum at −183°. Because it seemed reasonable to question the reliability of results for which the tungsten bridge wires were used, a second method (Fig. 2) was also employed. In this method, the copper–constantan thermo-junction, inserted at the point A, was pushed to the bottom of the platinum finger F, which was closed at its lower end. The platinum finger fitted loosely into a thin-walled copper sleeve which was embedded in the catalyst, the loose fit being necessary to facilitate the assembly of the apparatus. A reference junction not shown in Fig. 2 was inserted into the heavy copper jacket mentioned below. This calorimeter had the advantage that the gases never came in contact with the thermoelement. Both calorimeters contained the copper adsorbent granules in layers separated by copper gauze disks to improve the conditions for heat distribution.[2b] A heavy copper jacket

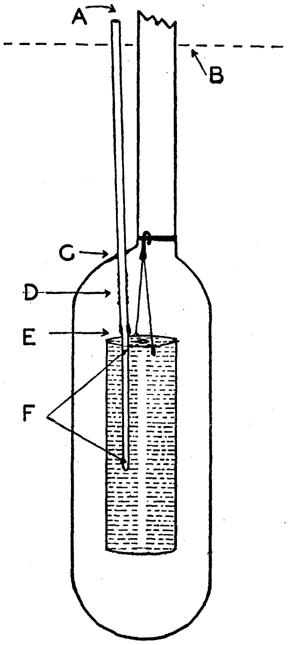

Fig. 2.—B, liquid oxygen level; C, ring seal; D, Pyrex to soft glass seal; E, soft glass to platinum seal.

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[1] Gould, Bleakney and Taylor, *J. Chem. Phys.*, **2**, 362 (1934).

(2) (a) Beebe, *Trans. Faraday Soc.*, **28**, 761 (1932); (b) Beebe and Wildner, THIS JOURNAL, **56**, 642 (1934).

1.1 cm. thick, suspended in the liquid oxygen bath and fitting closely around the Pyrex calorimeter chamber, served to integrate local variations in the bath temperature. The liquid oxygen[3] was contained in a large Dewar flask of 4.5 liters capacity. This large volume of liquid was essential to maintain sufficient constancy and uniformity of bath temperature.

The sensitivity of the single junction copper–constantan thermoelement was of course much less at −183° than at 0°; but this unfavorable factor was partially compensated because of the lower heat capacity of copper at the lower temperature. In the case of cylinder 1, for instance, the water equivalent was 3.93 as compared to 6.59 calories at 0°. The galvanometer deflection was 1 mm. per 0.0069° at a distance of one meter. The voltage sensitivity of the thermocouple in the region of −183° was calibrated against a secondary standard copper–constantan couple kindly provided by Professor Evald Skau of Trinity College, Hartford, Conn.

Materials.—In all, four different calorimeter cylinders filled with copper granules were used. Cylinder 1 with its charge of copper had been used for the measurements at 0° reported by Beebe and Wildner.[2b] This active copper, designated as copper 1, had been exposed to the atmosphere for some time, and after again reducing with hydrogen it had lost about 30% of its activity at the time of the previous measurements. At no time had the adsorbent been removed from the cylinder. On this as well as on all the other copper samples used, the rate of adsorption at −183° was practically instantaneous. Copper 2, used in cylinders 2 and 3, came from the same original batch as copper 1 but had been sealed in glass for nearly three years. Its adsorptive capacity was approximately the same as that of copper 1. Copper 4 used in cylinder 4 was prepared at the time of these experiments by reduction of copper oxide granules in hydrogen, first at 120°, and finally at 170°; its adsorptive capacity was about half that of copper 1. Cylinders 1 and 2 were used in method 1 (Fig. 1), and cylinders 3 and 4 in method 2 (Fig. 2). Because all the cylinders had the same dimensions, their weight when assembled varied little from that of cylinder 1 which was 71.5 g., of which 40.0 g. was due to active copper adsorbent.

Procedure.—Before each series of measurements the catalyst was outgassed for five hours at 170°. To hasten the establishment of thermal equilibrium between the calorimeter and its surroundings a small pressure of pure helium was admitted to the calorimeter which was then allowed to stand overnight in the liquid oxygen bath. In experiments by method 1, this helium was pumped out before the first increment of carbon monoxide was admitted, but with method 2 it was necessary to leave a small helium pressure (0.02 mm.) in the calorimeter vessel at the start of a series; otherwise the rate of transfer of heat from the active copper mass to the platinum finger containing the thermocouple was too slow to produce satisfactory time–temperature curves. In method 1 the uninsulated copper wire of the thermocouple was crowded against the copper gauze cylinders of the calorimeter probably in several places making much better thermal contact between the calorimeter and the thermocouple than the loosely fitting platinum finger of method 2. As in the previous work[2b] the time–temperature curves were photographically recorded.

Discussion of the Method

Previous experiments[2a] have demonstrated that two factors, (a) slow conduction of heat and (b) non-uniform adsorption, are unfavorable to satisfactory conditions for the heats of adsorption measurements; and the efficiency of our calorimeter in minimizing the effects of these factors at 0° has been discussed.[2b] Compared to 0°, effective heat transfer is favored at −183° by the greater thermal conductivity of copper at that low temperature; but this favorable factor is offset by the much lower rate of heat transfer by radiation and by the residual gases in the calorimeter. Judging from the similarity in form between the time–temperature curves obtained at the two temperatures, it would seem that the factors favorable and opposed to good heat distribution just about balanced each other. For the initial stages of adsorption at 0°, it was shown by experiment that the process was non-uniform, *i. e.*, adsorption occurred on those successive layers of adsorbent with which the carbon monoxide first came into contact.[2a] Although not demonstrated experimentally, it is probable that the same phenomenon is present at −183°. The calorimeter is designed to minimize, but does not completely eliminate, this effect with the result that the differential heats for the initial increments measured and reported below, are probably lower than the true differential heats for reasons previously given.[2b]

The time–temperature curves obtained by method 1 (Fig. 1) were similar to those at 0°, having the form of curves I, II and III in Fig. 2 of the paper by Beebe and Wildner,[2b] for initial, intermediate, and final increments of carbon monoxide added to the surface. Using method 2, all the time–temperature curves had the form of curve III mentioned above, the more rapid rise to a maximum and the subsequent more rapid cooling being due to the presence of the helium gas (0.02 mm.). Unlike those at 0°, these curves at −183° contained irregularities which were probably due to lack of complete uniformity in temperature of the liquid oxygen bath. The amplitude of these variations varied from 0.5 mm.

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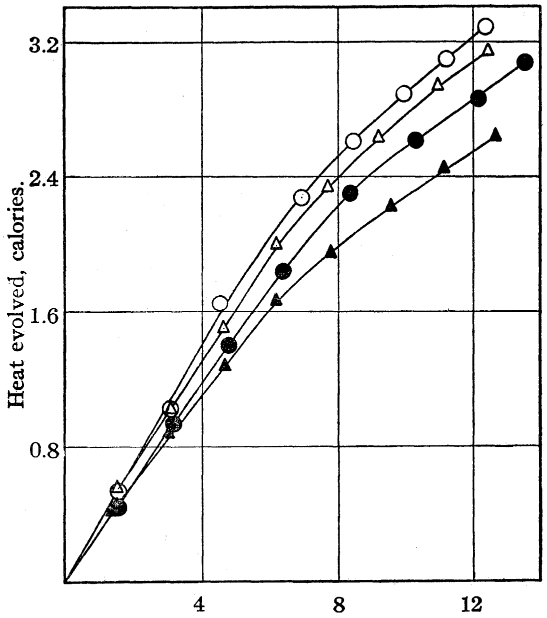
[3] This liquid oxygen guaranteed 99% pure was purchased from the Air Reduction Sales Company. Because of the high degree of purity of the oxygen and because a relatively small percentage of it was evaporated, no change in its boiling point was noticeable during the measurements.

in most of the curves to 2 mm. in the worst cases. It is roughly estimated that they introduced random errors of 5 to 10% in reading the temperature changes from the curves.

Results



Cc. adsorbed on 40.0 g. of copper.

Fig. 3.—○, Cylinder 2, series 1; △, cylinder 2, series 2; ●, cylinder 3, series 1; ▲, cylinder 3, series 2.

Three series of differential heats were measured for cylinder 1, and two each for cylinders 2, 3 and 4, making nine series in all. The results for the four series on copper 2 are shown in Fig. 3 in which the total heat evolved is plotted against cc. of carbon monoxide adsorbed. The total heat was calculated by summation of the measured heats for separate successive increments of gas. It is important to observe that method 1 (Fig. 1) was used in the measurements on cylinder 2, but that method 2 (Fig. 2) was used for cylinder 3; however, copper 2 was used in both cylinders. The fair concordance of the data obtained by the two methods is evidence for the reliability of both methods of measurement. The failure of the results for the four series to check more closely than they do is probably due to the lack of complete similarity of the copper surfaces used in the two cylinders, although they came originally from the same batch of copper, and also to the lack of complete reproducibility of these surfaces in successive series. In Table I is given a comparison of the volumes adsorbed at the arbitrarily chosen pressure of 0.8 mm. This table does not of course give any information concerning the relative percentages of active points in the surfaces used. In Table II are shown more complete details of two typical series. After the completion of series 2, cylinder 1 (Table II), the copper was outgassed for two hours at −183°. The increments a, b and c, then added, yielded low differential heats of the order of 3 kcal. per mole. Measurements on copper 4 which had lower adsorptive capacity than the others gave the following differential heats for successive increments: 7.3, 5.5, 4.9, 3.8, 4.0 kcal. per mole.

TABLE I

Cylinder no.	Series no.	Cc. adsorbed
2	1	12.40
2	2	12.20
3	1	13.45
3	2	11.80

TABLE II

	Volume of gas Admitted	Volume of gas Adsorbed	Resid. press. mm. $\times 10^3$	Galv. defl., mm.	Diff. heat of adsorp., kcal./mol.	Total vol. ads. cc.
		Cylinder 1, Series 2				
1	1.32	1.32	0	22.3	8.7	1.32
2	1.44	1.44	0	25.6	8.9	2.75
3	1.34	1.34	0	17.2	6.5	4.10
4	1.40	1.40	0	16.2	5.9	5.51
5	1.28	1.28	16	10.0	4.0	6.79
6	1.40	1.37	43	10.7	4.0	8.16
7	1.34	1.26	158	9.7	3.9	9.42
8	1.37	1.20	395	7.8	3.3	10.62
9	1.46	1.16	836	8.0	3.5	11.78
		Outgassed to	27			
a	1.52	1.46	103	9.9	3.3	9.3
b	1.40	1.25	331	7.9	3.2	10.6
c	1.40	1.12	751	7.1	3.3	11.7
		Cylinder 3, Series 1				
1	1.57	1.57	0	23.0	7.0	1.57
2	1.58	1.58	0	22.5	6.8	3.15
3	1.58	1.58	0	20.0	6.1	4.73
4	1.62	1.62	0	20.5	6.1	6.35
5	2.02	2.00	1	21.5	5.1	8.35
6	1.98	1.91	99	15.0	3.7	10.26
7	2.16	1.86	450	11.6	3.0	12.13
8	1.97	1.44	1050	10.1	3.4	13.56

Discussion

In all our measurements for carbon monoxide on copper at −183° the differential heats for the first few cc. of gas added to the surface have been of the order of 8 kcal. which, although less than the values at 0°,[2b,4] is several times greater than the heat of vaporization of carbon monoxide. It

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(4) Measurements of differential heats at 0° on copper 1 and copper 2 using the tungsten bridge calorimeter (Fig. 1), confirmed the previous work of Beebe and Wildner which showed that the heats were of the order of 19 to 14 kcal. per mole.

therefore seems probable that the adsorption is a combination of activated and van der Waals adsorption favoring the former for initial stages but changing in ratio progressively to the latter as successive increments of gas are added to the surface. This is in agreement with the conclusion of Benton and White[5] based upon indirect experimental evidence.

The technique worked out in detail for carbon monoxide on copper should be applicable to other gas–solid combinations at −183°. For reasons given in the introduction, direct experimental measurements of heats of adsorption are needed at low temperatures on chromium oxide. The technique described above is now being applied to the latter adsorbent.

Our thanks are due to the Committee on Grants-in-Aid of the National Research Council for supplying funds for technical assistance in this work.

Summary

1. A method has been described for the direct measurement of the differential heats of adsorption of carbon monoxide on copper at −183°.

2. The differential heats are of the order of 8 kcal. per mole in the initial stages, and decrease to 3 kcal. in the later stages of the adsorption.

3. The results seem to indicate that a considerable part of the adsorption for the initial increments of gas is of the activated type even at the low temperature of −183°.

Amherst, Mass. Received August 29, 1936

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[5] Benton and White, This Journal, **54**, 1385 (1932).

[Contribution from the Chemical Laboratory, University of Illinois]

X-Ray Diffraction Studies of Built Up Films[1]

By G. L. Clark and P. W. Leppla

The development by Langmuir and Blodgett[2] of a technique for the preparation of foliated films of any desired number of molecular layers permits for the first time the study of x-ray diffraction effects produced by a known number of planes. Clark, Sterrett and Leppla[3] reported distinct diffraction patterns from nine or more layers of stearates prepared by Blodgett's method. Langmuir and Schaefer[4] have since shown by chemical analysis of the unimolecular layer skimmed from solutions containing calcium or barium ions that the built up films vary continuously in composition from pure acid at *p*H 2 to pure soap at *p*H 11. In view of the fact that the soaps and the acids crystallize in different systems, and since, furthermore, several modifications of the fatty acids are known, the structure of the composite built up films was investigated by diffraction methods.

Experimental.—Films were prepared of stearates of lead, calcium and barium by means of a motor-driven device to ensure freedom from vibration and the highest possible perfection of the individual layers. To eliminate the necessity for oscillating the specimen in the path of the x-ray beam, curved surfaces were used as originally proposed by Trillat.[5] For the measurement of the long spacing, *d*, a radius of 15 mm. was employed. To each order corrections were applied for the actual position of the origin of the diffracted spot. To increase the intensity of the pattern for the study of films of only a few layers, the radius was increased to a maximum of 50 cm. Copper Kα radiation was used.

A double lining of lacquer overlaid with paraffin was used in the brass trough to prevent contamination of the solutions with copper ions. For the measurement of *p*H an antimony electrode was employed.

Since films do not adhere to glass at low *p*H, lacquered surfaces were used in the acid range. Molecules adhere to glass or metal by their polar groups and exist in an odd number of layers. On lacquer the hydrocarbon end of the chain is attached to the surface and the films exist in an even number of layers.

Composition of the Surface Film.—Unimolecular stearate films were skimmed from the surface of dilute calcium, barium and lead salt solutions at varying hydrogen-ion concentrations, the material air-dried, packed into tiny cells and transmission diffraction patterns registered. Side spacings characteristic of both the acid and the soap appeared in each case, the intensities indicating complete agreement with Langmuir and Schaefer's[4] conclusions.

Structure of the Built Up Films.—From the mechanism of the transfer process the gross structure readily may be inferred to be the alternating

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[1] From a thesis presented by P. W. Leppla to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1936. Presented before the 91st meeting of the American Chemical Society, Kansas City, Mo., April, 1936.

[2] Blodgett, This Journal, **57**, 1007 (1935).

[3] Clark, Sterrett and Leppla, *ibid.*, **57**, 330 (1935).

[4] Langmuir and Schaefer, *ibid.*, **58**, 284 (1936).

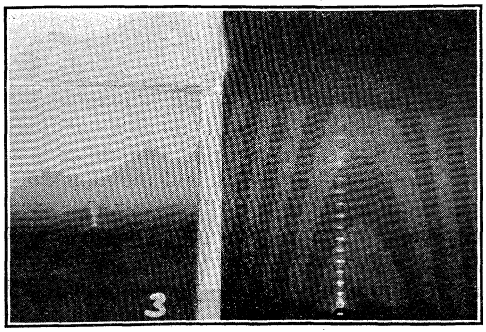
[5] Trillat, *J. phys. radium*, [6] **10**, 32 (1929).

type common to fatty acids and derivatives. In the ordinary crystal modification of stearic acid the chains are tilted at about 27° from the normal to the base and *d* is about 40 Å. In stearates of divalent metals the chains are perpendicular or very nearly so to the base and *d* is approximately 50 Å. The spacings observed for built up films and for ordinary preparations are given in Table I.

Table I

		Å.
Stearic acid	Built up film	39.7 ± 0.2
	Melted on glass	39.5 ± .2
Calcium stearate	Built up film	49.4 ± .2
	Powder by transmission	50.0 ± 0.5
Lead stearate	Built up film	49.6 ± .2
	Powder by transmission	49.7 ± .5

Based upon the spacing observed and the relative intensities of the odd and even orders, it was concluded that the structure of the composite films varies *discontinuously* with the *p*H, being that of the acid below *p*H 3 and that of the soap above *p*H 6. As might be expected from the difference in lattice energies, the stearates power in imposing the soap structure on the film is the greater, and films containing even a relatively high proportion of the acid still have the structure of the soap. At intermediate hydrogen-ion concentrations a pattern was obtained characterized by low intensity of the higher order reflections, indicating a distorted transition structure. Lead stearate films at *p*H 4 gave a totally different pattern indicative of an entirely distinct configuration.



3 layers 50 layers

Fig. 1.—Diffraction patterns of built up films of lead stearate.

By an ingenious method of interference of monochromatic light, Blodgett[2] has measured the over-all thickness of calcium stearate films, obtaining 48.8 Å. per double layer. It has been suggested that comparison of such measurements with those of x-ray diffraction affords a direct approach to absolute x-ray wave length values. No significance can be attached to the discrepancy between Blodgett's value and those of this investigation since different samples of stearic acid were employed, and it has been shown adequately that *d* values for fatty acids vary greatly with the purity of the specimen, and for at least three polymorphic structures.

Pure stearic acid films were transferred to lacquered surfaces from perchloric acid solutions of *p*H 2 to 5. Two side spacings appeared on the photographic film in a position indicating that all the chains were tilted in the same direction, sloping down with respect to the plane in which the surface was raised and lowered during the transfer process.

Intensity Measurements.—The use of a large radius of curvature resulted in such high intensities that good patterns were obtained from as few as three layers of lead stearate. Figure 1 is a reproduction of such a pattern secured in three-fourths hour from a Philips Metalix tube operating at 28 kv. and 25 ma., as compared with a pattern for 50 layers.

From a series of films with increasing numbers of layers the data shown graphically in Fig. 2 were obtained. The intensities were read from micro-

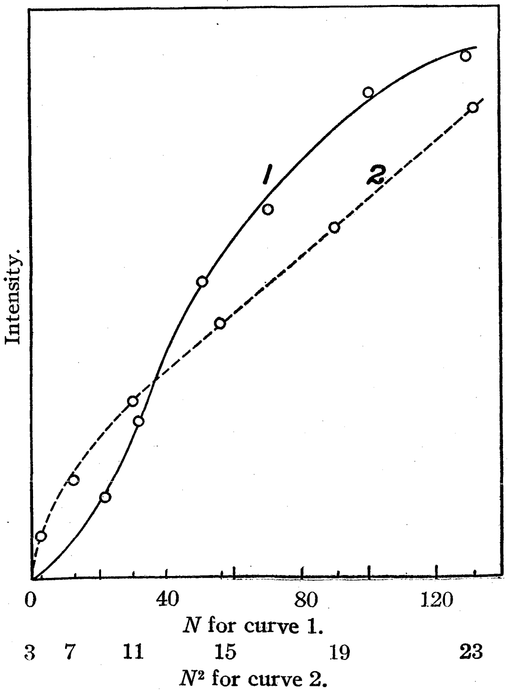


Fig. 2.

photometer traces and a blackening curve established from similar films developed simultaneously. In the experimental series the exposure time was varied systematically from one minute to one hour to keep the blackening between 25 and 50%. If intensities of interferences for the thinnest films are plotted against the *square* instead of the first power of the number of layers, the points between ten and thirty layers fall on a straight line. This is characteristic of an ideally imperfect diffracting medium. From a greater number of layers the intensity falls off, the upper layers shielding those below from the x-ray beam. Thus the irregularity of the first layers applied has become smoothed out and the planes approach perfection.

Test of the Laue Particle Size Equation.—The theoretically derived equation, $B = b + (0.9\ \lambda/D \cos \theta/2)$[6] has been used to calculate particle size in the colloidal range from the observed breadth of x-ray interferences. Until now it has been impossible to test the equation because of a lack of a comparison method. The expression is equally valid for the thickness of a built up film. The results of line breadth measurements are given in Table II. In general, agreement of observed and calculated values is good except for very thin films where the excess broadening observed is attributed to the previously mentioned distorted nature of the first layers applied.

TABLE II

Number of layers	Broadening			
	Obsd.		Av.	Calcd.
3	0.21	0.28	0.25	0.186
4	.27	.17	.22	.139
5	.10	.16	.13	.112
6	.15	.10	.13	.093
7	.04	.05	.05	.080
8	.06	.05	.06	.070
9	.05	.08	.06	.062
10	.05	.02	.04	.056
17	.04	.02	.03	.035
20	.02	.03	.03	.028
25	.01	.03	.02	.022
30	.02	.02	.02	.019
35	.02	.02	.02	.016

Summary

The structures of Blodgett's composite films of stearic acid and stearates have been investigated by x-ray diffraction methods. The structure and hence the thickness have been found to be that of the constituent present in greater proportion. The *d* spacings agree closely with those of the crystalline material.

Intensity measurements have been made from successively increasing numbers of planes and the degree of perfection inferred therefrom.

Laue's particle size equation has been tested by the use of films of known thickness.

URBANA, ILLINOIS RECEIVED AUGUST 6, 1936

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[6] B = breadth of interference at points of half-maximum intensity; b = apparatus constant for minimum width under experimental conditions; λ = x-ray wave length; θ = diffraction angle for given interference; D = size of particle, or thickness of film.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Reactions of Nickel Carbonyl with Oxides of Nitrogen[1]

BY J. C. W. FRAZER AND WM. E. TROUT, JR.[2]

M. Berthelot[3] passed nitric oxide into nickel carbonyl and obtained a solid product. Subsequent admission of small amounts of oxygen to the reaction vessel produced another solid. Berthelot characterized both solids as complex compounds but did not give analyses. Some confusion has arisen in the literature concerning these experiments, apparently due to the mistaken translation of "bioxyde d'azote" as nitrogen peroxide.[4] Attempts to determine the nature of the solids have not been wholly successful.[5,6]

This paper reports further observations concerning the reactions of nickel carbonyl with oxides of nitrogen.

Experimental

Nitrogen Peroxide and Nickel Carbonyl.—Nitrogen peroxide and nickel carbonyl reacted exothermally at temperatures as low as −78°. The reaction was carried out

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[1] Abstract of a dissertation submitted by Wm. E. Trout, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Johns Hopkins University.

[2] Present address: Department of Chemistry, Mary Baldwin College, Staunton, Virginia.

[3] Berthelot, *Compt. rend.*, **112**, 1343 (1891); *Bull. soc. chim.*, **7**, 431, 434 (1892).

[4] Muhlert, *Chem. Zentr.*, Vol. II, 1063 (1892); Gmelin–Kraut, "Handbuch d. anorg. Chem.," Heidelberg, Carl Winter, 1909, Vol. V, p. 107; Mellor, "Comprehensive Treatise of Inorganic Chemistry," Longmans, Green and Co., London, 1928, Vol. VIII, p. 546.

[5] Mond and Wallis, *J. Chem. Soc.*, **121**, 32 (1922).

[6] Reihlen, Gruhl, Hessling and Pfrengle, *Ann.*, **482**, 161 (1930).

in four ways: (1) nitrogen peroxide was permitted to expand into the vapor of nickel carbonyl at low pressures; (2) the gaseous reactants, transported in carbon monoxide or in nitrogen, were introduced into the reaction vessel in opposing jets; (3) nitrogen peroxide diluted with nitrogen was passed over liquid nickel carbonyl at or near 0°; (4) nitrogen peroxide was admitted to solutions of nickel carbonyl in hexane. Methods 2 and 3 appeared to be most satisfactory. Special care was taken to exclude air and moisture and to purify all materials.[1]

The gaseous products of this reaction contained as much as 97.8% of the carbon monoxide originally combined with the nickel in the reacting nickel carbonyl. Some carbon dioxide was detected, the amount appearing to vary with the rate of admission of nitrogen peroxide, or perhaps with the temperature attained by the glass near the reaction zone.

The solid products of the reaction were obtained as a light, bulky, greenish-yellow solid which adhered to the walls of the reaction vessel. When covered with liquid nickel carbonyl, the product was apparently insoluble and unchanged. Failure to obtain x-ray patterns of the solid suggested that the material was amorphous. The solid was hygroscopic, dissolving in the water absorbed, then appearing to hydrolyze to form a green gelatinous precipitate resembling nickelous hydroxide. When treated with dilute sulfuric acid, the solid readily dissolved and oxides of nitrogen escaped. This reaction was made use of in analysis. Analyses of the solid are indicated in Table I.

TABLE I

ANALYSES OF SOLIDS RESULTING FROM REACTION OF NICKEL CARBONYL WITH NITROGEN PEROXIDE

Numbers refer to methods of preparation listed above.

Sample no.	Percentage composition Ni	N	O
30[2]	36.43	17.55	47.82
31[2]	34.52	18.04	47.44
32[2,a]	35.50	17.26	47.24
34[2]	36.86	18.24	44.90
35[4]	32.25	18.84	48.91
36[4]	32.69	19.09	48.22
37[3]	35.20	17.88	46.92

[a] Adsorbed oxides of nitrogen were removed from this sample before analysis.

The ratio of nitrogen as nitrate to that as nitrite was determined on Sample 37 and was found to be: N (nitrate)/N (nitrite) = 0.7469.

Nitric Oxide and Nickel Carbonyl.—Reaction between these compounds was markedly *inhibited by carbon monoxide.* In the presence of carbon monoxide under partial pressure of approximately half an atmosphere, reaction between nitric oxide and *gaseous nickel carbonyl* was not detected below 62°, at which temperature a bronze film appeared on the heated glass. Addition of moisture to the gases did not alter the results. When nitrogen was substituted for the carbon monoxide, reaction between nickel carbonyl and nitric oxide began immediately but was soon retarded or stopped and was far from complete after twenty-four hours. Pure nitric oxide and gaseous nickel carbonyl reacted rapidly but incompletely at room temperature, although reaction was not detected at 0°.

When nitric oxide was passed over *liquid nickel carbonyl,* a greater pressure of carbon monoxide was necessary to inhibit the reaction than when both reactants were in gaseous form. When pure nitric oxide was passed over liquid nickel carbonyl at 0°, twenty-five and one-half hours were required for the preparation of a maximum yield of 0.2775 g. of the solid product mentioned below.

Reaction took place as usual between nitric oxide and nickel carbonyl at room temperature in a vessel from which the light was carefully excluded.

Analysis of the *gaseous products* of the reaction indicated that most of the carbon monoxide initially combined with the nickel was set free. A trace of carbon dioxide was detected.

Pure nitric oxide and liquid nickel carbonyl reacted at temperatures between −11 and 0° to form a blue gelatinous *solid product* which became pale blue, almost white, on removal of the excess liquid nickel carbonyl. At room temperature the reaction was complicated by the formation of bronze, brown or olive-green solids. Analyses of the solid products showed large variations as shown in Table II. The pale blue solid formed at 0° was insoluble in water, but dissolved readily in dilute sulfuric acid, liberating oxides of nitrogen. Concentrated sulfuric acid reacted slowly with the solid forming a yellow suspension and liberating oxides of nitrogen and traces of carbon monoxide and carbon dioxide. When heated in hydrogen a sample of the solid slowly turned brown: at 140° reaction was rapid, leaving a dark brown solid and liberating nitric oxide. When heated in oxygen another sample of the solid rapidly turned brown at 150° and nitrogen peroxide was formed. It is interesting to note that the similar solid prepared by Mond and Wallis[5] decomposed violently at 90° in an inert atmosphere.

TABLE II

ANALYSES OF SOLIDS RESULTING FROM REACTION OF NITRIC OXIDE WITH NICKEL CARBONYL

9, 10 prepared at room temperature; 11–13b at 0°

Sample no.	Percentage composition Ni	N	O
9	28.83	11.04	60.13
10	25.15	10.61	64.24
11	58.62	13.19	28.65
12	45.94	12.47	41.59
13a	39.19	14.35	46.46
13b	38.89	12.94	48.17

Ammonia, Nitric Oxide and Nickel Carbonyl.—In an attempt to stabilize the initially formed blue solid product of the reaction between nitric oxide and nickel carbonyl, ammonia at a partial pressure of 0.06 atm. was introduced into the nitric oxide and the resulting mixture was passed over liquid nickel carbonyl. Reaction occurred above −14° with the formation of a blue, gelatinous precipitate, lighter in color and more bulky than that obtained with nitric oxide alone. When the excess liquid nickel carbonyl was removed, a finely divided white solid remained, which dissolved readily in dilute sulfuric acid with the liberation of oxides of nitrogen. When exposed to the air the solid turned pink. Analyses of samples are indicated in Table III.

TABLE III

ANALYSES OF SOLIDS FORMED BY THE REACTION OF A MIXTURE OF NITRIC OXIDE AND AMMONIA WITH NICKEL CARBONYL

Sample no.	Percentage composition			
	Ni	NH_3	N (additional)	O
17	27.07	34.82	14.09	24.02
22	25.06	37.23	9.89	27.82

Ammonia and Nickel Carbonyl.—No reaction was detected with either gaseous or liquid reagents. The solubility of nickel carbonyl in liquid ammonia at its boiling point was apparently negligible.

Nitrogen Trioxide and Nickel Carbonyl.—Reaction of nitrogen trioxide with nickel carbonyl took place at −78° with the formation of a bright red solid, apparently formed only at temperatures at which the molecule N_2O_3 exists. The solid slowly lost its bright red color and became reddish-yellow when warmed to 60°. We were unable to analyze the red compound, but obtained a brown solid (apparently formed by the action of nitrogen peroxide on the red solid) which had the composition: Ni, 28.95; N, 22.95; O, 48.10.

Nitrous Oxide and Nickel Carbonyl.—Reaction between these substances was not observed at 0°, and at room temperature the rate of reaction was negligible. A mixture of nitrous oxide and gaseous nickel carbonyl exploded when ignited with a gas flame.

Nitric Oxide, Nickel Chloride and Grignard Reagents.—Nitric oxide was passed through suspensions formed by addition of nickel chloride (1) to an ether and benzene solution of phenylmagnesium bromide,[7] and (2) to an ether solution of ethylmagnesium bromide. The green solution obtained in the latter experiment was not as intense in color as that in the former. Attempts to isolate the green substances were unsuccessful due to their high solubility and sensitivity to air. That Job and Reich,[7] as they suggested, prepared the compound obtained by Mond and Wallis,[5] is made doubtful by the facts that the green substance in solution was not decomposed by dilute sulfuric acid, and that oxides of nitrogen were not liberated by this treatment.

Discussion of Results

The temperatures at which reaction was first detected between nickel carbonyl and oxides of nitrogen studied were roughly in the inverse order of the degree of oxidation of the nitrogen atom: NO_2, −78°; N_2O_3, −78°; NO, −11°; N_2O, above room temperature.

Nitrogen peroxide reacted with nickel carbonyl at −78° and above to form a solid in which the ratio of nitrate to nitrite was in agreement with the assumption that the solid consisted of a mixture of the nickel salts of these ions (calculated for $Ni(NO_2)_2 \cdot 0.7469Ni(NO_3)_2$, Ni, 35.20%: found Ni, 35.71). Most of the carbon monoxide combined with the nickel was liberated as such. The products of the reaction in hexane contained more nitrogen and oxygen than samples obtained by other methods.

Nitrogen trioxide reacted with nickel carbonyl apparently at temperatures at which the molecule N_2O_3 exists. The behavior of this solid suggests the possibility that it is an addition product.

Nitric oxide reacted with nickel carbonyl above −11° to liberate carbon monoxide and traces of carbon dioxide and to form solids which varied greatly in composition, even when prepared in consecutive vessels under the same conditions (13a and 13b, Table II). It will be noticed that the solid obtained at room temperature contained less nickel than that formed at 0° (9, 10, Table II).

The marked inhibiting effect of carbon monoxide on the reaction between nickel carbonyl and nitric oxide is somewhat similar to that reported by Dewar and Jones[8] on the reaction between nickel carbonyl and carbon disulfide. The phenomena in both cases are probably, as these authors suggested, explained by the influence of carbon monoxide on the stability of the nickel carbonyl in accordance with its reversible decomposition.

$$Ni(CO)_4 \rightleftarrows Ni + 4CO$$

for which the equilibrium relationship is

$$K = P_{Ni} \times P^4_{CO}/P_{Ni(CO)_4}$$

The possibility is suggested that the nitric oxide reacts not entirely with the nickel carbonyl but with its products of decomposition.

The appearance, analyses and manner of formation of the solids formed by the action of ammonia and nitric oxide on nickel carbonyl suggests the formation of complex compounds, such as $[Ni(NH_3)_5NO]NO_2$ and $[Ni(NH_3)_5NO]NO_3$ (Ni: calcd., 26.69 and 24.88%; found, 27.07 and 25.06%).

Ammonia did not react with nickel carbonyl at 0°, and the reaction between ammonia, nitric oxide and nickel carbonyl began at the same temperature as that between nitric oxide and nickel carbonyl. These facts suggest that the nickel carbonyl first reacts with the nitric oxide to form a product which further reacts with ammonia to form a complex compound, perhaps as indicated in the tentative equations

$$Ni(CO_4) + 2NO \longrightarrow Ni(NO)_2 + 4CO$$
$$Ni(NO)_2 + 5NH_3 \longrightarrow [Ni(NH_3)_5NO]NO$$

The $[Ni(NH_3)_5NO]NO$ may then be oxidized to form the compounds $[Ni(NH_3)_5NO]NO_2$ and

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[7] Job and Reich, *Compt. rend.*, **177**, 1439 (1923).

[8] Dewar and Jones, *J. Chem. Soc.*, **97**, 1226 (1910).

$[Ni(NH_3)_5NO]NO_3$. Briner and co-workers[9] have found that nitrogen peroxide is formed slowly in pure nitric oxide under pressure at ordinary temperature, and also in liquid nitric oxide under atmospheric pressure below its boiling point. The presence in the reacting gases of nitrogen peroxide so formed may explain the oxidation of the complex compound first formed, and may also explain the failure to obtain a pure solid product from the reaction of nitric oxide with nickel carbonyl.

In view of the unexplained erratic behavior of oxygen and nickel carbonyl,[10] the observations concerning mixtures of nitrous oxide and nickel carbonyl cannot be taken as final. Nitrous oxide may react equally unpredictably with nickel carbonyl.

Acknowledgments.—The authors wish to acknowledge their indebtedness to Drs. C. B. Jackson and O. G. Bennett for assistance in the preparation of the nickel carbonyl used, and to Messrs. P. M. Goodloe, J. H. Hopkins and J. W. Daum for assistance in the laboratory.

Summary

Some observations have been reported concerning the reactions of nickel carbonyl with nitrogen peroxide, nitric oxide, nitrous oxide, ammonia and a mixture of ammonia and nitric oxide.

The suggested relationship of the results of Job and Reich[7] to those of Mond and Wallis[5] was also investigated.

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[9] Briner, *et al.*, *Compt. rend.*, **149**, 1372 (1909); **156**, 228 (1931); *J. chim. phys.*, **23**, 157 (1926).

[10] Hieber and Kaufmann, *Z. anorg. allgem. Chem.*, **204**, 174 (1932); Berthelot, *Bull. soc. chim.*, **7**, 434 (1892); *Compt. rend.*, **113**, 679 (1892); Lenher and Loos, THIS JOURNAL, **22**, 114 (1900); Blanchard and Gilliland, *ibid.*, **48**, 872 (1926).

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, STATE UNIVERSITY OF IOWA]

Antioxidants and the Autoxidation of Fats. VII. Preliminary Classification of Inhibitors[1]

BY H. S. OLCOTT AND H. A. MATTILL

It was recently proposed[2] to give the name "inhibitols" to those as yet unidentified constituents of the unsaponifiable matter of various vegetables and vegetable oils which possess the capacity to delay oxidative rancidity in certain fats. This term indicates their activity as inhibitors and also the invariable occurrence of hydroxyl groups upon which their inhibiting action depends. Methods of preparation of inhibitol concentrates and some of their physical and chemical properties have been described in some detail.[2]

Inhibitol concentrates are effective antioxidants for animal fats and for highly purified unsaturated fatty acids and esters, but they have consistently failed to show any antioxygenic activity when added, even in relatively large amounts, to the vegetable oils from which they were obtained (Table I). The inactivity of inhibitols in vegetable oils is also implied in the experiments of Royce,[3] who added a crude sterol fraction of cottonseed oil to hydrogenated cottonseed oil without observing any prolongation of the induction period, in those of Greenbank and Holm[4] who reported an unsuccessful attempt to isolate an antioxidant from cottonseed oil, using vegetable oils as the assay substrate, and in those of Bau-

TABLE I

EFFECT OF INHIBITOLS ON DIFFERENT FATS

Substrate	Per cent. inhibitol concentrate added[a]	Induction period, days With inhibitor	Control
	Organoleptic method, 63°		
Cottonseed oil	0.10 C58	3.5, 4	4, 4.5
	.05 W5–10	3	3.5
	.05 W5–10	$6^1/_2$	8
	.05 C44	$8^1/_2$	8
Hydrogenated cottonseed oil	.02 W48	27, 31	28, 32
	.03 W5–10	42, 49	41, 49
Lard	.02 W5–10	9, 9	3, 3
	.01 W5–10	10.5, 11	4, 4
	Oxygen absorption method, 75°		
		Hrs.	Hrs.
Lard[b]	0.02 W5–10	50	10
Oleic acid	.03 W5–10	10	4
Methyl oleate	.02 W5–10	30	4

[a] W indicates wheat germ oil inhibitol, C that from cottonseed oil. [b] See also reference 2, Tables V and VI.

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[1] Presented before the Division of Agricultural and Food Chemistry at the 92nd meeting of the American Chemical Society, Pittsburgh, Pa., September 7 to 11, 1936.

[2] H. S. Olcott and H. A. Mattill, THIS JOURNAL, **58**, 1627 (1936).

[3] H. D. Royce, *Oil and Soap*, **9**, 25 (1931).

[4] G. R. Greenbank and G. D. Holm, *Ind. Eng. Chem.*, **26**, 243 (1934).

mann and Steenbock[5] who found that, in cottonseed oil, carotene losses were not reduced by an inhibitol-containing material like wheat germ oil.

These facts prompted an investigation of the factor or factors in the vegetable oils responsible for their refractoriness to protection by inhibitols and conversely, a study of the types of inhibitors which could protect these oils. The experiments to be described deal with the second of these two questions. Refined and hydrogenated cottonseed oils were used in most of the experiments, but the same phenomena were also demonstrable with palm, sesame, soy bean and other vegetable oils.

The oxygen absorption method which we have used[6] in the study of lard and its protection by inhibitors could not be applied satisfactorily to the study of vegetable oils. Whereas lard demonstrates a definite induction period after which the absorption of oxygen is rapid, vegetable oils absorb oxygen slowly and the end of the induction period is not sharply defined. Furthermore, vegetable oils are more stable than lard so that the oxygen absorption method is time consuming unless high temperatures are used. Since, in our hands, a temperature of 70–80° has proved to be a convenient one at which to measure oxygen absorption, we investigated several methods of reducing the induction period of these oils to convenient lengths at 75°, attempting at the same time to retain the properties of the original oils with regard to inhibitors, especially their absolute refractoriness to protection by inhibitols.

The most satisfactory method proved to be the use of the ethyl esters of the fatty acids, prepared as follows. Two parts of absolute alcohol containing 2–3% hydrogen chloride were added to one part of the fat and refluxed on a steam-bath for eighteen to twenty-four hours. The mixture was cooled and diluted with water. The ester layer was washed repeatedly with water to remove hydrochloric acid and ethyl alcohol, then centrifuged free from occluded water, and finally heated on a steam-bath in a vacuum to remove traces of solvents. Theoretically this light brown, mobile liquid, hereafter referred to as crude esters, contained the ethyl esters of the fatty acids, the unsaponifiable constituents of the original fat and possibly traces of unhydrolyzed glycerides; the glycerol and any water-soluble constituents should have been removed.

The product so obtained from a hydrogenated cottonseed oil could be used to assay inhibitors by the oxygen absorption method, since it had a convenient induction period at 75° (four to sixteen hours), and a rapid rate of oxygen absorption at the end. Furthermore, the protection afforded the crude esters by various inhibitors was qualitatively parallel to that conferred on the original fat; the crude esters were not protected by relatively large amounts of inhibitol concentrates but were protected to a remarkable degree by several substances which have been suggested for use as antioxidants in vegetable fats, namely, oxalic acid,[7] maleic acid,[4] sulfuric and phosphoric acids and their acid salts,[8] and lecithin.[9,10]

The effectiveness of so many substances that are alike only in the possession of an ionizable hydrogen atom prompted an investigation of the antioxygenic activity of other acids, both organic and inorganic. The results, summarized in Table II, permit of no generalizations, but suggest certain interesting relationships. In the aliphatic series, pyruvic acid is the only active compound not containing two free carboxyl groups; the adjacent carbonyl apparently has an activating effect. The two carboxyl radicals must not be separated by more than one CH_2 group unless an active group or groups, such as hydroxyl, or an unsaturated bond is also present. The inactivity of the salts and esters of the dicarboxylic acids indicates that the carboxyl groups must be free. Among the inorganic acids tested, sulfuric and phosphoric acids were the only ones to show marked antioxygenic action. Calcium acid phosphate was effective in contrast to the inactivity of the sodium and potassium salts, presumably due to its greater acidity. Any explanation of the action of these acids must take account of the fact that the medium in which they act is practically anhydrous. The solubility of cephalin doubtless accounts in part for its efficiency.

With the exception of hydroquinone, the phe-

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(5) C. H. Baumann and H. Steenbock, *J. Biol. Chem.*, **101**, 561 1933).

(6) R. B. French, H. S. Olcott and H. A. Mattill, *Ind. Eng. Chem.*, **27**, 724 (1935).

(7) T. H. Rogers, U. S. Patent 1,826,258; *C. A.*, **26**, 613 (1932).

(8) E. W. Eckey, U. S. Patent 1,982,907; 1,993,152; A. S. Richardson, F. C. Vibrans and J. T. R. Andrews, U. S. Patent 1,993,181; *C. A.*, **29**, 518, 2770 (1935).

(9) H. Bollman, U. S. Patent 1,464,557; *C. A.*, **17**, 3234 (1923).

(10) The antioxygenic action of commercial lecithin has been shown to be due to its contained cephalin, and the activity of cephalin in turn, appears to depend on the monobasic phosphoric acid radical [H. S. Olcott and H. A. Mattill, *Oil and Soap*, **13**, 98 (1936)].

TABLE II

THE ANTIOXYGENIC EFFECT OF ACIDIC AND PHENOLIC COMPOUNDS ON THE CRUDE ESTERS OF HYDROGENATED COTTONSEED OIL

Inactive Compounds[a]

Hydrochloric acid
Hydrobromic acid
Hydriodic acid
Iodic acid
Nitric acid
Boric acid
Arsenious oxide
Tungstic oxide
Sodium dihydrogen phosphate
Potassium dihydrogen phosphate
Formic acid
Acetic acid
Lactic acid
Succinic acid
Adipic acid
Mucic acid
Azelaic acid
Dihydroxystearic acid
Aspartic acid
Benzoic acid
Phthalic acid
Isophthalic acid
α-Naphthoic acid
β-Naphthoic acid
d-Camphoric acid
Tannic acid
Ethyl oxalate
Ethyl malonate
Ethyl tartrate
Sodium bitartrate
Sodium oxalate
Oxamide
Inhibitol concentrates

Active Compounds and Indices[b]

Sulfuric acid (95%)[c]	15–20	Maleic acid	4–6
Phosphoric acid (85%)[c]	15–20	Citric acid	10–15
Calcium dihydrogen phosphate	4–6	Malic acid	8–12
Cephalin	4–6	Pyruvic acid	10–15
Perchloric acid	3	Hydroquinone	1.2–1.6
Arsenic acid	3	Catechol	12
Oxalic acid	15–20	Pyrogallol	26
Malonic acid	10–15	α-Naphthol	9
Tartaric acid	10–15	1,5-Naphthalenediol	5

[a] For the most part these compounds were assayed by adding 1 mg. to 5 g. of the crude esters (0.02%). The induction period of the "protected" sample was never more than twice that of the control sample; in most cases, no antioxygenic action could be observed. When 5 mg. was used (0.1%), some of the compounds exhibited slight antioxygenic activity. Among these were lactic and phthalic acids, sodium and potassium dihydrogen phosphates, and ethyl tartrate.

[b] The index represents the ratio of the induction period with inhibitor to that of the control. For example, the data for several runs of tartaric acid: with inhibitor, 130, 100, 170 hours; without, 6, 9, 10. Most of the inhibitors were assayed at a 0.02% level. 1,5-Naphthalenediol was tested at 0.01%. All results were obtained at 75°.

[c] Dilution of the sulfuric and phosphoric acids with an equal amount of water did not decrease their activity.

nolic inhibitors were relatively as active on the ester preparations as on lard.[11,12]

The reactions of the vegetable oil crude esters to inhibitors thus provided an entirely different picture from that presented by lard and purified fatty acids, in which the acid inhibitors mentioned above are only very slightly antioxygenic if at all, while the phenolic inhibitors and the inhibitols are very efficient.[2] Crude methyl and ethyl esters prepared from lard responded to inhibitors in the same manner as did the original lard (Table III), indicating that the process of esterification was not responsible for the reaction toward inhibitors of the vegetable oil esters. Crude methyl esters of the vegetable oils reacted exactly like those prepared with ethyl alcohol.

TABLE III

THE EFFECT OF INHIBITORS ON LARD AND ON THE CRUDE ESTERS OF LARD

Substrate	% inhibitor added	Induction period, hours: With inhibitor	Induction period, hours: Control
Lard (75°)	0.20 cephalin	8	5
	.20 tartaric acid	15	9
	.20 malonic acid	13	9
	.20 citric	16	11
	.20 phosphoric acid	19	10
	.20 oxalic acid	38	13
	.20 W5-10	62	15
	.01 hydroquinone	410	14
Crude methyl esters of lard (60°)	.20 cephalin	10	9
	.20 tartaric acid	14	9
	.10 W5-10	45	9
Crude ethyl esters of lard (65°)	.10 tartaric acid	4	2
	.10 malonic acid	4	1.5
	.10 citric acid	4	1.5
	.10 phosphoric acid	5	1.5
	.10 oxalic acid	25	2
	.10 W5-10	12	1.5
	.02 hydroquinone	60	2

When the crude esters were distilled *in vacuo*, 95% distilled below 160° at 0.1 mm. The properties of the water-white distillate, with regard to its amenability to protection by various inhibitors, were strikingly different from those of the crude esters. The inhibitols were effective, although not as active as in lard. Hydroquinone was an efficient inhibitor, and the dibasic and inorganic acids were relatively ineffective (Table IV). This table also demonstrates the same significant difference in the reactions of palm oil esters to different inhibitors before and after distillation.

From these results it is apparent that, unless some destruction or alteration occurred during the distillation, the residue should contain compounds which could (a) inhibit the antioxygenic activity of inhibitols and hydroquinone and (b) activate the acid type inhibitors.

It was possible to demonstrate (b) but not (a) by adding small amounts of the residue to the distilled esters. The acid type inhibitors were effec-

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(11) H. A. Mattill, *J. Biol. Chem.*, **90**, 141 (1931).

(12) H. S. Olcott, THIS JOURNAL, **56**, 2492 (1934).

TABLE IV

THE EFFECT OF INHIBITORS ON THE DISTILLED ESTERS OF HYDROGENATED COTTONSEED OIL, AND ON THE CRUDE AND DISTILLED ESTERS OF PALM OIL

Substrate	% inhibitor added	Induction period, hrs. With inhibitor	Control
Distilled ethyl esters of hydrogenated cottonseed oil	0.02 citric acid	3	3
	.20 tartaric acid	6	6
	.02 maleic acid	4	3
	.20 cephalin	5.5	6
	.10 malonic acid	6	6
	.10 W5–10	52	6
	.02 hydroquinone	77	2
Palm oil crude ethyl esters	.02 tartaric acid	94	11
	.10 W5–10	11	11
	.02 hydroquinone	16	11
Distilled ethyl esters of palm oil	.02 tartaric acid	18	6
	.10 W5–10	24	6
	.02 hydroquinone	280	6

TABLE V

EFFECT OF MIXTURES OF INHIBITORS ON VARIOUS SUBSTRATES

% inhibitor added	Induction period, hrs. With inhibitor	Control
Distilled ethyl esters of hydrogenated cottonseed oil		
0.04 W5–10	9.5	5
.10 tartaric acid	8	5
.04 W5–10 + 0.10% tartaric acid	148	5
.02 W5–10	7.5	5
.10 cephalin	4	5
.02 W5–10 + 0.10% cephalin	78	5
.02 citric acid	3.5	3
.02 W5–10 + 0.02% citric acid	98	3
.02 H_3PO_4	4.5	4
.02 W5–10 + 0.02% H_3PO_4	73	4
Lard		
0.02 W5–10	30	7
.10 tartaric acid	17	7
.02 W5–10 + 0.10% tartaric acid	84	7
.10 cephalin	5	7
.02 W5–10 + 0.10% cephalin	69	7
.10 malonic acid	5	4
.02 W5–10 + 0.10% malonic	89	4
.02 $Ca(H_2PO_4)_2{\cdot}H_2O$	11	10
.02 W5–10 + 0.02% $Ca(H_2PO_4)_2{\cdot}H_2O$	93	10
Palm oil fatty acids		
0.10 W5–10	8	3
.10 tartaric acid	7	3
.10 W5–10 + 0.10% tartaric acid	88	3
Methyl oleate		
0.02 W5–10	22	10
.02 W5–10 + 0.1% tartaric acid	136	10
Octadecene		
0.10 W5–10	86	13
.10 tartaric acid	13	13
.10 W5–10 + 0.10% tartaric acid	304	13

tive for this mixed substrate but the antioxygenic action of inhibitols was not suppressed. A series of investigations designed to determine the nature of the compound present in the residue and responsible for the activation of the acid type inhibitors, disclosed that it occurred in the nonsterol unsaponifiable fraction and that it was destroyed by acetylation but not by hydrogenation. These were also properties of the inhibitols, and it was possible to demonstrate that a highly concentrated inhibitol fraction exhibited this remarkable synergism with acid type inhibitors when the distilled esters of hydrogenated cottonseed oil were used for the substrate fat (Table V). Apparently the inhibitol originally present in the vegetable oil and remaining in the residue when the crude esters were distilled, is responsible for the activation of the acid type inhibitors in the crude esters.

This synergistic effect of inhibitol and some one of the acid inhibitors could also be demonstrated in lard, purified fatty acids and esters and octadecene (Table V), but not in vegetable oils.

The close relationship between hydroquinone and the inhibitols led to an investigation of the effect of mixtures of phenolic and acid inhibitors. The synergistic effect could easily be demonstrated, for example, with orcinol and phosphoric acid (Table VI). Other combinations of phenolic and acidic inhibitors varied in their effectiveness. Citric and tartaric acids did not show the synergistic effect with orcinol when assayed on lard fatty acids.

It is thus apparent that the observation of Holmes, Corbet and Ragatz[13] on the superior stabilizing effect of combinations of lecithin and hydroquinone on vitamin A over that of either alone, is only an individual case of a more or less general phenomenon.

Based upon our experiments we have tentatively classified the inhibitors studied into three groups: (1) the acid type inhibitors, (2) inhibitols and hydroquinone, and (3) the phenolic type including α-naphthol, pyrogallol, catechol and others. Table VII outlines the qualitative differences in behavior of these kinds of inhibitors on various substrates. The boundaries between the three types are not especially well defined. For example, oxalic acid has a definite antioxygenic action on lard, greater than that of the other acid type inhibitors. The anomalous behavior of hy-

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[13] H. N. Holmes, R. E. Corbet and R. A. Ragatz, *Ind. Eng. Chem.*, **28**, 133 (1936).

TABLE VI

SYNERGISTIC EFFECT OF ORCINOL AND PHOSPHORIC ACID

Substrate	% inhibitor added	Induction period, hrs. With inhibitor	Induction period, hrs. Control
Lard (75°)	0.02 orcinol	75	12
	.10 phosphoric acid	21	12
	.02 orcinol + 0.10% phosphoric acid	314[a]	12
Lard fatty acids (60°)	.02 orcinol	29	2.5
	.10 phosphoric acid	5	2.5
	.02 orcinol + 0.10% phosphoric acid	300[a]	2.5
	.02 orcinol + 0.10% citric acid	30	2.5
	.02 orcinol + 0.10% tartaric acid	41	2.5

[a] When discontinued, these samples were still fresh.

droquinone in contrast to the other phenolic inhibitors is in accord with the observations of others concerning hydroquinone in gasoline.[14]

TABLE VII

QUALITATIVE DIFFERENTIATION OF THREE TYPES OF INHIBITORS

	Acid type[a]	Inhibitols and hydroquinone[b]	Phenolic type[c]
Vegetable oils	+	−	+
Crude vegetable oil esters	+	−	+
Distilled vegetable oil esters	−	+	+
Lard and lard esters	−	+	+
Purified fatty acids and esters	−	+	+

[a] Oxalic acid protects lard to an appreciable extent (Table III).

[b] Hydroquinone is effective in vegetable oils, but is included in this grouping because it is relatively ineffective on crude vegetable oil esters.

[c] Includes some natural products, such as gossypol, gallic acid, as well as catechol, pyrogallol, α-naphthol, etc.

In general, any type 1 inhibitor when used with any type 2 or 3 compound, prolongs the induction period of certain fats and other unsaturated compounds to a much greater extent than would be expected from a summation of the effects of each used alone.

There is, of course, an almost infinite number of possible combinations of antioxidants, some of which should be utilizable not only in the edible fat industry, but wherever compounds or mixtures are subject to oxidative deterioration.

In conclusion, it may again be emphasized that the complex reactions which result in rancidity are subject to many factors, some unknown, which operate to make duplication of results uncertain at times. The data recorded in this paper are merely representative of those obtained from a large number of experiments and assays.

Further observations on the causes of the fundamental differences between vegetable and animal fats, with respect to their reactions toward different inhibitors, will appear in subsequent publications.

Acknowledgment.—The authors are indebted to Lever Brothers Company for a grant in support of this work and to Dr. Lyle A. Hamilton for technical assistance.

Summary

The crude esters of hydrogenated cottonseed and other vegetable oils, prepared by refluxing the oil with absolute methyl or ethyl alcohol containing dry hydrogen chloride, are protected to a remarkable degree by oxalic, malonic, maleic, citric and other aliphatic dibasic acids, by phosphoric and sulfuric acids and cephalin, and by some phenolic inhibitors. Hydroquinone is only slightly effective and inhibitol concentrates prepared from the unsaponifiable fraction of vegetable oils are inactive.

When the esters are partially purified by fractional distillation *in vacuo*, they are only slightly protected by the acids or cephalin, but are protected by hydroquinone and the inhibitols.

The acid inhibitors and inhibitol concentrates have a pronounced synergistic effect when used together in the distilled ester preparation; the protection afforded by the mixture is much greater than by either alone. This phenomenon can also be demonstrated in lard, and in purified fatty acids and esters, and also with certain mixtures of phenolic and acid type inhibitors.

Based upon these observations, a tentative classification of inhibitors into three groups is proposed: Group 1, acid type inhibitors; Group 2, inhibitols and hydroquinone; Group 3, other phenolic inhibitors.

IOWA CITY, IOWA

RECEIVED SEPTEMBER 2, 1936

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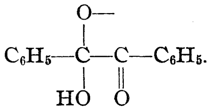
(14) C. D. Lowry, Jr., G. Egloff, J. C. Morrell and C. G. Dryer, *Ind. Eng. Chem.*, **25**, 804 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Kinetics of the Benzilic Acid Rearrangement

BY F. H. WESTHEIMER[1]

Introduction

In 1932 Whitmore[2] advanced a general theory which postulated a positive ion as the intermediate in all molecular rearrangements. Not only a large amount of qualitative evidence, but also the quantitative work of Meerwein,[3] support this hypothesis, at least for the Wagner–Meerwein (retropinacol) rearrangement. Ingold,[4] in 1928, put forth another general theory of rearrangements in which a negative ion was assumed as the intermediate; later[5] he pointed out that it is difficult to reconcile Whitmore's views with the facts of the benzilic acid rearrangement. The present work, a quantitative study of the benzilic acid rearrangement, supports Ingold's contention that the intermediate is the negative ion  $C_6H_5\text{—}\overset{\text{O—}}{\underset{\text{HO}}{C}}\text{—}\underset{\text{O}}{\overset{}{C}}\text{—}C_6H_5$. Another study, which will be presented elsewhere, deals with the rearrangement of benzil *o*-carboxylic acid, especially as concerns the salt effect.

Method

Lachman,[6] in 1924, showed that there are three reactions which take place when benzil, in aqueous alcoholic solution, is treated with alkali

$$C_6H_5COCOC_6H_5 + KOH \longrightarrow (C_6H_5)_2COHCOOK$$
$$C_6H_5COCOC_6H_5 + KOH \longrightarrow C_6H_5COOK + C_6H_5CHO$$
$$2C_6H_5COCOC_6H_5 + C_2H_5OH \longrightarrow C_{30}H_{24}O_4$$

The second of these three reactions, a cleavage, goes on only in the presence of alcohol, and to the extent of only a few per cent. when the alcohol is less than half of the total solvent. The third reaction, the production of "ethyl dibenzil," also a minor reaction, again occurs only in the presence of alcohol. The structure of "ethyl dibenzil"[7] is unknown. The first reaction, the rearrangement of benzil to benzilic acid, is quantitative in aqueous solution; in aqueous alcohol yields of 90–95% are obtained. Since benzil, even in the absence of salt, is soluble only to the extent of 0.3 g./l. at 100°, it was necessary to employ 32% alcohol in this kinetic study. The secondary reactions interfered but slightly with the results obtained.

The rate of rearrangement of benzil was measured at 100° in 32% alcoholic solutions of potassium and barium hydroxides, and in phenol-phenolate ion and *o*-chlorophenol-*o*-chlorophenolate ion buffers. While many studies have been made of the *pK* of phenol and chlorophenol at room temperature,[8] the value of these constants at 100° was unknown. In order to ascertain the hydroxyl ion concentrations of the buffer solutions, the hydrolysis constants of phenolate and of *o*-chlorophenolate ions were measured at 100° in 32% alcohol by conductivity.

Ampoules, filled with the reacting solution, were removed from the thermostat at stated times for analysis. Since it would have been difficult if not impossible to determine the concentration of benzilic acid, acidimetrically, by difference, especially in the buffered solutions, an extraction method was employed. The contents of the ampoules were acidified and the organic matter brought into ether using a continuous extractor. Subsequently the ether was distilled off, the benzilic acid taken up in alcohol–water and titrated with 0.01 *M* carbonate-free alkali, using thymol blue as the indicator. When buffered solutions were employed, they were neutralized, bicarbonate solution added, and the mixture extracted. This removed the phenol or *o*-chlorophenol; after acidifying again, the benzilic acid was obtained by a second extraction.

A difficulty, encountered in connection with the buffers, was the air oxidation of the alkaline phenol solution. This produced a red indicator-type dye which effectively obscured the thymol blue end-point. It was impossible to obtain consistent results until the ampoules were evacuated and filled with nitrogen before sealing. The ampoules were of a type which prevented mixing of the phenol with the alkali until they were inverted.

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(1) National Research Fellow in Chemistry.

(2) Whitmore, THIS JOURNAL, **54**, 3274 (1932).

(3) Meerwein and van Emster, *Ber.*, **53**, 1815 (1920); *ibid.*, **55**, 2500 (1922).

(4) Ingold, *Ann. Rep. Chem. Soc.*, **25**, 124 (1928).

(5) Ingold, *ibid.*, **30**, 177 (1933).

(6) Lachman, THIS JOURNAL, **46**, 779 (1924).

(7) Jena, *Ann* , **155**, 77 (1870); Owens and Japp, *Am. Chem. J.*, **7**, 16 (1885–86).

(8) Murray and Gordon, THIS JOURNAL, **57**, 110 (1935), and references contained therein.

TABLE I

TYPICAL VELOCITY DETERMINATION

Cc. stands for the number of cc. of 0.01 *M* potassium hydroxide used in titration, x, for the concentration of benzilic acid, $a - x$ the concentration of benzil, $b - x$ the concentration of potassium hydroxide present at any time; t is quoted in minutes. The standard equation, employing natural logarithms, was used for the calculation.

Cc.	x	$a - x$	$b - x$	$\text{Log}\,\frac{a\,(b - x)}{b\,(a - x)}$	D		$k \times 10$	Dev.
2.72	0.00149	0.00505	0.0485	0.099				
4.06	.00222	.00432	.0478	.160	0.061	15.2	2.13	0.18
5.00	.00274	.00380	.0473	.211	.112	33.3	1.78	.17
5.91	.00323	.00331	.0468	.267	.168	45.7	1.94	.01
6.62	.00362	.00292	.0464	.319	.220	61.3	1.89	.06
7.48	.00409	.00245	.0459	.389	.290	76.8	2.00	.05
						Average	1.95	0.09 or 5%

Since the analyses proved accurate to 1%, velocity constants could be obtained.

Experimental

The thermostat is a large copper tank designed as in Fig. 1. A hot plate boils water in the lower compartment. Steam fills the boiler, heats the wells (which are filled with paraffin) and the condensate is returned from the reflux to the lower compartment. The cold end of the condenser is attached to a pressure regulator, of the type designed by Coffin,[9] with picein. By maintaining constant pressure, constant temperature was assured. The thermostat, which required no attention whatsoever, operated at 100.04 ± 0.03° for a period of five months. The absolute temperature was determined with a Bureau of Standards calibrated thermometer.

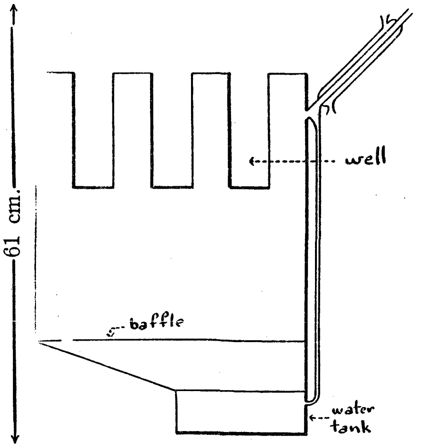

Fig. 1.—The thermostat.

Conductivity Apparatus.—The conductivity cell was a Washburn[10] type B cell, made of Jena glass, with 1.3-cm. smooth platinum electrodes 8 cm. apart. The conductivity apparatus was of the standard Washburn type.

Extractors were designed as in Fig. 2. They were constructed entirely of glass, using interchangeable ground-glass joints. Blanks showed that benzilic acid, introduced with alcohol as in the actual experimental conditions, could be removed quantitatively in one hour. The precision was 1%. When buffers were used, the solution was brought to the methyl orange end-point, and 10 cc. of 0.1 *M* sodium bicarbonate solution added. The solution was extracted for two hours in the case of phenol, three hours in the case of *o*-chlorophenol. Three cc. of 1 *M* hydrochloric acid was then added through the funnel and the solution extracted for one hour after the acid had permeated the entire aqueous layer (as shown by the methyl orange color). Blanks showed that this method removed the benzilic acid from phenol with an accuracy of 1%.

Materials.—The benzil was an Eastman chemical, recrystallized twice from carbon tetrachloride, twice from alcohol. The corrected m. p. was 94.4°. Eastman chlorophenol was three times vacuum distilled from an ordinary Claisen flask; the corrected freezing point was 9.1° over a few hundredths of a degree range. After five vacuum distillations and subsequent fraction freezing, Eastman recrystallized phenol froze at 40.5° over 0.1° range. The alcohol was freed of aldehyde by the method of Dunlap.[11] All salts were recrystallized from water. Only carbonate-free alkali was employed.

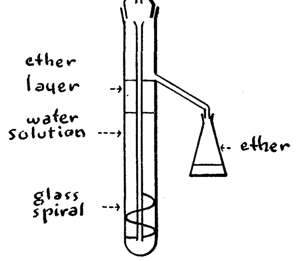

Fig. 2.—Continuous extractor.

Results

The reaction between benzil and OH^- ion is bimolecular. This conclusion is based not only on the fact that a constant is obtained with a bimolecular equation, but also on the fact that the constant remains sensibly the same while the concentrations of the reactants are varied tenfold. The small deviations observed which are outside the possible experimental error may be due to the fact that the side reactions, referred to above,

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(9) Coffin, THIS JOURNAL, **55**, 3646 (1933); Crist and Roehling, *ibid.*, **57**, 2196 (1935).

(10) Washburn, *ibid.*, **38**, 2431 (1916); Washburn and Parker, *ibid.*, **39**, 235 (1917).

(11) Dunlap, *ibid.*, **28**, 395 (1906)

are more prominent in one case then in the other. A typical run, in which the average deviation is of the usual magnitude, is recorded.

The rate constants obtained using varying initial concentrations of benzil and of hydroxyl ion (but a constant ionic strength of 0.3) are shown in Table II.

TABLE II

BIMOLECULAR RATE CONSTANT FOR THE BENZILIC ACID REARRANGEMENT

Concn. of benzil	Concn. of KOH	Concn. of KCl	k
0.008	0.15	0.150	2.17×10^{-1}
.006	.05	.250	1.95×10^{-1}
.006	.015	.285	1.79×10^{-1}
.003	.005	.295	2.12×10^{-1}
.02	.05	.250	1.85×10^{-1}

While the variation is somewhat greater than the experimental error, it is indeed small for a tenfold change in the concentration of both reactants. Such variation as there is in the rate constant with change in hydroxyl-ion concentration must be discounted in view of the evidence, reported below, obtained with buffered solutions. A small change in the extent of the side reactions with increasing concentration of benzil would account for that part of the variation in the constant which exceeds the experimental error. The effect of increased salt concentration upon the reaction is small, but positive, as is shown in Table III.

TABLE III

THE SALT EFFECT IN THE REARRANGEMENT OF BENZIL

Concn. of benzil	Concn. of OH⁻	Concn. of KCl	μ	k
0.008	0.05		0.05	1.89×10^{-1}
.006	.05	0.25	.30	1.97×10^{-1}
.007	.05	.70	.75	2.15×10^{-1}

If the reaction is truly a bimolecular one between benzil and hydroxyl ion, the rate should be the same regardless of what metallic hydroxide is employed. In solutions of low ionic strength, the rate with barium hydroxide indeed proved approximately equal to that with potassium hydroxide; there is, however, a large positive salt effect with increased concentration of barium chloride. The results are tabulated below.

TABLE IV

THE SALT EFFECT WITH BARIUM CHLORIDE ON THE REARRANGEMENT OF BENZIL

Concn. of benzil	Concn. of OH⁻	Concn. of $BaCl_2$	μ	k
0.006	0.0100		0.015	2.61×10^{-1}
.007	.0100	0.050	.165	3.69×10^{-1}
.007	.0100	.242	.740	5.13×10^{-1}

In buffered solution, the pseudomonomolecular rate constants drifted to lower values of k as the run progressed. Some, at least, of this effect was due to the fact that the buffer does not hold the hydroxyl ion concentration constant, but this concentration diminishes during the run. It is, however, possible to separate this effect from any real drift which may occur. The following approximation formula was developed to compensate for the change in hydroxyl ion concentration during the course of the reaction

Let x = concentration of benzilic acid
a = original concentration of benzil
b = original concentration of phenolate ion
c = original concentration of phenol
K_h = hydrolysis constant of phenolate ion

$$\frac{dx}{dt} = k(\text{Benzil})(\text{OH}^-) \text{ and } (\text{OH}^-) = K_h \frac{(\text{Phenolate ion})}{(\text{Phenol})}$$

$$\text{So } \frac{dx}{dt} = kK_h(a - x)\frac{(b - x)}{(c + x)}$$

Since b and c are large compared with x, little error is introduced by replacing $(b - x)/(c + x)$ by the expression $\frac{b}{c}\frac{1}{1 + [(b + c)/bc]x}$. Making this substitution, and integrating the resultant equation, we obtain

$$2.303\left(1 + \frac{b + c}{bc}a\right)\log\frac{a}{a - x} - \frac{b + c}{bc}x = \frac{b}{c}kK_h t$$

Here the left side of the equation embodies the correction; the product $(b/c)kK_h$ can be considered a new constant k'. The results obtained with this equation still have, on the average, somewhat of a drift, although this hardly exceeds the experimental error. Typical values for k', obtained over about 50% reaction, are 1.70, 1.31, 1.46, 1.45, 1.38. The values of k' in various buffer solutions are recorded below.

TABLE V

RATE OF REARRANGEMENT OF BENZIL IN BUFFERED SOLUTIONS

Concn. of benzil	Concn. of KCl	Concn. of phenolate ion	Ratio of phenolate ion to phenol	k'
0.012	0.185	0.115	2.00	4.71×10^{-4}
.010	.250	.050	1.00	2.40×10^{-4}
.011	.118	.182	1.00	2.32×10^{-4}
.009		.300	1.00	2.44×10^{-4}
.009	.268	.032	0.50	1.40×10^{-4}
.009	.108	.192	.50	1.46×10^{-4}

Using *o*-chlorophenol and *o*-chlorophenolate ion, the results given in Table VI were obtained.

The results with phenol were easier to reproduce than the very slow rates obtained with *o*-chlorophenol.

TABLE VI

RATE OF REARRANGEMENT OF BENZIL IN BUFFERED SOLUTIONS

Benzil concn.	0.008	0.010
o-Chlorophenolate ion concn.	.026	.190
Ratio of *o*-chlorophenolate ion to *o*-chlorophenol	3.00	3.00
Potassium chloride concn.	0.274	0.110
$k' \times 10^4$	.92	.72

It is at once obvious from these figures that the rate is dependent upon the buffer ratio but not upon the concentration of the phenolate ion present. That is to say, the reaction is not one involving general base catalysis, for, if it were, the rate would increase, at constant buffer ratio, as the concentration of the phenolate ion increases. Furthermore, the change in rate with change in buffer ratio is approximately that which would be predicted if the reaction is strictly between benzil and OH^- ion.

TABLE VII

HYDROLYSIS OF PHENOLATE AND *o*-CHLOROPHENOLATE IONS AT 100° IN 32% ALCOHOL

Compound	Concn.	Compound	Concn.	Resistance
KOH	0.01500			776.8
KOH	.003106			3602.8
Phenolate	.2620	Phenol	0.3640	120.46
Phenolate	.2617	Excess KOH	.00151	107.41
o-Chlorophenolate	.3055	*o*-Chlorophenol	.1670	106.30
o-Chlorophenolate	.3038	Excess KOH	.00150	102.46

Phenolate ion is 7.3% hydrolyzed in the presence of 0.6% excess potassium hydroxide. *o*-Chlorophenolate ion is 1.7% hydrolyzed in the presence of 0.5% excess potassium hydroxide.

The rates in buffered and unbuffered solutions enable us to determine the hydrolysis constant of phenolate and of *o*-chlorophenolate ions. From Table V, the average value for phenol of ck'/b (which is equal to kK_h) is 2.54×10^{-4}, with an average deviation of 8%. Likewise, from Table I, the average value of the bimolecular constant k is 1.98×10^{-1}, with an average deviation of 7%. The value for K_h from kinetic measurements, then, is 1.28×10^{-3} for phenol, and likewise is 1.37×10^{-4} for *o*-chlorophenol.

The hydrolysis constant of a weak acid can be determined independently by measuring, by conductivity, the degree of hydrolysis of the potassium salt. A difficulty arose here in the manner in which the measurements should be made. For, to be comparable to the kinetic data, the conductivity measurements should be made at an ionic strength of 0.3. While these were the experimental conditions used, it is necessary to bear in mind that the conductivities of two salts in the same solution are not necessarily the sum of their separate conductivities, and that there is a certain solvent effect due to the presence of undissociated phenol or *o*-chlorophenol. Furthermore, these effects are magnified in solutions of moderate concentration.[12]

In the calculations using the data of Table VII below, the conductivities of the phenolate and *o*-chlorophenolate ions were corrected for the hydroxyl ions in the buffer solutions before calculating the percentage hydrolysis. $(\text{Phenol})(OH^-)/(\text{Phenolate ion} = K_h$. The final results are, then, given in Table VIII.

TABLE VIII

HYDROLYSIS CONSTANTS OF PHENOLATE AND *o*-CHLOROPHENOLATE IONS

	K_h	
Compound	Kinetics	Conductivity
Phenol	1.28×10^{-3}	1.61×10^{-3}
o-Chlorophenol	1.37×10^{-4}	1.15×10^{-4}

Before the significance of these figures can be appreciated, the possible errors must be evaluated. The error in the quotient of the two velocity constants may well be 10 or 15%. An error of 0.1% in the percentage hydrolysis of phenolate ion would mean an error of about 3% in the value of K_h; a similar error in the case of *o*-chlorophenolate ion would represent an error of a little more than 10%. If, then, there are no errors introduced because of the divergence from ideality of solutions as concentrated as 0.3 molar, we would expect that the constants obtained by the two different methods would agree within about 20%. The disagreement, while a trifle greater than this, is of this order of magnitude, and the pK of phenol and chlorophenol determined by the two methods agree within 0.1 pK unit.

Since the values of the hydrolysis constants determined by the two methods agree as well as

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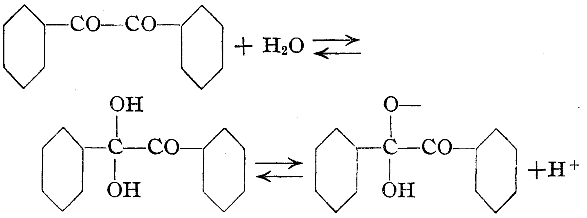
[12] MacInnes, Shedlovsky and Longsworth, *Chem. Rev.*, **13**, 29 (1933).

can be expected, we are justified in the assumption, used in the calculation of the hydrolysis constants from the kinetic data, that the bimolecular rate constant holds throughout the entire range of acidities studied. Essentially, the hydroxyl ion concentration has been varied 425-fold without changing the velocity constant by more than the experimental error.

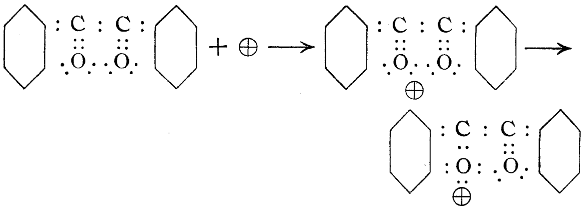
Peroxide Effect.—The work of Kharasch and Foy[13] on the oxygen catalysis of the Cannizzaro reaction suggested that the effect might be present in the benzilic acid rearrangement. Using the same precautions with which the results of Kharasch were repeated, no retardation was noted in the rearrangement. If such a catalysis exists, it levels off too rapidly to invalidate the kinetic data recorded above.

Discussion of Results

In aqueous solution, benzil undoubtedly exists in equilibrium with its hydrate, and with the negative ion which results from the ionization of the hydrate

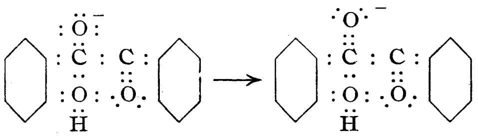


Whitmore[2] suggested that the first reaction is one between a positive ion and benzil, followed by a shift of electrons to form a carbonium ion, the true, unstable intermediate.



However, regardless of whether this primary addition is the slow step, or merely an equilibrium supplying the starting product for some other slow step, the theory would demand a strong positive ion catalysis. Such does not exist, and Whitmore's hypothesis cannot possibly be correct in this case. As a carbonium ion is the most likely intermediate in the Wagner–Meerwein rearrangement,[3] it is necessary to postulate more than one type of ionic intermediate for molecular rearrangements.

Ingold[4] suggested that the negative ion which results from the ionization of benzil hydrate is the first intermediate; a shift of electrons so that ten surround one C atom forms the true, unstable intermediate.



The kinetic data give no indication of whether this second hypothesis is correct, but they do very definitely point to this negative ion as the intermediate.[14] No other assumption would explain the fact that the rearrangement of benzil is bimolecular over more than a four hundredfold change in hydroxyl ion concentration.

This ion could be formed by one of three mechanisms, namely, by general base catalysis, in which case a base would remove a hydrogen ion from the hydrate, by addition of an hydroxyl ion to benzil, or by direct ionization of the hydrate. The fact that the rate is independent of the concentration of phenolate ion is definite proof that the reaction is not an example of general base catalysis. The kinetic data afford no means of differentiating between the other two possibilities.

Furthermore, the ionization cannot be extensive in any of the solutions studied. For, if it were, a simple calculation shows that the rate would vary with *less* than the first power of the hydroxyl ion concentration; such is not the case. Moreover, a doubly ionized benzil molecule is also impossible, for if such an ion were involved, the reaction would of necessity show a large positive salt effect. Therefore, not only can the reaction adequately be explained on the basis of this ion as intermediate, but most other likely hypotheses can be eliminated definitely.

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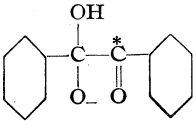
(13) Kharasch and Foy, THIS JOURNAL, **57**, 1510 (1935).

(14) Dr. P. D. Bartlett has pointed out in discussion that the fact that this migration occurs in a negative rather than a positive ion is not so foreign to Whitmore's generalization as might appear. According to this viewpoint, the essential feature of rearrangements is the migration of some group R: with an electron pair to a position having electron-attracting character. In the pinacol rearrangement such a position must be produced by the formation of a positive ion. Benzil, on the other hand, has an electron-attracting center permanently in the starred carbon atom of the carbonyl group:



The appearance of a negative charge on the other CO group facilitates the release of the adjacent phenyl group with its electron pair.

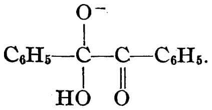
Acknowledgment.—The author owes an especial debt of gratitude to Professor L. P. Hammett for his advice and assistance. He wishes also to thank Professor J. J. Beaver for the use of his conductivity apparatus.

Summary

1. The rate of the rearrangement of benzil to benzilic acid has been measured in solutions of hydroxyl ion and in phenol–phenolate and *o*-chlorophenol–*o*-chlorophenolate ion buffers, all in 32% alcohol at 100%. The reaction is strictly bimolecular.

2. The hydrolysis constants of phenolate and of *o*-chlorophenolate ions have been measured, in 32% alcohol at 100°, by conductivity.

3 The conclusion is drawn that the rearrangement proceeds through the ion



$C_6H_5\text{—}\overset{O^-}{\underset{HO}{C}}\text{—}\underset{O}{C}\text{—}C_6H_5$.

NEW YORK, N. Y. RECEIVED JULY 27, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Rate of Exchange between Chloride Ion and Chlorine in Aqueous Solution

BY F. A. LONG AND A. R. OLSON

Two investigations dealing with the rate of exchange between halide ions and halogens have been published recently. Grosse and Agruss[1] studied the exchange between bromine and bromide ion and Hull, Shiflett and Lind[2] that between iodine and iodide ion. Both of these investigations employed radioactive indicators to follow the reactions. We can conclude from the results of these investigators that considerable interchange takes place during the course of several minutes, but no attempt was made in either investigation to ascertain the order of magnitude of the rate of the interchange reaction.

In studying the mechanism of the rearrangement of chloroacetylaminobenzene, Olson, Porter, Long and Halford[3] found that it was necessary to know whether such an interchange was fast or slow compared to the rate at which chlorine reacts with acetanilide in aqueous solution. Since this latter reaction is itself extremely fast, it is obvious that we could draw no inferences from the published investigations which would be valid in this work. We have therefore determined the relative speed of these two fast reactions by passing non-radioactive chlorine into an aqueous solution of acetanilide and radioactive chloride ion, followed by an examination of the distribution of the radioactivity in the products of the reaction. Radioactivity in the resulting chloroacetanilide will thus indicate that the chlorine has interchanged with the chloride ions before chlorinating the acetanilide. Even though the chlorination of acetanilide is immeasurably fast, we found the exchange reaction to be complete within the limits of experimental error.

Experimental

0.033 Mole of acetanilide was dissolved in 35 cc. of 95% alcohol, 515 cc. of 1 *N* sulfuric acid added and 0.0825 mole of radioactive sodium chloride was dissolved in this mixture. The concentrations in the resulting 550 cc. of solution were thus 0.06 *M* acetanilide and 0.15 *M* chloride ion. Fifty cc. of this solution was withdrawn for radioactive analysis and, to the remaining 500 cc., 0.00617 mole of chlorine was added with vigorous shaking. The chlorine disappeared rapidly and a precipitate of chloroacetanilide appeared almost immediately. The organic matter, chloroacetanilide and unreacted acetanilide, was then extracted with two portions of ether, the ethereal solution evaporated to dryness and the solid material fused with potassium hydroxide in a nickel crucible. The resulting fused mass was dissolved in water and acidified with nitric acid. To this solution, containing chloride ion from the chloroacetanilide only, and to the 50-cc. initial sample, excess silver nitrate solution was added. Weighed amounts of the dried silver chloride precipitates were dissolved in ammonium hydroxide and radioactive determinations were then made by the method described by Olson, Libby, Long and Halford.[4] The control sample was made by using 0.4 g. of silver chloride. From the fusion we were able to obtain only 0.33 g. of silver chloride and so 0.07 g. of non-radioactive silver chloride was added. In comparing the radioactive analyses this factor must be taken into account.

In Fig. 1 we have plotted the time against the logarithm of the net count times the dilution. The circles represent the observed data and the straight lines have been drawn with a slope corresponding to the known half-life of radioactive chlorine (thirty-seven minutes). Our radioactive material exhibited some gamma radiation but

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[1] A. V. Grosse and M. S. Agruss, THIS JOURNAL, **57**, 591 (1935).

[2] D. E. Hull, C. H. Shiflett and S. C. Lind, *ibid.*, **58**, 535 (1936).

[3] A. R. Olson, C. W. Porter, F. A. Long and R. S. Halford, to be published soon.

[4] A. R. Olson, W. F. Libby, F. A. Long and R. S. Halford, THIS JOURNAL, **58**, 1313 (1936).

any contribution due to this was ignored in calculating our results. During the run the counting apparatus developed some instability as was shown by a variation of the background count and so the accuracy is not as great as we could have expected for this type of experiment. However, the errors are not large enough to throw any doubt on our conclusions.

Figure 1 shows immediately that considerable interchange must take place since the chlorine in the final product is highly radioactive. A comparison of the readings for the two samples at any given time shows that the activity of the silver chloride from the chloroacetanilide is about 79% of that of the control sample.

Discussion and Calculations

The particular concentrations that we used were chosen, first, so that the ratio of chloride ion to acetanilide would be small enough so that the chlorine would not have too great a chance of interchanging before colliding with an acetanilide molecule, and second, with the ratio of radioactive chloride ion to the amount of chlorine rather large so as to permit simplification in calculating the results. Every molecule of chlorine that reacts with acetanilide forms one molecule of chloroacetanilide and sets free one chloride ion. Thus, if a is the initial amount of radioactive chloride ion and x is the amount of chlorine introduced at any time, then, since all chlorine that goes into solution reacts almost immediately, the total amount of chloride ion, radioactive or non-radioactive, is $a + x$. If all of the chlorine becomes radioactive before reacting with the acetanilide, the amount of radioactive chloride ion in solution would be $a - x$. To correct for the fact that as the reaction progresses the chlorine has a decreasing probability of becoming radioactive, we must alter the above amount to $a - x\ (a - x)/(a + x)$. As the reaction progresses the probability that the chlorine will become radioactive decreases for two reasons: first, because the total amount of chloride ion increases and, second, because the amount of radioactive chloride ion decreases. Thus the probability that a chlorine molecule will become radioactive is equal to $[a - x\ (a - x)/(a + x)]/(a + x)$. Then the decrease in radioactivity of the chloride ion in solution will be very nearly equal to the integral from zero to x of $\frac{a - x(a - x)/(a + x)}{a + x}\,dx$. This, of course, will also be the total amount of radioactivity to be found in the chloroacetanilide. In our experiment the ratio of x to a is 1 to 13.35. Putting these values into the above integral we find that the radioactivity of the chlorine in the chloroacetanilide should be 93% of the original radioactive chloride ion. When we apply the further correction of 33/40 due to the undersized sample we find that the radioactivity of the silver chloride from the chloroacetanilide should be about 77% of that for the control sample, assuming complete interchange between chlorine and chloride ion. This agrees very well with our experimental value of 79%. Therefore we can conclude that the establishment of the equilibrium between chlorine and chloride ions in an acidified aqueous solution is extremely rapid.

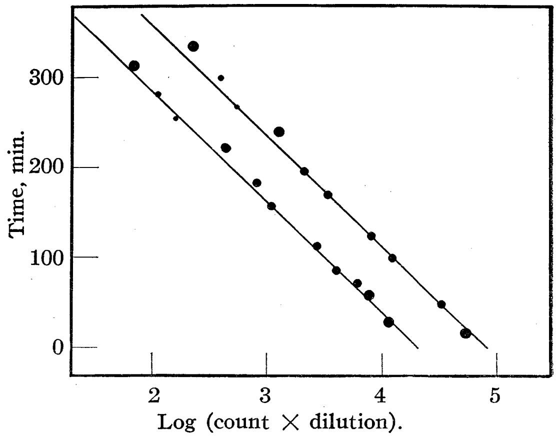

Fig. 1.—The upper curve, which is for the control sample, has been displaced to the right by one-half a unit.

In conclusion we express our indebtedness to Professor E. O. Lawrence and his colleagues for supplying us with the radioactive sodium chloride.

BERKELEY, CALIF. RECEIVED AUGUST 19, 1936

[Contribution from the Chemical Laboratory of Harvard University]

The Activity of Sodium in Dilute Sodium Amalgams

By H. E. Bent and E. Swift, Jr.

The thermodynamic properties of sodium amalgams have been investigated previously by a number of workers.[1] The potentiometric method of Richards and Conant used, as an electrolyte, an aqueous solution of sodium hydroxide. Lewis and Kraus,[2] in determining the standard electrode potential of sodium used a solution of sodium iodide in ethylamine. By combining these two sets of data one can calculate the activity of sodium in dilute sodium amalgams referred to the pure metal as the standard state. Recently, however, it has been shown that the potential of a concentration cell may be affected by the nature of the electrolyte.[3] The explanation for this behavior is not known but presumably the electrolyte either alters the number of equivalents of alkali metal transferred per faraday due to the formation of a complex ion or gives rise to some side reaction. It therefore seemed desirable to check data previously reported by the use of other solvents and with varying concentrations of electrolyte.

A further reason for again studying these amalgams arose in the effort to interpret the shape of the curve obtained by plotting the values of the logarithm of the activity coefficient against the concentration of the sodium. The variation in the values determined for the most dilute solutions on account of reaction with the aqueous electrolyte made it impossible to distinguish between a physical and a chemical explanation for the deviations from Raoult's law in this region.

Finally, it seemed worth while to develop the technique of these measurements to a considerably higher point before studying further amalgams of the other alkali metals. We are interested in having data on the thermodynamic properties of alkali metal amalgams in connection with a program of studying the free energy of formation of various organo metallic compounds with the aid of amalgams.

The most accurate element in this investigation seemed to be the determination of the potential between amalgams of various concentrations. We therefore attempted to bring the various other errors down to the order of 0.01%. We first investigated a number of solvents in order to find one which would dissolve sufficient sodium iodide to give a good conductivity and still not react with the sodium amalgam or metallic sodium. Great care was exercised in filling the cells and in controlling the temperature during measurement. Finally, considerable time was spent in improving the accuracy of the analysis and discovering the sources of error in this determination.

Solvent.—The solvents heretofore used in the study of amalgam concentration cells have been water, ethylamine and ether. Water obviously is far from ideal on account of its rapid reaction with amalgams. Ethylamine, used by Lewis and Kraus, is very much better but even this solvent reacts slowly with metallic sodium. Ether is better from the standpoint of reaction with the metal. However, as shown by Gilfillan, the electromotive forces obtained by dissolving organo metallic compounds in ether are not reproducible and do not agree with those obtained with other solvents.

Dimethylethylamine was prepared by treating dimethylamine with diethyl sulfate at 80° for twenty-four hours. The yield was very poor—about 1%. The product was purified by distillation and dried before using. Dimethylamine, diethylamine and ethylamine were purchased from Eastman Kodak Co. and purified and dried before use. The amine was first dried by distillation onto calcium oxide or activated alumina and then onto sodium benzophenone. It was sealed in glass capsules which were later broken into an evacuated system. The sodium iodide was fused in vacuum in a platinum boat according to the method of Forziati.[4] As will be seen from Table I only ethylamine and dimethylamine dissolve sufficient sodium iodide to be suitable solvents.

Table I

Specific Conductance

	Mhos
Dimethylethylamine + NaI (satd.)	$<10^{-10}$
Diethylamine	3×10^{-12}
Diethylamine + NaI (satd.)	3×10^{-9}
Dimethylamine	1×10^{-10}
Dimethylamine + NaI (satd.)	2×10^{-4}
Ethylamine	1×10^{-9}
Ethylamine + NaI (satd.)	$>1 \times 10^{-4}$

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[1] (a) Richards and Conant, This Journal, **44**, 601 (1922); (b) Bent and Hildebrand, *ibid.*, **49**, 3011 (1927); (c) Gilfillan and Bent, *ibid.*, **56**, 1505 (1934).

[2] Lewis and Kraus, *ibid.*, **32**, 1459 (1910).

[3] Bent and Gilfillan, *ibid.*, **55**, 247 (1933).

[4] Forziati, *ibid.*, **58**, 2220 (1936).

These two amines were then compared to determine the relative speed of the reaction with alkali metal. For this purpose sodium–potassium alloy was introduced into a small tube connected to a second tube carrying a pair of platinum electrodes. The amine could be distilled into the tube containing the electrodes to measure its conductivity or the solution could be poured in and the course of the reaction followed by the change in conductivity. It was found that ethylamine reacted about one hundred times faster than dimethylamine and gave solutions which were of the order of one hundred times more conducting as a result of reaction with the alloy. This treatment is probably much more severe than necessary but gives a rapid method of comparing the inertness of the two liquids. The ethylamine very quickly became colored and at times bubbles could be observed rising from the surface of the alloy in contact with this liquid, while the dimethylamine remained perfectly clear. The results of these experiments are recorded in Table II and indicate clearly that dimethylamine is much to be preferred.

TABLE II

SPECIFIC CONDUCTANCE OF AMINES IN CONTACT WITH NaK ALLOY

Time, hrs.	Dimethylamine	Ethylamine
0	10^{-10}	10^{-9}
1	10^{-9}	5×10^{-8}
24	2×10^{-9}	4×10^{-7}
48	3×10^{-9}	6×10^{-7}

Analysis.—Since the analysis of the amalgams is the part of the problem which introduces the greatest part of the experimental error, a great deal of time was spent in improving this procedure. A great many precautions were taken in standardizing the acid used in the titration and in extracting the sodium from the amalgam. Only a few of these will be mentioned here. The carefully purified sodium carbonate was fused in a stream of dry carbon dioxide. All titrations were carried out in quartz flasks with air, free from carbon dioxide, passing through the flask at the end-point. Weight burets were used, one containing sulfuric acid approximately 0.5 *N* and the other acid approximately 0.01 *N*. Standard base was not used in the titration, the initial alkaline solution being decanted from the amalgam in order that an excess of acid could be added to remove the last of the sodium. The initial alkaline solution was then added and the titration carried just to the end-point with brom thymol blue. All amalgams were prepared by distilling mercury onto sodium which had been filtered through several constrictions. The amalgam was then transferred to storage flasks and capsules which had been baked and evacuated at 450°. Samples were removed for analysis or for the preparation of a cell by means of tips broken by magnetic hammers. The general style of cell was the same as that used by Gilfillan.[5] No stopcocks were used at any point in the line, however. With the aid of the above precautions the precision of the analysis appeared to be 0.02% as judged by the agreement of successive runs.

Thermostat.—The temperature of the thermostat was controlled by means of a 24-junction copper–constantan thermocouple. The potential from this thermocouple was balanced by a small potentiometer which was kept, with dry cells used for its operation, in another thermostat at 25°. When off balance the current generated deflected a spot of light thrown by a spot light onto a galvanometer and reflected to a photocell. The remainder of the control is illustrated in Fig. 1. This use of the thyratron in a phase-shift circuit results in an adjustment of the current sixty times a second. This arrangement was worked out with the details as shown in the figure by Professor W. B. Nottingham of Massachusetts Institute of Technology and proved very satisfactory. There was no tendency of the temperature to oscillate and the temperature could be kept constant at any desired point to 0.01°. Greater precision could have been obtained by using a larger thermostat and a thermocouple with a greater number of junctions or a more sensitive galvanometer. All that was necessary to operate the cell at lower temperature was to adjust the temperature roughly by an increase in the flow of cooling water and then to set the potentiometer for the desired temperature. Switch "G" was added in order to allow the temperature to be raised rapidly.

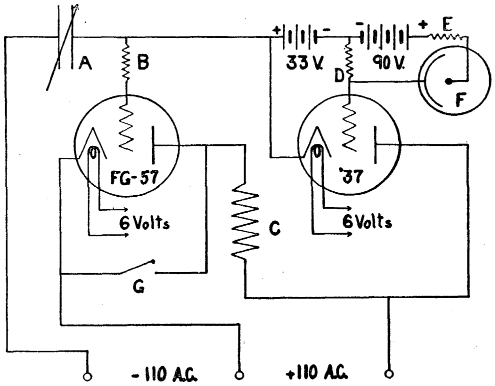

Fig. 1.—Control circuit used for thermostat: A, 0.0001 mfd. variable condenser; B, 50,000-ohm variable resistance; C, 125-watt "lagless" heater (in bath); D, 10-megohm resistance; E, 2-megohm resistance; F, photoelectric cell, type 71-A; G, switch used for rapid heating.

Experimental Results

Seven cells were constructed including eight amalgams of varying concentrations, one of which was two phase. One cell was designed to permit successive dilution of the electrolyte. Over a range of one thousandfold in the concentration of sodium iodide there was no change in the e. m. f. which was greater than the experimental error. However, in the case of the most dilute solutions the resistance was so high that it was difficult to obtain measurements which were reproducible to better than about 1%. This experiment proves that there is no variation in e. m. f. with this electrolyte comparable to the 50% variation found by Gilfillan with ether solutions of organo metallic

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[5] Bent and Gilfillan, THIS JOURNAL, **55**, 3989 (1933).

TABLE III

MOLE FRACTION OF AMALGAMS AND OBSERVED E. M. F.

No.	N_2	5°	15°	25°	Reference electrode
1	Two phase	0.01600 ± 20	0.02348 ± 1	0.03157 ± 5	4
2	0.0489708	....	.05582	.05732	5
3	.0394227	.03920	.04020	.04131	5
4	.0336062	.02980	.03066	.03151	5
5	.0177086	.00000	.00000	.00000	5
6	.0120373	− .01418	− .01460	− .01501	5
7	.0042270	− .04631	− .04777	− .04921	5
8	.00042375	− .10497	− .10844	− .11193	5
3	.0394227	− .81600	− .81445	− .81338	Sodium
3	.0394227			− .81336	
7	.0042270			− .89418	Sodium

compounds. The cross checks obtained by comparing various pairs of amalgams in a single cell were usually good to 0.01 mv. The values for pairs of amalgams occurring in different cells were good to 0.03 mv. From all of these cells data were obtained over many weeks and at 5, 15 and 25°. Two cells contained metallic sodium. The results are given in condensed form in Table III. From these data three equations were obtained by the method of least squares to represent log a_2/N_2 as a function of N_2. The form of expression found satisfactory is of the familiar type, log $a_2/N_2 = a + bN_2 + cN_2^2$, the last term contributing relatively little to the expression. The average deviation of the experimental points from the curve was 0.0015, which corresponds to about 0.06 mv. error in the e. m. f. or about 0.1% in the analysis of the more concentrated amalgams. It was found possible to combine these three equations, obtained by least squares

$$\log a_2/N_{2_{25°}} = -12.81441 + 15.6130N_2 + 7.530N_2^2$$
$$\log a_2/N_{2_{15°}} = -13.32030 + 15.87260N_2 + 7.110N_2^2$$
$$\log a_2/N_{2_{5°}} = -13.86807 + 16.1820N_2 + 5.970N_2^2$$

into a single simple equation involving the temperature without seriously sacrificing the accuracy of the data. This equation is

$$\log a_2/N_2 = \frac{-8387.6}{T^{1.138}} + \frac{338.2}{T^{0.54}} N_2 + 7.0N_2^2$$

Values of log a_2/N_2 calculated by means of this equation usually differed from those calculated by the three separate equations given above by less than 0.001. From this more general equation the following equations have been derived for the partial molal free energy, entropy and heat content of sodium and mercury, following the methods used by Bent and Gilfillan.

$$\overline{F}_2 = 4.57393\ T \log N_2 - \frac{38364.30}{T^{0.138}} + 1546.9N_2T^{0.46} + 32.0N_2^2T$$

$$\overline{S}_2 = -4.57393 \log N_2 - \frac{5294.27}{T^{1.138}} - \frac{711.574}{T^{0.54}} N_2 - 32.0N_2^2$$

$$\overline{H}_2 = \frac{-43658.57}{T^{0.138}} + 835.3N_2T^{0.46}$$

$$\overline{F}_1 = 4.57393\ [T \log N_1 - 169.1N_2^2\ T^{0.46} - (338.2T^{0.46} + 14T) \text{ x } (N_2^3/3 + N_2^4/4\ldots)]$$

$$\overline{S}_1 = -4.57393\ [\log N_1 - \frac{77.786}{T^{0.54}} N_2^2 - \left(\frac{155.57}{T^{0.54}} + 14\right)(N_2^3/3 + N_2^4/4\ldots)]$$

$$\overline{H}_1 = 4.57393\ [-91.3\ N_2^2T^{0.46} - 182.6T^{0.46}\ (N_2^3/3 + N_2^4/4\ldots)]$$

Introducing the values for the e. m. f.'s of sodium to the saturated amalgams into the equation obtained by the method of least squares for each temperature and solving for the concentration, three values were obtained for the solubility of sodium in mercury.

TABLE IV

SOLUBILITY OF SODIUM IN MERCURY

Temp., °C.	Mole fraction of Na
5	0.043955
15	.04870
25	.05380

Our results may be compared first with those of Lewis and Kraus. They report an e. m. f. between an amalgam whose concentration is 0.2062 wt. % sodium and pure sodium of 0.8456 which is equal to 0.8453 international volt.[6] We find from our equation a value for this e. m. f. of 0.8448 using the equation derived from the experimental data at 25° and a value of 0.8449 v. using our more general equation which includes the temperature. The disagreement between our value and that of Lewis and Kraus is considerably more than the experimental error which they attribute to their result. A check on our result has been obtained by A. F. Forziati using entirely different apparatus in work soon to be reported. His measure-

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(6) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 415.

ments agree with our results for the e. m. f. between sodium and an amalgam of a given concentration to 0.1 mv. Our agreement with Lewis and Kraus in the temperature coefficient of this cell is not entirely satisfactory. They report a value of −0.0000408 v. per degree for the range 10–35°. As will be seen from Table V the temperature coefficient is changing rather rapidly with the temperature. The average value which we obtained by calculating the activity at 10 and 35° does not agree well with that of Lewis and Kraus and the value at 25° is still further from their value.

TABLE V

CALCULATED VALUES OF dE/dT

Temp., °C.	$-dE/dT$
5	0.000059
15	.000043
25	.000029
10–35	.000032

We have also compared our data with those of Richards and Conant. Their experimental data are shown by crosses on our plot in Fig. 2. They did not determine the potential of any amalgam against sodium. Their points have been placed on our plot by arbitrarily adding a constant to the values of log a_2/N_2 which would give the best agreement with their data. The agreement of their data with those reported in this investigation seems remarkably good considering the difficulties which they encountered in working with water solutions. Their data have been calculated in a similar manner by Bent and Hildebrand but these results do not entirely agree with our present calculations, apparently due to some error in the earlier calculations.

We have also compared our temperature coefficients with those observed by Richards and Conant. The agreement here is remarkably good, probably within our experimental error.

TABLE VI

COMPARISON OF dE/dT WITH DATA OF RICHARDS AND CONANT

Amalgams of R. and C.	dE/dT R. and C.	dE/dT B. and S.
18–20	0.093	0.091
18–19	.156	.151
20–21	.164	.158
21–22	.059	.062

Finally, from our equations we have calculated the free energy of formation of $NaHg_4$ and values for the solubility of sodium in mercury. These data were obtained from measurements on the two-phase amalgam. The potential between the two-phase amalgam and sodium is shown in Fig. 2 and gives, with the aid of the equation for the curve, the concentration of the liquid phase. From the activity of sodium and mercury in this amalgam we then calculate the value −18,296 kcal. for ΔF.

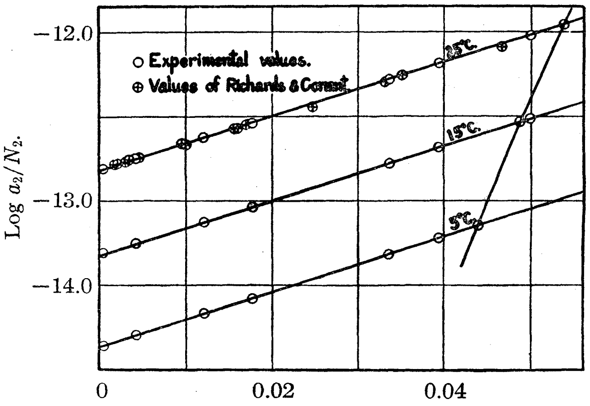

Fig. 2.—○, Experimental values; ⊕, values of Richards and Conant.

The choice of explaining the deviation from ideal solution by either compound formation or a more general physical picture seems to be pretty clearly answered by our data. Whatever compounds may be present at higher concentrations the behavior of the dilute amalgams cannot be explained by such assumptions alone. The plot of log a_2/N_2 is perfectly straight down to our most dilute amalgam. It has been shown by Bent and Hildebrand that even a compound containing as much mercury as $NaHg_{16}$, which is about as much as one can reasonably postulate, still gives a slight upward curvature in the very dilute range of concentration.

Summary

1. The thermodynamic properties of dilute sodium amalgams have been determined by means of concentration cells containing sodium iodide in dimethylamine as the electrolyte.

2. The solubility of sodium in mercury has been determined at 5, 15 and 25°.

3. The experimental results are compared with those of Richards and Conant on concentration cells and Lewis and Kraus on the sodium electrode.

4. The data on very dilute amalgams indicate that deviations from Raoult's law, which can be

largely attributed to the existence of compounds, cannot be quantitatively explained by the assumption that compounds exist which dissolve in mercury to give ideal solutions.

MALLINCKRODT CHEMICAL LABORATORY
CAMBRIDGE, MASS. RECEIVED AUGUST 14, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Activity of Sodium and Mercury in Solid Sodium Amalgams

BY H. E. BENT AND A. F. FORZIATI

The number and composition of the solid phases containing sodium and mercury have been the subject of much difference of opinion.[1] A study of the activity of sodium in the solid phase might well be expected to throw added light on this complex system.

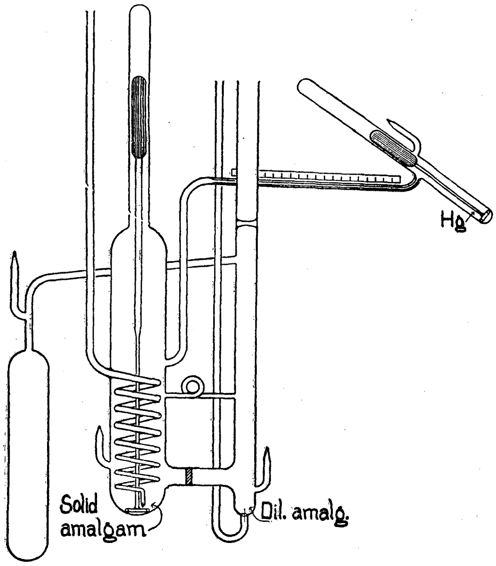

Fig. 1.

A second reason for studying the solid compounds of sodium and mercury arises in connection with the investigation of organo-metallic compounds. It is possible to determine the free energy change associated with the addition of sodium to various organic compounds by shaking the materials to be investigated with liquid sodium amalgams.[2] Many compounds, however, exhibit a stability which would necessitate the use of solid sodium amalgams in such an equilibrium determination. Recently the investigation of unsaturated hydrocarbons[3] has emphasized the need of studying such solid sodium amalgams.

We have constructed cells in which one electrode is a dilute sodium amalgam and the other a solid amalgam, Fig. 1. The solid amalgams may be diluted by small additions of known quantities of mercury, thus covering the whole concentration range with one cell. The electrolyte is a solution of sodium iodide in dimethylamine. This solvent has been found to be well suited to cells of this type.[4] From the activity of the sodium the activity of the mercury can be calculated and the free energy of formation of the various solid phases.

Materials

All materials were handled in carefully evacuated and baked out glass apparatus. Stopcocks were replaced by glass tips to be broken by magnetic hammers.

Mercury was purified by washing with nitric acid and distillation.

Sodium was melted and allowed to flow through several constrictions in order to remove surface impurities. In one cell sodium was prepared by repeated distillation and this material compared with that which had only been filtered. These results justify the procedure of using material which has been subjected only to the removal of surface impurities.

Ethylamine and Dimethylamine.—Ethylamine was used in the earlier cells but is not entirely satisfactory as it reacts slowly with the amalgams. Dimethylamine has been shown by E. Swift, Jr., to be much less reactive and still to dissolve enough sodium iodide to serve as a good electrolyte. The amines were prepared in each case by treating the hydrochloride with sodium hydroxide. Much of the water vapor is removed by a reflux condenser. The amine is dried by allowing it to stand first over calcium oxide or activated alumina and then distilling it into a tube containing benzophenone and sodium–potassium alloy. The ketyl dissolves in the amine and indicates by its intense violet color the absence of all water. The amine is next shaken with fused sodium iodide in order to produce practically a saturated solution.

Sodium Iodide.—This material was first recrystallized and then fused in a covered platinum boat in a vacuum. Considerable difficulty is encountered in the process of fusion unless adequate precautions are taken. The vapor pressure of the iodide is so great at its melting point that it distils out of the platinum boat and condenses over the

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(1) Paranjpe and Joshi, *J. Phys. Chem.*, **36**, 2474 (1932).

(2) Bent *et al.*, THIS JOURNAL, **52**, 1498 (1930); **53**, 1786 (1931); **54**, 3250 (1932); **57**, 1217, 1242, 1259, 1452, 1455 (1935); **58**, 1367 (1936).

(3) Bent and Keevil, *ibid.*, **58**, 1367 (1936).

(4) Bent and Swift, *ibid.*, **58**, 2216 (1936).

surface of the quartz tube. This difficulty was avoided by covering the platinum boat with a tight fitting platinum cover. A small hole in the cover allowed a heavy platinum pin to project above the cover. When the iodide fuses the pin drops down into the boat thus indicating that the process is complete.

Experimental Procedure

The technique of handling cells containing solid sodium amalgams requires some comment as a great deal of difficulty was encountered. The high melting point of some of the amalgams (355°) makes it impossible to melt such an amalgam without distillation of mercury. Furthermore the amalgam adheres to the glass if clean and on cooling will crack even very rugged cells. It is almost impossible to keep amalgams in capsules and then introduce them into the cell as distillation is serious at the melting point and the labor of preparing and analyzing amalgams over the whole concentration range would be almost prohibitive.

Many types of cells were constructed and in most cases some useful data were obtained. The early cells contained ethylamine as the solvent. Later cells contained dimethylamine which is much more inert. Without going into the details of all of the types of cells investigated we will describe only the type used in constructing cells 10 and 11. Figure 1 illustrates the chief features of the cell. Contact is made with the solid amalgam by means of a long spiral which dips into the amalgam at the bottom. This was the only style of cell which was not cracked by the solidification of the amalgam. A stirrer which may be moved magnetically is also included in this cell in order to ensure homogeneity of the amalgam. A sintered Pyrex disk prevents any liquid amalgam from spattering or being dumped into the wrong electrode. A connecting tube above the level of the electrolyte equalizes the pressure on both sides and prevents undue stirring and bubbling of the electrolyte. The chief point of interest, perhaps, in this cell is the dilution device. Two types have been tried in different cells. The first type is perhaps a little more simple to construct but not quite so convenient to operate. By tipping the whole apparatus mercury in the reservoir is allowed to run into a short section of capillary which is within the reservoir. On turning the apparatus rapidly into a vertical position this slug of mercury runs down into a horizontal calibrated section of capillary tubing where it is measured by determining its length. Further tipping then pours this mercury into the cell. By this device it is possible to start with a small amount of a concentrated amalgam and carry it through practically the whole concentration range, admitting either large or small quantities of mercury as desired. A second device which accomplishes the same purpose is a little magnetic lift. In this case the apparatus need not be tipped. The reservoir is set at an angle of about 45° and within the mercury reservoir is a glass cylinder containing soft iron. To the end of this cylinder is attached a glass rod which terminates in a ring of glass which is ground to fit the inside of the tube and to be flat on its upper surface. This gives a right angle at the point of contact of ring and tube. When the cylinder is raised a drop of mercury is carried upward to the point at which it runs into the side-arm and down into the capillary to be measured. After a little practice this was found to be a much easier method of diluting the amalgam.

Other experimental details were very similar to those previously recorded.[5] A type K potentiometer was used with a type HS galvanometer sensitive to 10^{-10} amp. The resistance of the cells was of the order of one megohm. Usually a cell could be measured to 0.01 mv. However, the e. m. f. fluctuated from day to day in the most favorable cases by several hundredths of a millivolt and, in the case of some unstable amalgams to be discussed later, by several hundredths of a volt.

In the case of low melting amalgams the electrolyte was poured into the side bulb before diluting the amalgam. The amine could then be cooled with Dry-Ice while the mercury was being added and the amalgam melted and stirred. The highest melting amalgams could only be studied by admitting nitrogen into the system as otherwise it was impossible to melt the amalgam without a great deal of distillation.

Experimental Results

The experimental results are recorded in Table I and in Fig. 2. It would be impossible to give all of the observations without taking up an inordinately great amount of space. Eleven cells were studied, in some cases over a period of several months. In the early part of the work it seemed almost impossible to discover any meaning in the data. The e. m. f.'s were frequently very fluctuating and often an amalgam gave a higher e. m. f. after adding mercury than it did before. Gradually, however, as data were accumulated, it became evident that cells were likely to be very unstable when the composition was very near that of one of the compounds. When the composition was about half-way between that of two compounds the e. m. f. was usually very satisfactory. Frequently just after diluting an amalgam the e. m. f. would be very low and gradually rise and become steady when it came to the value at which other amalgams had become steady. A possible explanation for this phenomenon would

TABLE I

OBSERVED ELECTROMOTIVE FORCE

Composition of solid electrode	Mole fraction of reference electrode	Obsd. e. m. f.
Na + liq.	0.03270	0.8150
Na_3Hg + Na_3Hg_2	.03270	.7950
Na_3Hg_2 + NaHg	.03270	.7600
NaHg + Na_7Hg_8	.03270	.7400
Na_7Hg_8 + $NaHg_2$	.03270	.6500
$NaHg_2$ + $NaHg_4$	.03206	.1800
$NaHg_4$ + liq.	.03206	.0350

The error in the e. m. f. in most cases is probably not greater than 1 mv. although it may be as large as 5 mv. in the case of the fourth value in the column.

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[5] Bent and Gilfillan, THIS JOURNAL, **55**, 3989 (1933).

be that on cooling a liquid amalgam a solid solution is first formed which gradually goes over into the two stable crystalline compounds. Another curious phenomenon was that frequently an e. m. f. was observed corresponding to a pair of compounds which could not possibly represent the over-all composition of the electrode. In fact further dilution would in these cases sometimes raise the e. m. f. to that to be expected from the total composition of the electrode, as is shown by the points in Fig. 2. This phenomenon can only mean that, on cooling, the liquid becomes supersaturated with respect to several compounds simultaneously and that it is more or less a matter of chance which compounds are formed. The curious part of this behavior, however, is that these metastable compounds are able to dominate the situation and determine the value of the e. m. f. of the cell.

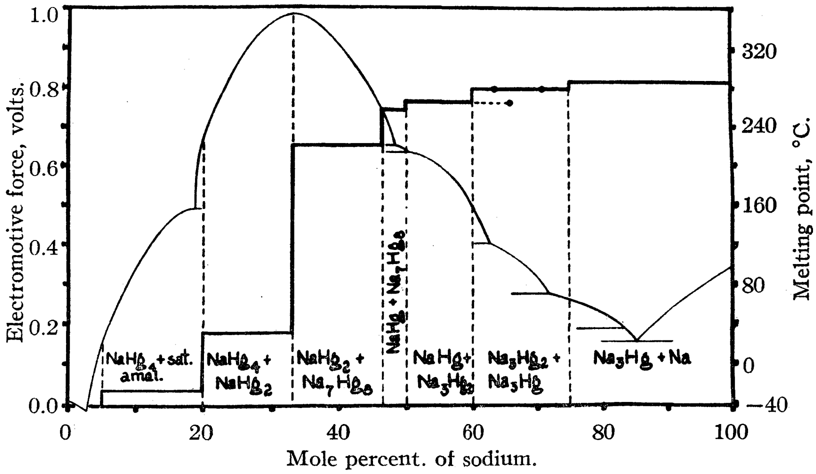

Fig. 2.

The experimental results given in Fig. 2 and in Table I give the e. m. f. produced by the difference in the activity of sodium in a dilute amalgam and a solid amalgam. A typical half cell reaction at the solid amalgam electrode is $2NaHg_2 = NaHg_4 + Na^+ + (-)$ and at the dilute amalgam electrode is $Na^+ + (-) = Na_{\text{dil. amalg.}}$. Since it has been shown[6] that the activity of sodium in a saturated amalgam in which the mole fraction of sodium is 0.857 is the same as that of solid sodium, our measurements may all be referred to pure metal by taking our first electrode as our point of reference. This then gives the activity of sodium in the various two-phase solid amalgams as shown in the first five entries in Table II. These data we hope to use in interpreting reactions involving solid sodium amalgams.

Knowing the activity of sodium over the whole range of concentration one would expect to be able to calculate the activity of mercury by a process similar to that employed in using the partial molal equation[7]

$$\log \frac{a_1}{N_1} = -\int_0^{N_2} \frac{N_2}{N_1} \, d \log \frac{a_2}{N_2}$$

In this case the process is one of summation due to the formation of definite compounds. Table II gives the data for the activity of mercury over the whole range of concentration and also the free energy of formation of the various solid compounds. The first five equations represent the reactions involved in our cells, giving rise to the observed e. m. f.'s. The values of ΔF are calculated from the experimental measurements. The value for reaction 6 has been taken from the data of Bent and Swift.[4] Reactions 7–11 are of interest in indicating the relative stability of the various compounds and are also useful in calculating the activity of mercury in these solid amalgams. Reactions 12–16 describe the changes involved in starting with sodium and adding mercury. If a cell were possible which would be reversible to mercury rather than to sodium the e. m. f. would be determined by these equations. The next-to-the-last column in the table gives the method of computing the various values of ΔF. The numbers in parentheses refer to equations given in the same table. The equations when combined as indicated give the desired reaction and the corresponding value for ΔF.

The last column of the table gives the activity of sodium (a_2) and the activity of mercury (a_1) in solid amalgams of various concentrations. The liquid phase, occurring at 85 atom % sodium is not discussed here as it has been reported previously.[6] The activity of sodium in this liquid amalgam is practically the same as that of the pure metal.

The equations written in Table II are deduced

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(6) Gilfillan and Bent, THIS JOURNAL, **56**, 1505 (1934).

(7) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 269.

TABLE II

		$-\Delta F$, kcal.	Equations used	a_2
1	$Na_3Hg_2 + 3Na = 2Na_3Hg$	1.384		0.459
2	$2NaHg + Na = Na_3Hg_2$	1.269		.117
3	$Na_7Hg_8 + Na = 8NaHg$	1.730		.0539
4	$4NaHg_2 + 3Na = Na_7Hg_8$	11.417		.00162
5	$NaHg_4 + Na = 2NaHg_2$	14.672		1.75×10^{-11}
6	$4Hg + Na = NaHg_4$	18.296		
7	$2Hg + Na = NaHg_2$	16.484	$^1/_2((5) + (6))$	
8	$8Hg + 7Na = Na_7Hg_8$	77.353	$(4) + 4(7)$	
9	$Hg + Na = NaHg$	9.885	$^1/_8((3) + (8))$	
10	$2Hg + 3Na = Na_3Hg_2$	21.039	$(2) + 2(9)$	a_1
11	$Hg + 3Na = Na_3Hg$	11.212	$^1/_2((1) + (10))$	6.0×10^{-9}
12	$NaHg_2 + 2Hg = NaHg_4$	1.812	$(6) - (7)$	0.217
13	$Na_7Hg_8 + 6Hg = 7NaHg_2$	38.035	$7(7) - (8)$	2.25×10^{-5}
14	$7NaHg + Hg = Na_7Hg_8$	8.158	$(8) - 7(9)$	1.05×10^{-6}
15	$Na_3Hg_2 + Hg = 3NaHg$	8.616	$3(9) - (10)$	4.8×10^{-7}
16	$Na_3Hg + Hg = Na_3Hg_2$	9.827	$(10) - (11)$	6.2×10^{-8}

partly from the work of Vanstone,[8] Schuller[9] and Kurnakow[10] and partly from the results of this investigation. Vanstone and Schuller agree very well in the formulas to be assigned to the various compounds. Both agree in writing $NaHg_4$, $NaHg_2$, NaHg, Na_3Hg_2 and Na_3Hg. The compound Na_7Hg_8 is perhaps not quite so certain. Schuller writes $Na_{12}Hg_{13}$. Kurnakow agrees with the above list although he does not report either of these last two compounds or Na_3Hg_2.

The results of our investigation agree perfectly with the list of Vanstone. We are not able to contribute anything very definite to the discussion of the compound Na_7Hg_8 although we did have a few points which could most readily be interpreted as due to some such compound. The evidence is very good, however, in the case of the compound $NaHg_4$. The change in e. m. f. was abrupt and large at 20 atom % sodium and the e. m. f. beyond this point is that observed between a saturated amalgam and one in which the concentration of sodium is 3.27 atom %.[4] This clearly indicates that no compound was present such as $NaHg_5$ or $NaHg_6$ as has been previously suggested.

The activities listed in the last column give information which will be useful in studying chemical reactions involving solid amalgams. The activity of mercury gives a measure of the efficiency of sodium in replacing liquid air or Dry-Ice as a mercury trap in a vacuum line.[11] At 25° the vapor pressure of mercury above liquid 85 atom per cent. amalgam is 1.2×10^{-11} mm. while the vapor pressure of mercury at the temperature of Dry-Ice is 10^{-9} mm. Hence this liquid amalgam should be one hundred times as good as Dry-Ice in removing mercury vapor in a vacuum line. We may also conclude from the data in the last column that on heating a solid amalgam the metal which will distil will probably be mercury. This follows from the fact that at room temperature the ratio of the vapor pressure of mercury to that of sodium is about 10^{11}. Consequently, even in amalgams rich in sodium the mercury will have the higher vapor pressure. At elevated temperatures it is not as easy to make predictions. Undoubtedly the mercury will have the higher pressure from all amalgams except possibly those richest in sodium. The higher heat of vaporization of sodium would tend to increase its vapor pressure faster than that of mercury but this would be complicated by the change in the stability of the various compounds which would probably tend to increase the vapor pressure of mercury.

Conclusions

1. A potentiometric method is described for studying intermetallic compounds at room temperature.
2. Values are given for the free energy of formation of $NaHg_4$, $NaHg_2$, NaHg, Na_3Hg_2 and Na_3Hg. The value for Na_7Hg_8 is not so reliable.
3. The activity of mercury and sodium in solid amalgams of all concentrations is computed.

MALLINCKRODT CHEMICAL LABORATORY
CAMBRIDGE, MASS.

RECEIVED AUGUST 15, 1936

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[8] Vanstone, *Trans. Faraday Soc.*, **7**, 42 (1911).

[9] Schuller, *Z. anorg. Chem.*, **40**, 385 (1904).

[10] Kurnakow, *ibid.*, **23**, 434 (1900).

[11] Poindexter, *Phys. Rev.*, **28**, 208 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. II. The Reaction of Carbonates with Dichlorodiethylenediaminocobaltic Chloride

BY JOHN C. BAILAR, JR., FRANK G. JONELIS AND E. H. HUFFMAN

The factors which commonly determine whether a Walden inversion will occur when a group attached to an asymmetric atom is replaced by another group are the nature of the reagent, its concentration, the temperature and the solvent. That the first of these factors is effective in bringing about a Walden inversion in the reactions of complex inorganic compounds was shown by the discovery that levo-dichlorodiethylenediaminocobaltic chloride reacts with silver carbonate to give a levo carbonato product, while potassium carbonate gives the corresponding dextro salt[1]

$$[\mathrm{Coen_2Cl_2}]^+ \longrightarrow {}^2[\mathrm{Coen_2CO_3}]^+$$

$$l \underset{\text{alc. HCl}}{\overset{\mathrm{K_2CO_3}}{\rightleftarrows}} d$$

$$l \xrightarrow{\mathrm{Ag_2CO_3}} l$$

The present study had for its purpose the determination of the influence of the second two factors mentioned above, *viz.*, the effect of changing concentration of the reagent and the effect of temperature.

Effect of Concentration.—The dichlorodiethylenediaminocobaltic chloride was treated with varying amounts of silver carbonate and the optical rotation of the product was determined. Table I shows that increasing the number of moles of silver carbonate changed the rotation of the product from dextro to levo.

TABLE I

Molar ratio $\frac{Ag_2CO_3}{\text{complex salt}}$	Specific rotation of product
0.75	+362°
1.12	+288°
1.5	−102°
3.0	−160°
4.5	−180°

The data show that changing the concentration of the reagent silver carbonate is certainly an important factor in determining whether a Walden inversion takes place.

On the other hand, potassium carbonate produced the dextro salt at all concentrations (Table II).

TABLE II

Molar ratio $\frac{K_2CO_3}{\text{complex salt}}$	Specific rotation of product
1.0	+240°
1.5	+140°
3.0	+110°
5.0	+ 80°

The marked racemization during the reaction with the higher concentration of potassium carbonate may be due to the formation of the optically inactive *trans* hydroxy-aquo complex $[\mathrm{Coen_2(H_2O)(OH)}]^{++}$ by the strongly basic solution.

Holmberg[3] and Bancroft and Davis[4] have shown that *l*-bromosuccinic acid and silver oxide react to give *l*-malic acid if the silver oxide is present in limited amount, but *d*-malic acid if it is present in large amount. The rotation of the product is apparently a function of the acidity of the solution. It is evident that neither the acidity nor the carbonate ion concentration is the determining factor in the reaction of carbonates with levo-dichlorodiethylenediaminocobaltic chloride, for the more silver carbonate is present, the more strongly levorotatory the product is, while potassium carbonate, which furnishes an abundance of both hydroxyl and carbonate ions, yields a dextrorotatory product.

Effect of Temperature.—The same reaction was carried out at six different temperatures. The data which are summarized in Table III show that the chief effect of low temperatures is to decrease the rate of reaction, and the effect of higher temperatures is to cause racemization.

TABLE III

Temp., °C.	Specific rotation of product
0	− 10°
15	−100°
25	−106°
50	− 78°
75	− 28°
90	0°

Using a smaller amount of silver carbonate, dextrorotatory products were obtained, the com-

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[1] Bailar and Auten, THIS JOURNAL, **56**, 774 (1934).

[2] The symbol "en" represents ethylenediamine.

[3] Holmberg, *J. prakt. Chem.*, **87**, 456 (1913).

[4] Bancroft and Davis, *J. Phys. Chem.*, **35**, 1253 (1931).

pound prepared at 0° having a smaller rotation than that prepared at 25°.

The reaction of mercurous carbonate with the dichloro salt is of some interest. Mercurous ion and silver ion are both univalent and form insoluble chlorides and carbonates, and they have about the same ionic radii.[5] They might, therefore, be expected to behave similarly. It was found, however, that *l*-dichlorodiethylenediaminocobaltic chloride reacts with an excess of mercurous carbonate to give the dextrorotatory carbonato salt. The reaction is much slower than that with silver carbonate.

The discovery that the amount of reagent employed affects the rotatory power of the product in this reaction suggested a reëxamination of the reaction between oxalates and dichlorodiethylenediaminocobaltic chloride.[1] Varying the relative amounts of the reactants did not bring about an inversion in this case, however, though the magnitude of the rotatory power was varied somewhat.

Experimental

The materials used were prepared as described in the earlier paper. It has been found that the dextro-ammonium-α-bromo-camphor-π-sulfonate used in resolving the dichloro salt can be recovered in 85–90% yield by adding an excess of ammonium carbonate to the solution and evaporating to crystallization. Attempts to recover the complex inorganic salt have not been successful. The levo-dichlorodiethylenediaminocobaltic chloride used in this study had a specific rotation of +650°, as measured for a 0.05% solution for the D line of sodium.[6]

All measurements reported in this paper are for the D line of sodium, and, unless otherwise stated, for solutions having a concentration of 0.1%. In most cases, the carbonato salts were not isolated, but the solutions containing them were simply diluted to the proper concentration.

Effect of Varying the Proportions of $\left[\mathrm{Co}^{\mathrm{en}_2}_{\mathrm{Cl}_2}\right]\mathrm{Cl}$ and Silver Carbonate.—Three grams of levo-*cis*-dichlorodiethylenediaminocobaltic chloride was ground in a mortar with 2.14 g. of silver carbonate (molar ratio 1:0.75). The mixture was shaken in 10 cc. of water until the color change indicated that reaction was complete. The solution was allowed to stand for a day to ensure racemization of the unreacted dichloro salt, and the silver chloride was removed by filtration. One hundred cubic centimeters of absolute alcohol was added to precipitate the carbonatodiethylenediaminocobaltic chloride, which was filtered off at once. On standing, the filtrate yielded a second crop of the material. The first precipitate had very little optical activity; the second had a specific rotation of +362°. The experiments using larger amounts of silver carbonate were carried out in the same way. The negative ion of the complex compound is chloride in some cases, and carbonate in others, but this does not affect the specific rotations.

A sample of the dextro carbonato compound was prepared for analysis by adding 3.8 g. of silver carbonate in small portions to 2.4 g. of levo $[\mathrm{Coen_2Cl_2}]\mathrm{Cl}$ while the mixture was ground with water in a mortar. The complex compound was present in excess until the very end of the reaction. The product had a specific rotation of +370° and showed C, 22.34; H, 6.30, and N, 19.22. Calcd. for $[\mathrm{Coen_2CO_3}]\mathrm{CO_3{\cdot}3H_2O}$: C, 22.29; H, 6.47; N, 18.92. A sample of this material was reconverted to the dichloro salt by alcoholic hydrogen chloride. This salt had a specific rotation (0.05% soln.) of +240°. Chlorine, 37.08. Calcd., 37.37.

A sample of the levorotatory carbonato salt (C, 22.12; H, 6.43; N, 19.08) with a specific rotation of −180° was converted to the dichloro compound (Cl, 37.60) having a specific rotation (0.05%) of −132°.

The Effect of Varying the Concentration of Potassium Carbonate.—Samples of 0.3 g. of *l*-$(\mathrm{Coen_2Cl_2})\mathrm{Cl}$ were mixed with varying amounts (0.145, 0.218, 0.436 and 0.725 g.) of potassium carbonate and dissolved in 10 cc. of water at room temperature. At the completion of the reaction, 1 cc. of each solution was diluted to 33 cc. to give a 0.1% solution and the rotation was taken. The excess carbonate remaining in solution does not affect the rotation, as was shown by adding potassium carbonate to the solutions and taking the rotations again.

The Effect of Changing Temperature.—Intimate mixtures of 0.3 g. *l*-$[\mathrm{Coen_2Cl_2}]\mathrm{Cl}$ and 0.5 g. of silver carbonate were shaken in 10 cc. of water at 0, 15, 25, 50, 75 and 90° until the color of the reaction mixture indicated complete reaction. This required eight hours at 0°, but only a few seconds at 90°. At the three higher temperatures, the solution was cooled as quickly as possible after the reaction was ended. The silver salts were filtered out and 1 cc. of each filtrate was diluted to 33 cc. to give a 0.1% solution.

In the same manner 0.3 g. of *l*-$[\mathrm{Coen_2Cl_2}]\mathrm{Cl}$ was allowed to react with 0.3 g. of silver carbonate at 0 and 25°. In this case the solutions were allowed to stand until the unreacted dichloro salt had racemized. The observed rotations were +0.13 and +0.24°.

The Reaction with Mercurous Carbonate.—An intimate mixture of 0.4 g. of $[\mathrm{Coen_2Cl_2}]\mathrm{Cl}$ and 4 g. of mercurous carbonate was moistened with enough water to make a paste and ground intermittently until the color indicated completion of the reaction. This required about eight hours. Enough water was added to dissolve the complex, the solution was filtered, and the carbonato salt precipitated by adding alcohol and ether. It has a specific rotation of +120°.

The Reaction with Oxalates.—Samples of $[\mathrm{Coen_2Cl_2}]\mathrm{Cl}$, each weighing 0.30 g., were allowed to react with 0.245, 0.49 and 0.735 g. of $\mathrm{K_2C_2O_4{\cdot}H_2O}$ in 10 cc. of water at room temperature. After dilution of 1 cc. of each solution to 33 cc., they showed specific rotations of +160, +200 and +220°. The soluble potassium salts remaining in the solutions do not affect the rotatory power, as was shown by

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(5) Pauling, This Journal, **49**, 765 (1927).

(6) Mathieu, who confirmed the results of our earlier investigation [*Bull. soc. chim.*, [5] **3**, 495 (1936)], commented on the great discrepancy between the rotation of the dichloro salt as given by us (M_{D} −600°) and as found by him (M_{D} +2500°). This is no doubt due to differences in the concentrations of the solutions, which affect the specific rotatory power enormously, causing a change in sign at about 0.17%. This will be discussed in detail in a subsequent paper.

adding a large amount of potassium oxalate to each of them and taking the rotations again.

Likewise, three samples were ground with 0.31, 0.62 and 0.93 g. of silver oxalate and allowed to react in 10 cc. of water. After filtration and dilution (1 to 33 cc.) the solutions showed specific rotations of +170, +390 and +430°.

Another sample, weighing 0.6 g., was dissolved in 20 cc. of water. Eight-tenths of a gram of silver oxalate was added in small portions while the mixture was ground continuously, so that the complex was present in great excess until the end of the reaction. The solution was diluted as before and showed a rotation of +240°.

Summary

It has been shown that levo-dichlorodiethylenediaminocobaltic chloride reacts with a limited amount of silver carbonate to give the dextro carbonato salt, whereas a larger amount of silver carbonate causes inversion in the direction of rotation to give the levo salt.

The reaction with potassium carbonate gives the dextro salt, no matter what the concentration of the reagent.

It appears that temperature is not an important factor in determining whether a Walden inversion occurs in this reaction.

Mercurous carbonate, present in large excess, reacts with levo-dichlorodiethylenediaminocobaltic chloride to give the dextro-rotatory carbonato salt. In this respect it is like potassium carbonate, and unlike silver carbonate.

URBANA, ILL. RECEIVED AUGUST 4, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Molecules. III. The Reaction of Ammonia with Levo-Dichlorodiethylenediaminocobaltic Chloride

BY JOHN C. BAILAR, JR., J. H. HASLAM AND ELDON M. JONES

One of the mechanisms suggested for the Walden inversion postulates that every reaction which involves a single step in the substitution of one group by another on a tetrahedral atom should lead to inversion.[1,2] Accordingly, if the over-all reaction takes place in an odd number of steps the product should be the enantiomorph of the original material, but if it takes place in an even number of steps, the starting material and the product should have the same configuration.

The object of the present study was to see whether this theory might be applied to reactions of the octahedral complex inorganic compounds. The reaction studied was that between ammonia and levo-dichlorodiethylenediaminocobaltic chloride[3]

$$\underset{\text{levo } cis}{[\mathrm{Coen_2Cl_2}]\mathrm{Cl}} \longrightarrow \underset{\substack{trans\text{, levo } cis \\ \text{or dextro } cis}}{[\mathrm{Coen_2(NH_3)Cl}]\mathrm{Cl_2}} \longrightarrow \underset{\substack{trans\text{, levo } cis\text{, or} \\ \text{dextro } cis}}{[\mathrm{Coen_2(NH_3)_2}]\mathrm{Cl_3}}$$

The two chloride groups of the complex ion are attached to the cobalt in exactly the same way and occupy like positions in the molecule. It seems logical to assume, therefore, that the same mechanism functions in their displacement from the complex. If this is correct, the conversion of the dichloro salt to the diammino salt must take place in an even number of steps, and the theory mentioned would allow no inversion. However, as the data in Table I show, the reaction does lead to a Walden inversion, the product prepared at low temperatures being levorotatory while that prepared at higher temperatures is dextrorotatory. It is of some interest to note that this is the first case of a Walden inversion of complex inorganic compounds brought about by a change in temperature.

TABLE I

Reagent	Temp., °C.	$[\alpha]^{25°}_{\mathrm{E}}$ (av.)
Liquid NH_3	−77	−32
Liquid NH_3	−33	−22
Liquid NH_3	+25	+29
Gaseous NH_3	+80	+43
NH_3 in CH_3OH	+25	+31
NH_3 in C_2H_5OH	+25	+29

It is possible, of course, that the displacement of a negative chloride group by a neutral ammonia molecule produces such a profound change in the complex ion that the second step of the reaction does not follow the same mechanism as the first. The theory of Bergmann, Polanyi and Szabo and of Olson might be more applicable if the chloride groups were displaced by other univalent

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[1] Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, **B20**, 161 (1933).

[2] Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[3] The symbol "en" represents ethylenediamine.

negative groups. A search for an example of the Walden inversion in such a case is now under way. It seems probable that the two steps of the reaction here reported do not follow the same mechanism, or that the theory of Bergmann, Polanyi and Szabo and of Olson cannot be applied to this case.

A study of the octahedral model will show that if the substitution of the ammonia molecules for the chloride groups follows purely mechanical laws, both *cis* and *trans* isomers will be formed at each step of the reaction. The formation of a *trans* form at any point would, of course, cause racemization. Fortunately, the formation of the *cis* isomer is favored under the conditions of this reaction. In no case did the diammino compound contain more than 10% of the *trans* form, and the rotations, while small, were unmistakable.

Experimental

The dichlorodiethylenediaminocobaltic chloride used was prepared and resolved as previously described.[4] Several different batches were used, but all had about the same specific rotation: +650° for a 0.05% solution for the D line of sodium. The diamino compound rotates yellow light very feebly, so rotations on it were taken at the E line (5270 Å.). The instrument used was a Schmidt and Haensch polarimeter graduated to one-thousandth of a degree, and fitted with a prism to select the desired wave length. The solutions used had a concentration of 0.1%.

The amount of *trans* diamino salt formed in the experiments was determined by precipitating it from the mixture with sodium dithionate in acid solution, according to the directions of Werner.[5] The separation afforded by this method is not entirely quantitative, but was deemed satisfactory for the purposes of this investigation. Since the amount of *trans* salt in every case was very small, it was not removed from those samples which were examined for optical activity, but allowance was made for it in making up the solutions. That the presence of the *trans* salt does not affect the rotation of the *cis* salt was shown by polarimetric examination of various mixtures of the two.

The Reaction of Liquid Ammonia and levo cis ($Coen_2Cl_2$)-Cl at −77°.—One-half gram of levo *cis*($Coen_2Cl_2$)Cl was placed in a small flask in a bath of solid carbon dioxide. Fifty cubic centimeters of liquid ammonia was added and the flask was stoppered and allowed to stand until the reaction was complete—forty-eight to sixty hours. It is easy to follow the progress of the reaction as the original purple color of the solution changes to bright red (the chloro-ammino compound) and then to yellowish-brown (the diammino compound). The ammonia was allowed to evaporate, and the material was examined. Four samples gave specific rotations of −35, −29, −30 and −34°.

The Reaction with Liquid Ammonia at −33°.—The reaction was carried out as before, but the ammonia was allowed to evaporate freely from a well insulated flask, which was fitted with a trap to avoid entrance of moisture. The amount of ammonia used for one-half gram of the sample was varied between 10 and 50 cc. without appreciably affecting the results. Specific rotations of −21, −27, −24, −17, −22, −20 and −25° were obtained.

The Reaction with Liquid Ammonia at +25°.—Two-tenths of a gram of the dichloro salt was placed in one arm of a Y-tube and from 6 to 12 cc. of liquid ammonia in the other. After sealing, the tube was allowed to come to room temperature. The salt is deliquescent toward ammonia and some of the gas distilled over before room temperature was reached. When the temperature reached 25°, the whole of the liquid was poured onto the solid. In other respects the experiment was like the preceding ones. Six samples gave specific rotations of +17, +24, +13, +40, +42 and +37°.

The Reaction with Gaseous Ammonia at +80°.—A half gram of finely powdered dichloro salt was placed in a tube in a bath at 80°. Dry ammonia gas was passed over it until the reaction was complete. Six samples gave specific rotations of +31, +43, +40, +53, +56, +49 and +52°.

Samples of the dichloro salt were placed in an atmosphere of ammonia at room temperature over a year ago. The first step of the reaction was complete in about a month—the second step is now progressing very slowly.

The Reaction with Ammonia Dissolved in Absolute Methyl and in Absolute Ethyl Alcohols at +25°.—One-half gram of the dichloro salt was placed in 35 cc. of the saturated alcoholic ammonia solution. The salt did not dissolve appreciably, so the reaction was slow. After three or four days, the alcohol was evaporated, and the residue examined. Four samples prepared in methyl alcohol gave specific rotations of +29, +27, +34 and +36°. The samples prepared in ethyl alcohol gave rotations of +21, +28, +36 and +33°.

We are indebted to Mr. J. P. McReynolds for some of the polarimeter readings.

Summary

It has been shown that a Walden inversion takes place in the reaction of ammonia with levo-dichlorodiethylenediaminocobaltic chloride, the optical rotatory power of the diamminodiethylenediaminocobaltic chloride formed being conditioned by the temperature at which the reaction is carried out. Prepared at the temperature of boiling ammonia or lower, the product is levorotatory; at 25° and higher, it is dextrorotatory.

It seems probable that the two steps of the reaction do not follow the same mechanism, or that the mechanism of the Walden inversion proposed by Bergmann, Polanyi and Szabo and by Olson is not applicable to this case.

Urbana, Ill. Received August 4, 1936

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[4] Bailar and Auten, This Journal, **56**, 774 (1934).

[5] Werner, *Ann.*, **386**, 204 (1912).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity of Lithium Carbonate from 16 to 300°K. The Entropy and Heat of Solution of Lithium Carbonate at 298°K. The Entropy of Lithium Ion

BY OLIVER L. I. BROWN AND WENDELL M. LATIMER

The heat capacity of lithium carbonate has been determined from 16 to 300°K. in order to evaluate more accurately the entropy of lithium ion in aqueous solution.

Material.—A C. P. grade of lithium carbonate was shaken with distilled water saturated with carbon dioxide. The solution was filtered through sintered glass and the filtrate boiled to precipitate lithium carbonate. This procedure was repeated with the product thus obtained. The final product was dried at 110° and for a short time at 200°. The carbonate was definitely crystalline, and analysis by titration with weight burets, using sulfuric acid standardized against sodium carbonate, showed 99.82, 99.82 and 99.79% lithium carbonate.

Heat Capacity Measurements.—The measurements were made with a calorimeter and cryostat similar to that previously described.[1] One calorie was assumed equal to 4.1833 int. joules. The molecular weight of lithium carbonate was taken as 73.88. Measurements were made on a sample of 61.814 g. (weight *in vacuo*). The heat capacity measurements are summarized in Table I, and are plotted as a function of temperature in Fig. 1.

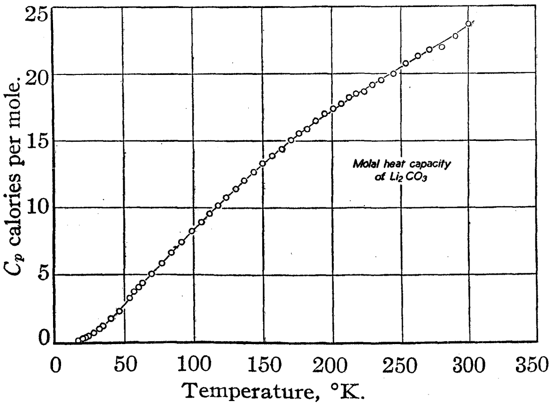

Fig. 1.—Molal heat capacity of lithium carbonate.

Entropy of Lithium Carbonate.—The entropy at 298.1°K. was obtained by graphical integration of the integral $S = \int C_p d \ln T$ between 16.68 and 298.1°K. combined with an extrapolation from 16.68 to 0°K. using the Debye specific heat equation. The calculation is summarized in Table II.

TABLE I

MOLAL HEAT CAPACITY OF LITHIUM CARBONATE

T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.
16.68	0.16	136.89	12.02
20.10	.25	143.65	12.66
22.30	.33	149.97	13.31
24.77	.44	156.44	13.83
28.59	.67	163.38	14.44
32.35	.94	170.12	15.04
35.04	1.18	176.09	15.52
40.49	1.74	181.98	15.98
46.56	2.32	187.97	16.48
49.33	2.73	194.44	17.00
53.58	3.24	200.85	17.40
56.96	3.70	206.78	17.74
60.16	4.03	212.47	18.21
63.18	4.35	217.84	18.48
69.90	5.03	223.23	18.64
76.94	5.83	229.21	19.16
83.96	6.61	235.84	19.50
91.32	7.41	244.66	19.94
98.90	8.21	253.68	20.73
105.47	8.92	262.21	21.31
111.32	9.53	270.72	21.76
117.68	10.16	279.51	21.96
123.83	10.74	289.58	22.76
130.59	11.40	300.20	23.69

TABLE II

ENTROPY OF LITHIUM CARBONATE

0–16.68°K.	Debye extrapolation	0.05
16.68–298.1°K.	Graphical from data	21.55 ± 0.05
	Entropy at 298.1°K.	21.60 E. U.

Heat of Solution of Lithium Carbonate.—The heat of solution of lithium carbonate was determined with the calorimeter previously described.[2]

The integral heat of solution of one mole of lithium carbonate in 1900 moles of water at 298.1°K. was found to be −3371 and −3395 cal. The average value −3383 cal. was corrected for the heat of hydrolysis of carbonate ion and extrapolated to infinite dilution on the assumption that the heat of dilution was the same as for lithium sulfate. In this way the theoretical heat of solution of lithium carbonate in an infinite amount of water with no hydrolysis was found to be −4200

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[1] Latimer and Greensfelder, THIS JOURNAL, **50**, 2202 (1928).

[2] Brown, Smith and Latimer, *ibid.*, **58**, 1758 (1936).

cal./mole. The probable error resulting from these corrections is difficult to estimate, but may be as high as 200 cal.

Entropy of Solution of Lithium Carbonate.—Seyler and Lloyd[3] measured the solubility of lithium carbonate at 298.1°K., in water solutions containing various amounts of carbon dioxide. They measured the total carbonate and bicarbonate by titration. By plotting the reciprocal of the mean molality of lithium ion and carbonate ion against the square root of the ionic strength, a fairly good straight line was obtained, from which the activity coefficient of lithium carbonate at saturation was found to be 0.59. The calculation is not of high accuracy but fortunately this does not affect greatly the free energy of solution. For example, a change of 10% in the activity coefficient would change the free energy of solution only about 180 cal., which corresponds to 0.3 E. U. in the entropy of lithium ion. The solubility of lithium carbonate in pure water is 0.169 *M* according to the same authors, so that $\Delta F^\circ = 3280$ cal./mole.

The entropy change when the solid salt dissolves to form a hypothetical one molal solution is given by the expression

$$\Delta S^\circ = (\Delta H - \Delta F^\circ)/T = (-4200 - 3280)/298.1 = -25.1 \text{ E. U.}$$

Entropy of Lithium Ion.—The entropy of carbonate ion[4] is −12.7 E. U., so that the entropy of lithium ion is given by the expression

$$S^\circ_{\mathrm{Li^+}} = {}^1/_2(\Delta S^\circ + S^\circ_{\mathrm{Li_2CO_3}} - S^\circ_{\mathrm{CO_3^{--}}}) = {}^1/_2(-25.1 + 21.6 + 12.7) = 4.6 \text{ E. U.}$$

Because of the absence of calorimetric data on lithium compounds, the entropy of lithium ion previously has been calculated from the entropy change of the lithium electrode reaction, even though the uncertainties were quite large.[5] The value thus obtained (−1.8 E. U.) differs by 6.4 E. U., or about 1900 calories, from the value calculated above. Since we believe the possible uncertainty introduced into the entropy of solution of lithium carbonate by the troublesome corrections for hydrolysis are not greater than one E. U. in $S^\circ_{\mathrm{Li^+}}$, we must conclude that the discrepancy is due to errors in the entropy change of the electrode reaction.

Summary

The heat capacity of lithium carbonate has been measured from 16 to 300°K. The entropy of lithium carbonate at 298.1°K. obtained from these data is 21.60 E. U. The heat of solution in water at 298.1°K. has been determined. The entropy of lithium ion calculated from these and other data has been found to be 4.6 E. U.

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[3] Seyler and Lloyd, *J. Chem. Soc.*, **111**, 994 (1917).

[4] Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

[5] Latimer, *Chem. Rev.*, **18**, 351 (1936).

BERKELEY, CALIF. RECEIVED SEPTEMBER 8, 1936

[CONTRIBUTION FROM VALENCIA HIGH SCHOOL]

The Boyle Temperature and a General Equation of State

BY GEORGE WOOLSEY

If a general equation of state is possible the Boyle temperature, the temperature at which $\left(\frac{\partial PV/T}{\partial P}\right)_T = 0$, at zero pressure must be either the same temperature or a function of RT_c/p_cv_c (*n* in my notation) for all pure non-associating and non-dissociating substances. Empirically the older data seem to indicate that the Boyle temperature, T_B (reduced), is a function of *n*. For example, taking T_B as the temperature for which the second virial coefficient equals zero, Holborn and Otto[1] found

Substance	Ne	He	H_2	O_2	A	N_2
T_B	3.00	3.65	3.21	2.72	2.73	2.56
n	3.254	3.261	3.282	3.423	3.424	3.428

Recomputing the values for oxygen and argon, using more recent values for critical temperatures, gives 2.74 and 2.72, respectively. These figures seem to indicate quite definitely that T_B is a function of *n*.

However, using data compiled by Beattie and Bridgeman,[2] approximate values of T_B are obtained which indicate that the other possibility, that T_B is a constant, is the correct one.

Substance	Ne	H_2	O_2	A	N_2	CH_4
T_B	<2.77	Between 3.7 and 2.5	>2.4	2.5	Between 2.56 and 2.33	2.48
n	3.245	3.282	3.423	3.424	3.428	3.448

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[1] Holborn and Otto, *Z. Physik*, **33**, 9 (1925); **38**, 365 (1926).

[2] Beattie and Bridgeman, "A New Equation of State for Fluids," *Proc. Am. Acad. Arts Sci.*, **63**, No. 5 (1928).

An additional value is found from the work of Bartlett, *et al.*, THIS JOURNAL, **52**, 1363–1374 (1930).

Substance	CO
T_B	Between 2.78 and 2.41
n	3.404

These data indicate that the value $T_B = 2.5$ for all of these substances is very nearly correct. The use of this relationship, $T_B = 2.5$, enables the constants of the equation[3]

$$PV + \frac{AV - AB}{T^xV^2 + CT^yV + DT^z} = nT + (B + K)\,P + q\log(P + 1)/T^w$$

to be determined in a way which is much more convenient than that used before. (The equation as given here contains the expression T^w which was not previously used. Work with the equation indicates that the logarithmic term should be an inverse function of the temperature.)

To make use of the above relationship the equation is divided by T and the expression for $(\partial PV/T/\partial P)_T$ is obtained by differentiation and set equal to zero at $P = 0$ when $T = T_B$. Two substitutions, $PV = nT$ when $P = 0$ and $dV/dP = T/P(\partial PV/T/\partial P)_T - V/P$ are used to obtain the final expression. This is

$$q = 2.30259\ T_B^w\ \{A/nT_B^{(x+1)} - (B + K)\}$$

Letting $n = n_0 = 3.25$, $T_B = 2.5$, $A = C^2 + 3C + 3 - D$ and $B + K = C + 3 - n - 0.30103\,q$, the following expressions for q are found for various values of x and w.

x	w	$-q$
0	1	$0.966720\,(C^2 - 5.125C + 5.03125 - D)$
0.5	1	$.61140\,(C^2 - 9.8467C + 6.21168 - D)$
1	1	$0.386691\,(C^2 - 17.3125C + 8.078125 - D)$
0	1.5	$.643843\,(C^2 - 5.125C + 5.03125 - D)$
0.5	1.5	$.407191\,(C^2 - 9.8467C + 6.21168 - D)$
1	1.5	$.257535\,(C^2 - 17.3125C + 8.078125 - D)$

Work with $w = 0$ or 0.5 is found to lead to unusable results.

The constants for the equation of state are determined for the various values of x, w and q from this table by substituting $V = 0.36$ at $P = 20$ and $V = 0.4$ at $P = 10$, with $T = 1$ for both, and solving the resulting simultaneous equations for C and D. These values are then checked at three points on the critical isotherm as indicated.

x	w	C	D	q	$(B + K)$	A	$-AB$
0	1	0.9237	2.4824	1.2875	0.2861	4.1419	8.7402
0.5	1	.8390	0.2943	1.0027	.2871	5.9266	0.1298
1	1	.9859	−4.1268	1.5046	.2829	11.0564	−17.4489
0	1.5	.9298	+3.1629	1.3085	.2859	3.4910	+11.4296
0.5	1.5	.8973	1.1216	1.1972	.2869	5.3753	3.3713
1	1.5	1.0210	−2.2272	1.6299	.2804	9.3327	− 9.9556

		P (calcd.) at			
			P exp.	0.5	5	2
			V	5.2[a]	0.454	0.55
x	w		T	1	1	1
0	1			0.544	4.9	1.85
0.5	1			.499	4.95	2.00
1	1			.417	8.24	Impossible
0	1.5			.539	4.86	1.78
0.5	1.5			.511	4.94	1.94
1	1.5			.455	12.5	Impossible

[a] Additional data obtained since the preceding paper[3] indicate that $V = 5.2$ at $P = 0.5$ is a better value than the previously used $V = 5.4$.

This table shows that $x = 0.5$ is a much better value than $x = 0$ or $x = 1$. A point in the liquid phase in equilibrium with the vapor, $T = 0.85$, $P = 0.3745$ and $V = 0.49048$, is used to determine one relation between y and z. When these values are substituted in the equation of state the equations $0.85^y + 0.7152 \times 0.85^z = 2.0509$ when $w = 1$ and $0.85^y + 2.5484 \times 0.85^z = 4.2074$ when $w = 1.5$ are obtained. Another relation between y and z is obtained by making use of the fact that for $V = 1$ the $(AV - AB)/(T^{1/2}V^2 + CT^yV + DT^z)$ term must be a maximum at the critical temperature. Differentiating the denominator with respect to T and setting it equal to zero gives the relation $0.5 + yC + zD = 0$. Solving these two equations in y and z gives $y = 0.333$ and $z = -2.67$ when $w = 1$; and $y = 1.8$ and $z = -1.88$ when $w = 1.5$. The table below shows that the values with $w = 1.5$ give the better solution.

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(3) Woolsey, THIS JOURNAL, **58**, 984–987 (1936).

T	8	8	4	4	0.85	0.85
V	1.56	2.80	0.91	1.54	5.8264	.49048
P (calculated) ($w = 1$)	19.77	10.15	18.3	9.50	0.355	(.373)
P (calculated) ($w = 1.5$)	20.34	10.31	20.04	10.07	.366	(.379)
P (experimental)	20	10	20	10	.3745	.3745[a]

[a] Used to obtain the relation between y and z.

The use, then, of the Boyle temperature has resulted in a modification of the form of the general equation of state by showing that the logarithmic term is a function of T and it has simplified considerably the determination of the constants of the equation. Using the critical point, the ideal gas value at low pressure, two points on the critical isotherm at high pressure, the Boyle temperature, one point in the liquid phase and the second term maximum at the critical point, an equation

$$PV + \frac{5.3752V + 3.3713}{T^{0.5}V^2 + 0.8973T^{1.8}V + 1.1216T^{-1.88}} = 3.25T + 0.2869P + 1.1972T^{-1.5}\log(P + 1)$$

is found which fits fairly closely at the eight other widely divergent points which were tested.

PLACENTIA, CALIF.

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[CONTRIBUTION FROM THE DIVISION OF PLANT NUTRITION, UNIVERSITY OF CALIFORNIA]

Age and the Chemical Composition of White Fir Wood

BY IRVING H. ISENBERG

The effect of age on the chemical composition of wood has been studied by few investigators. The composition of sapwood and heartwood has been compared,[1–4] separate trees examined[4,5] or a single constituent determined in one tree.[6,7] It would seem that differences due to age may be studied best by demarking zones of various ages on a cross-section from a definite height in a selected tree, in order to eliminate environmental factors as far as possible. The material should be examined for all important constituents.

Selection of Material

In the past, little effort has been made to record data on the environment in which the wood to be analyzed was grown. Since there is a possibility that environment and chemical composition may be correlated, such data may be of value in the future.

The wood used for this study was obtained from a white fir tree (*Abies concolor*) growing in a mixed conifer stand near Quincy, California. It was a healthy tree, approximately 100 feet tall and 185 years old. The diameter, breast high, was 23 inches (58 cm.). Classed as a dominant number three,[8] it had a long, pointed crown of medium width. The site was such that a tree dominant throughout its life had an average height of 125 feet (38 meters) at 300 years of age; the elevation 3900 feet (1150 meters); the slope 50%; and the exposure northwesterly. The average annual precipitation is 35 to 40 inches (89 to 101 cm.), with little during the summer season.

Preparation of Material

A section 7 inches (17.8 cm.) thick and 17 inches (43 cm.) in diameter, without the bark, was sawed from the white fir tree described above, at a point 12 feet (3.66 m.) above the ground level. The age at this point was one hundred and sixty years. This cross-section was carefully marked, following the 15th, 40th, 85th and 125th annual ring from the periphery, thus dividing the piece into five bands or zones. These zones were chiseled to sticks approximately 0.2 × 0.2 × 3.5 inches (0.51 × 0.51 × 8.9 cm.) and after drying at room temperature, chopped in a Wiley mill until all the sawdust passed a 60-mesh screen. In common with standard procedure, all sawdust passing an 80-mesh screen was discarded. Knots and compression wood areas were eliminated.

Data concerning these zones are listed in Table I. The total (T) was mixed from weighted proportions of the zones. The wood was 65.4% sapwood and 34.6% heartwood. The average apparent specific gravity of the sapwood was 0.425 and of the heartwood 0.440.

TABLE I

MEASUREMENTS ON AGE ZONES

No. of rings from periphery	Symbol	Sap- or heart-wood	Radial width of zone, in.	Area of zone, sq. in.	% of total	% of sap- or heart-wood
1–15	A	S	0.5	23.0	10.1	15.5
16–40	B	S	1.25	60.6	26.8	40.9
41–85	C	S	1.75	64.6	28.5	43.6
86–125	D	H	2.38	57.0	25.1	72.5
126–160	E	H	2.62	21.6	9.5	27.5
1–160	T	..	8.50	226.8	100.0	..

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(1) E. Gäumann, *Flora*, **23**, 344 (1928).

(2) G. J. Ritter and L. C. Fleck, *Ind. Eng. Chem.*, **15**, 1055 (1923).

(3) G. J. Ritter and L. C. Fleck, *ibid.*, **18**, 576 (1926).

(4) C. G. Schwalbe and E. Becker, *Z. angew. Chem.*, **33**, 14 (1920).

(5) P. Klason, *Cellulosechem.*, **12**, 36 (1931).

(6) G. De Chalmot, *Am. Chem. J.*, **16**, 611 (1894).

(7) B. Johnsen and R. W. Hovey, *J. Soc. Chem. Ind.*, **37**, 132T (1918).

(8) D. Dunning, *J. Agric. Research*, **36**, 755 (1928).

Methods

Methods of the Forest Products Laboratory[9] were used to determine ash, solubility in cold water, hot water, 1% sodium hydroxide, ether, and alcohol–benzene, pentosans (thiobarbituric acid used as precipitant), cellulose and lignin.[10] Nitrogen was determined by the method given in Schorger.[11] The Zeisel method, as modified by Dore,[12] was used to determine methoxyl content. Acetic acid was determined by the toluenesulfonic acid method of Freudenberg.[13]

Carbon dioxide determinations, using Dore's modification[14] of the LeFevre method for the determination of uronic acid, were made on the total sawdust. Mannan was determined on this material by Schorger's method[11] (p. 537).

Results

The averages for all data collected on age zones are gathered in Table II. In each case the value calculated for the total from the zones is listed so that it may be compared with the figure determined experimentally. All results are the average of at least two check determinations. Values are expressed in per cent. of oven-dry (105°) weight of the wood.

TABLE II

SUMMARY OF RESULTS

		Solubility in					
Zone	Ash	Cold water	Hot water	Ether	Alcohol–benzene	1% NaOH	Acetic acid
A	0.38	1.46	2.35	0.21	0.92	11.28	1.64
B	.37	0.51	1.29	.19	.96	10.66	1.70
C	.38	.21	1.19	.20	.94	9.95	1.71
D	.63	2.16	2.83	.26	1.74	11.72	1.33
E	.64	1.55	2.04	.22	1.49	10.77	1.25
T	.43	1.12	1.89	.23	1.43	11.38	1.64
Calcd. T	.46	1.04	1.83	.22	1.20	10.79	1.56

Zone	Methoxyl	Nitrogen	Pentosan	Lignin	Cellulose	Pentosan-in-cellulose
A	4.68	0.08	8.68	26.62	64.63	6.96
B	4.62	.06	8.46	27.29	64.56	6.33
C	4.40	.06	8.62	27.65	64.60	7.18
D	4.68	.06	8.83	27.31	64.53	5.75
E	5.06	.06	10.98	28.00	63.65	9.16
T	4.57	.06	8.86	27.43	64.47	7.31
Calcd. T	4.62	.06	8.73	27.40	64.49	..

The total sawdust contained 5.98% mannan and yielded 0.86% carbon dioxide in the uronic acid determination. The methoxyl content of the lignin isolated from total sawdust was 14.81%, or 4.06% calculated on the total wood. Compared to 4.57%, 89% of the methoxyl content was retained in the lignin.

Discussion

No previous data have been reported in the literature for the proximate analysis of the wood of white fir. The values found for the total wood, *i. e.*, the sample commonly used for analysis, compared favorably with the data recorded for other coniferous woods[11] (p. 34). In many points the composition of white fir resembled that of white spruce.

The carbon dioxide from total sawdust amounted to 0.86%. If the carbon dioxide is assumed to be due principally to uronic acid residues, the value for pentosan must be corrected. The total sawdust yielded 5.09% of furfural (equal to 8.86%, pentosan). The carbon dioxide content of 0.86% is equal to 3.44% uronic anhydride. Norris and Resch[15] found that the furfural resulting from galacturonic anhydride, on distillation with 12% hydrochloric acid, was only 43% of the theoretical, or 23.50% of the uronic anhydride. Using this figure, 0.81% of furfural was due to uronic anhydride. Apparently the difference, 4.28%, was the furfural due to pentosans. Accordingly the pentosan content was 7.33%, instead of 8.86%. Anderson[16] found 1.00% carbon dioxide in the wood of white spruce.

Inspection of the data for the five age zones showed the ash content to be constant within the sapwood and within the heartwood, but the values for the latter were approximately 50% higher than those of the sapwood. Other investigators[1–3] have found ash content higher in the sapwood in some instances and higher in the heartwood in others. The wood from older trees often is lower in per cent. ash than that from a younger tree of the same species.

The values for solubility in cold water, hot water, and 1% sodium hydroxide decreased from the outer to the inner sapwood, then rose sharply in the outer heartwood to their highest value and dropped slightly in the inner heartwood. Solubility in ether and alcohol–benzene had a constant value in the sapwood with an increase in the outer heartwood followed by a slight decrease in the inner heartwood.

Acetic acid values were constant within the sapwood and within the heartwood but were ap-

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(9) M. W. Bray, "Chemical Analysis of Pulps and Pulp Woods," Mimeographed, Forest Products Laboratory, Madison, Wisconsin, 1928.

(10) G. J. Ritter, R. M. Seborg and R. L. Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **4**, 202 (1932).

(11) A. W. Schorger, "Chemistry of Cellulose and Wood," McGraw-Hill Book Co., Inc., New York, 1926, p. 507.

(12) W. H. Dore, *J. Ind. Eng. Chem.*, **12**, 472 (1920).

(13) K. Freudenberg, *Ann.*, **433**, 230 (1923).

(14) W. H. Dore, THIS JOURNAL, **48**, 232 (1926).

(15) F. W. Norris and C. E. Resch, *Biochem. J.*, **29**, 1590 (1935).

(16) E. Anderson, *J. Biol. Chem.*, **91**, 559 (1931).

preciably higher in the former. This holds in all American conifers examined.[2,3] When the sapwood sawdust or the total sawdust was heated with absolute alcohol and *p*-toluenesulfonic acid in the Freudenberg method, a violet coloration first appeared. The reaction which caused this is unknown but the coloration suggests a possible method for distinguishing sapwood from heartwood in doubtful cases.

The methoxyl and pentosan values were practically constant in the four outer age zones, but both showed a sharp rise in the inner heartwood. This trend in the methoxyl content paralleled, to a certain extent, that of lignin, especially in regard to the final rise in the inner heartwood.

Nitrogen content was practically the same throughout the section but was slightly higher in the outer sapwood. One might expect this since most of the living cells were in this zone and conduction of nitrates occurred there also.

The lignin content showed appreciable increase from the periphery to the pith.

The cellulose content was nearly constant in the four outer zones but showed a considerable decrease in the inner heartwood. The pentosan in cellulose was irregular. Johnsen and Hovey[7] determined the cellulose in a balsam fir 10.5 inches (26.6 cm.) in diameter with 64 annual rings and found an increase from pith to sapwood, as follows: pith to 15th ring, 51.14%, 20th to 35th, 53.26% and sapwood, 54.21%.

Since in most determinations the values calculated for the total wood from the data of the individual age zones agreed very well with the values determined experimentally (compare last two rows, Table II), it was decided to calculate values for the sapwood and heartwood so that they might be compared with values found by Ritter and Fleck for other American conifers.[2,3] This was done from the data in Table I, Column 7.

In the American conifers they examined, Ritter and Fleck[2,3] found that the cold-water, hot-water, ether and alkali-soluble components were higher in the heartwood than in the sapwood and that, with the exception of lignin in white cedar, the cellulose and lignin contents were lower in the heartwood. White fir showed similar results for the extractives and cellulose but the lignin behaved like that of white cedar and was higher in the heartwood. Apparently, then, white cedar and white fir can be classed in a separate group from the others examined. Acetic acid was also higher in the sapwood of white fir as it was in all the woods they analyzed. In white fir both methoxyl and pentosan values were higher in the heartwood. Ritter and Fleck found fluctuations for these determinations. In general, the calculated sapwood and heartwood values agree with the data reported for American conifers.

TABLE III

CALCULATED VALUES FOR SAPWOOD AND HEARTWOOD

(% Oven-dry Weight)

Determination	Sapwood	Heartwood
Ash	0.38	0.63
Cold water	.53	1.99
Hot water	1.41	2.61
Ether	0.20	0.25
Alcohol–benzene	.94	1.67
1% NaOH	10.45	11.46
Determination	**Sapwood**	**Heartwood**
Acetic acid	1.70	1.31
Methoxyl	4.53	4.78
Pentosan	8.56	9.42
Nitrogen	0.06	0.06
Lignin	27.34	27.50
Cellulose	64.59	64.29

Comparison of our data for *Abies concolor* with those of Gäumann for *Abies pectinate*,[1] although different methods were used, showed the ash, lignin and solubility in ether to be higher in the heartwood in both cases. Gäumann found other extractives to be higher in the sapwood while the opposite was true in white fir. The values he found for pentosan and cellulose fluctuated throughout the year.

Summary

The effect of age on the chemical composition of white fir wood was studied. Values, calculated from the age zone data, for the composition of the sapwood and heartwood agree in general with the data reported by other investigators for American conifers.

BERKELEY, CALIF. RECEIVED AUGUST 18, 1936

[CONTRIBUTION FROM THE DEPARTMENTS OF BIOLOGICAL CHEMISTRY AND MEDICINE, HARVARD MEDICAL SCHOOL, AND THE MEDICAL CLINIC, MASSACHUSETTS GENERAL HOSPITAL]

Studies of the Pernicious Anemia Principle in Liver. III. The Isolation and Properties of a Substance with Primary Therapeutic Activity[1]

BY Y. SUBBAROW, BERNARD M. JACOBSON AND VILMA PROCHOWNICK

This communication is a detailed account and an extension of results previously reported in a preliminary form.[2]

It has already been found[3] that a therapeutically active extract of liver can be prepared by adsorption of Cohn's fraction G on norit, elution of the adsorbate by hot ethyl alcohol, and subsequent concentration of the elute by vacuum distillation (fraction B). The copious precipitate appearing on further concentration of the elute (fraction C) has been characterized as a complex purine.[4] The filtrate (fraction D) from 100 g. of fresh liver concentrated to 3 cc. is light brown in color, and contains 10 to 12 mg. of total nitrogen. This filtrate is the starting point of the preparation described below.

Experimental

After acidification of 150 cc. of the filtrate (derived from 5 kg. of liver) to *p*H 2 with hydrochloric acid, 16 g. of English fuller's earth was added, and the mixture was stirred mechanically for thirty minutes at room temperature. The precipitate was filtered off and washed once with 50 cc. of water. To the filtrate and washings were added 10 volumes of 95% ethyl alcohol and 10 volumes of ether, and the mixture was left in the cold room for twenty-four to thirty-six hours. The resulting precipitate was then filtered off. The precipitate (fraction H[5]) was obtained in a yield of 1 g. (20 mg. from 100 g. of liver) and contained 12 to 13% nitrogen.

One gram of this precipitate was dissolved in 50 cc. of water and the solution was brought to *p*H 3 with 10 *N* sulfuric acid. A crystalline precipitate immediately separated. This precipitate consisted mainly of calcium sulfate, and on the basis of spectroscopic examination contained traces of silver, copper, iron, aluminum and lead, all of the latter in a concentration of less than 0.01%, and probably derived from the fuller's earth. The filtrate of the calcium sulfate precipitate was then added to 40 cc. of water containing 1 g. of Reinecke salt[6] at 40°. After remaining in the cold room for twenty-four hours a crystalline precipitate formed which was filtered off and washed once with 50 cc. of ice-cold water. The precipitate was suspended in 300 cc. of 0.03 *N* sulfuric acid at 30–35°, and the Reinecke acid was removed by repeated extraction with 500 cc. of a mixture of equal volumes of amyl alcohol and ether. After several such extractions the color was entirely removed, and the solution was concentrated *in vacuo* to a volume of 25 cc. To this concentrate were added 10 volumes of acetone and 10 volumes of ether, and the mixture was kept in the cold room for forty-eight hours. A microcrystalline precipitate separated in a yield of 100 mg. (2 mg. from 100 g. of fresh liver). This precipitate is termed fraction I.

Fraction I was also prepared without the use of fuller's earth. To 1 liter of fraction D were added 7 liters of 95% ethyl alcohol and the mixture was kept at room temperature for five hours. The resulting precipitate, which contain none of fraction I, was filtered off. To the filtrate 3 liters of ethyl alcohol and 10 liters of ether were added, and the mixture kept in the cold room for forty-eight hours. The resulting precipitate, termed fraction E, was filtered off and dissolved in 500 cc. of water. To this was added 200 cc. of a 5% solution of rhodanilic acid in methyl alcohol. After forty-eight hours in the cold room a crystalline precipitate separated which was filtered off, and freed of rhodanilic acid by means of pyridine, with subsequent removal of the pyridine by ether, the method of regeneration described by Bergmann.[7] The regenerated rhodanilate solution was then precipitated by Reinecke salt as described above, and the subsequent procedure was followed. The yield of fraction I was approximately the same as that obtained by the previous method.

Properties of Fraction I.—The microcrystalline material, derived from either the crystalline rhodanilate or directly from the crystalline reineckate, is white and dissolves readily in water, forming a colorless solution. The sulfate is readily soluble in dilute alcohol, but is very little soluble in absolute alcohol. The sulfate can be precipitated from an aqueous solution acidified to *p*H 2.5 with sulfuric acid by the addition of acetone and ether. Repeated precipitation did not change the nitrogen content. The sulfate decomposes without melting above 290°. In 0.8% aqueous solution the sulfate has an optical activity $[\alpha]^{28}\text{D}$ −85.4 ±2°. *Anal.* Found: C, 41.56; H, 6.74; N, 13.13; S, 4.6. 3.4% of the 4.6% S is present as inorganic sulfate. The ash content of this sample was 1.6%. Spectroscopic examination disclosed that almost all of the ash consisted of chromium, evidently derived from the decomposition of the Reinecke salt. The amino nitrogen (Van Slyke[8]) was determined after interaction with nitrous acid at the end of

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(1) This investigation has been supported by grants from the Ella Sachs Plotz Foundation, the Proctor Fund of the Harvard Medical School, the Milton Fund of Harvard University and the Lederle Laboratories, Inc.; and by Therapeutic Research Grant No. 267 of the Council on Pharmacy and Chemistry of the American Medical Association.

(2) Subbarow and Jacobson, *J. Biol. Chem.*, **114**, cii (1936).

(3) Subbarow, Jacobson and Fiske, *New Eng. J. Med.*, **214**, 194 (1936).

(4) Subbarow, Jacobson and Fiske, *ibid.*, **212**, 663 (1935).

(5) Due to the possibility of conflict in terminology with the fraction G of Cohn, we have omitted the use of the letter G in designating our fractions.

(6) Dakin and West, *J. Biol. Chem.*, **109**, 489 (1935).

(7) Bergmann, *ibid.*, **110**, 471 (1935).

(8) The authors are indebted to Mr. Leon Rosenfeld for assistance in these determinations.

five minutes and at the end of sixty minutes, with the following results:

PER CENT. AMINO N FOUND

	5 min.	60 min.
Before hydrolysis	5	14.7
After hydrolysis for 6 hours in 2 *N* HCl	75	87

Under the usual conditions fraction I does not show a ninhydrin reaction, but after neutralization to *p*H 7 a slight reaction is observed. Fraction I reduces the Folin–Ciacalteau phenol reagent,[9] gives a positive orcin test, and a weak diazo reaction. The Sagakuchi, Millon, glyoxylic acid and biuret tests are negative.

Fraction I is readily precipitated by phosphotungstic acid and is partially precipitated by Hopkins' reagent ($HgSO_4$ in H_2SO_4). The reineckate can be recrystallized readily from hot water, but due to the decomposition products formed during the successive regenerations this salt is not suitable for further purification. A crystalline rufianate is readily obtained with the following composition: C, 46.5; H, 4.84; N, 4.23; S, 6.6. For further purification the rufianate is also not practicable due to the necessity of using large amounts of amyl alcohol in regeneration. Furthermore, if the rufianic acid is removed with barium the resulting barium rufianate precipitate adsorbs the fraction I.

An aqueous solution of fraction I, when exposed to ultraviolet light, exhibits an intense blue fluorescence. The absorption spectrum in the ultraviolet of an aqueous solution of fraction I (C 0.5 mg. per cc., L 1 cm.) as depicted in Fig. 1, shows an inflection between 2480 and 2560 Å.[10]

Therapeutic Activity.—That fraction H is therapeutically active is evidenced by satisfactory clinical and hematological improvement in four patients suffering from pernicious anemia, following the administration of the material by intramuscular injection. The therapeutic activity of fraction I has been tested similarly in two patients, with resulting moderate clinical and hematological improvement. The data are presented in Table I.

TABLE I

THE THERAPEUTIC ACTIVITY OF FRACTION H AND FRACTION I

Fraction no.	H	H	H	H	I	I
Patient no.	16	15	21	22	23	13
Total amount fraction administered, mg.	60	20	20	20	7.6	4
R. b. c. at beginning, millions per cu. mm.	1.05	1.28	1.15	0.88	2.41	1.40
R. b. c. at end, millions per cu. mm.	2.42	1.93	1.80	1.60	3.10	2.35
Reticulocytes at peak, %	31.0	24.4	30.2	24.6	6.6	12.0
Day of reticulocyte peak	6th	7th	5th	5th	4th	5th
Length of period, days	18	8	8	8	10	10

Since this paper has gone to press fraction I regenerated from the rufianate has been tested for its therapeutic activity on two patients. The resulting hematopoietic responses were similar to the responses to fraction I described in Table I.

It is to be noted that all of the experimental periods of therapeutic trial are of short duration, and are not adequate for an estimate of the capacity of fraction H and of fraction I to induce a complete clinical and hematological remission. It has already been reported[11] that the complete therapeutic activity of commercial liver extract probably depends upon its content of several chemically distinct substances. Fractions H and I, in the light of the present evidence, probably exert a primary or initiating therapeutic action, which is augmented by the addition of several other substances derived from crude liver extract. The evidence for this view, and the details of the therapeutic activities of fractions H and I, will be discussed in a forthcoming publication.

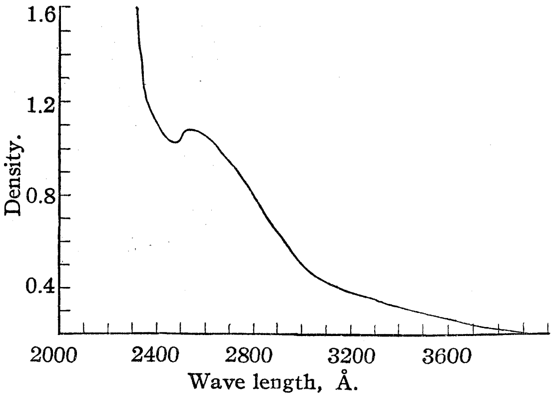

Fig. 1.

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(9) Folin and Ciacalteau, *J. Biol. Chem.*, **73**, 627 (1927).

(10) For the determination of the absorption spectrum the authors are indebted to Prof. George R. Harrison of the Massachusetts Institute of Technology.

(11) Fiske, Subbarow and Jacobson, *J. Clin. Investigation*, **14**, 709 (1935).

There has recently been reported by Laland and Klem[12] the separation from liver of an amorphous, reddish-yellow material, in a yield of 0.35 mg. from 100 g. of fresh liver, with the following composition: C, 53.64; H, 6.85; N, 13.33; S, 0.74 (ash content 2.05%). The absorption spectrum in the ultraviolet showed two points of inflection, one between 2500 and 2650 Å. and another between 3450 and 3500 Å. The similarity between the nitrogen content and one point of inflection of the absorption spectrum of the material of Laland and Klem and fraction I is worthy of note. The material of Laland and Klem has been found to be therapeutically active, in doses of 0.7 mg., by Strandell, Poulsson and Schartum-Hansen.[13] Proof is still lacking that the chemically active material reported in this paper is a single pure chemical substance.

Summary

There is described the isolation from commercial liver extract of a microcrystalline white substance, as a sulfate, in a yield of 2 mg. from 100 g. of fresh liver, exhibiting intense blue fluorescence when exposed to ultraviolet light, and exerting therapeutic activity in pernicious anemia.

BOSTON, MASS. RECEIVED AUGUST 19, 1936

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[12] Laland and Klem, *Acta Med. Scand.*, **88**, 620 (1936).

[13] Strandell, Poulsson and Schartum-Hansen, *ibid.*, **88**, 624 (1936).

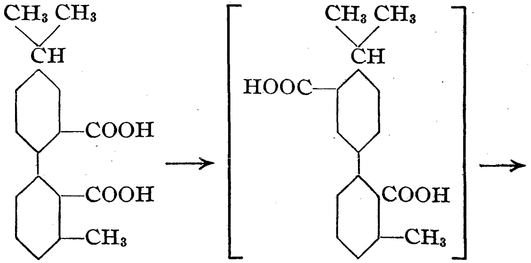
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

Investigations in the Retene Field. VII. Certain Fluorenones and Phenanthridones from Retenediphenic Acid

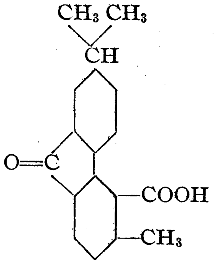
BY DAVID E. ADELSON[1] AND MARSTON TAYLOR BOGERT

In a previous publication[2] it was shown that the oxidation of retenequinone in glacial acetic acid solution with 30% hydrogen peroxide yielded retenediphenic acid. This paper is concerned with the preparation and proof of structure of some additional derivatives of retenediphenic acid and with the establishment of the configuration of compounds previously reported.[2]

When retenediphenic acid (I) was treated with 95% sulfuric acid, a rotation of one of the rings of the biphenyl nucleus took place and the hypothetical intermediate (II) thus formed lost a molecule of water in two ways to yield 6-methyl-2-isopropylfluorenone-5-carboxylic acid (III) and 1 - methyl - 7 - isopropylfluorenone - 5 - carboxylic acid (IV).

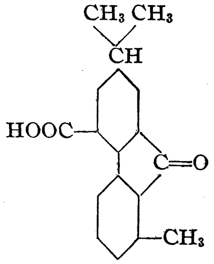


(I) (II)



(III)

and



(IV)

At 110° the principal product was the keto acid (III), while the isomeric acid (IV) was isolated when the reaction was carried out at room temperature. At 60° there resulted a mixture of acids which could not be separated by fractional crystallization; at 175° complete sulfonation took place. These keto acids, (III) and (IV), were characterized by conversion into the oximes, the methyl esters and the oximes of the latter.

At 110° the action of 95% sulfuric acid on the 3-methyl-4′-isopropyl-2′-carbomethoxybiphenyl-2-carboxylic acid (V) resulted in a mixture of the keto acids, (III) and (IV), and the methyl ester of (IV). This is similar to the experience of Underwood and Kochmann,[3] who studied the action of sulfuric acid on methyl acid diphenate. At room temperature, however, 95% sulfuric acid converted the acid ester (V) into the methyl ester

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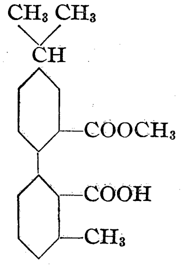
(1) Fritzsche Fellow in Organic Chemistry, Columbia University, 1935–1936.

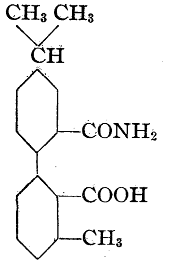
(2) Adelson, Hasselstrom and Bogert, THIS JOURNAL, **58**, 871 (1936).

(3) Underwood and Kochmann, *ibid.*, **46**, 2074 (1924).

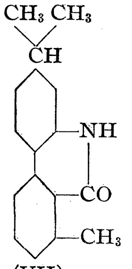
of (IV) in quantitative yield. The last reaction furnished the important link essential to the determination of the structures of the compounds reported in this and the previous paper.[2]



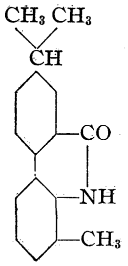
(V)



(VI)



(VII)



(VIII)

Concentrated ammonium hydroxide converted the acid methyl ester (V) into 6-methyl-5′-isopropyl-1′-diphenamic acid (VI) which yielded 8-methyl-2-isopropylphenanthridone (VII) when subjected to the Hofmann degradation. This phenanthridone (VII) was isomeric but not identical with the product obtained from the Beckmann rearrangement of 1-methyl-7-isopropylfluorenonoxime.[4] The previously reported phenanthridone is therefore 1-methyl-7-isopropylphenanthridone (VIII). Oxidation of (VII) yielded hemimellitic acid, thus indicating that the amide group in the amic acid (VI) and the ester group in the acid methyl ester (V) were in the same benzene nucleus as the isopropyl group. From this it followed that the action of 95% sulfuric acid on (V) at room temperature should yield the methyl ester of (IV) and that the acid (III), isomeric with (IV), should not yield retene ketone (1-methyl-7-isopropylfluorenone) upon decarboxylation, and such was actually found to be the case.

As a by-product in the action of 95% sulfuric acid on retenediphenic acid at 110°, there was formed a small amount of a neutral body. Its structure has not yet been determined.

Pyrolysis of retenediphenic acid yielded retene ketone.[5,6] This is analogous to the behavior of diphenic acid, which yielded fluorenone under similar treatment.[7,8] A better yield of retene ketone was obtained by dry distillation of retenediphenic anhydride.[2] Fluorenone has been obtained from diphenic anhydride in similar fashion.[8] The over-all yield of the ketone, based on retene, was 21%, whereas the older method of preparation[6] gave a yield of 13%.

So far as our experiments have gone, only one of the possible stereoisomers was encountered in these reactions.

Acknowledgments—We are indebted to Dr. Torsten Hasselstrom for preliminary work on the preparation of 6-methyl-2-isopropylfluorenone-5-carboxylic acid and for authentic samples of 1-methyl-7-isopropylphenanthridone and retene ketone.

Experimental

6 - Methyl - 2 - isopropylfluorenone - 5 - carboxylic Acid (III).—A solution of 10 g. of retenediphenic acid in 25 cc. of 95% sulfuric acid was maintained at 110–115° for twenty minutes, cooled and poured onto cracked ice. The yellow solid which this precipitated was dissolved in ether, and the solution washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent yielded 9 g. of a mixture of keto acids, (III) and (IV). Because of the similarity of their solubilities in organic solvents, their separation proved very difficult. Fractional crystallization of the mixture from benzene gave 3 g. of the keto acid (III), which was then recrystallized from 90% formic acid, appearing as long, yellow needles, m. p. 156–156.5° (corr.).

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.11; H, 5.76. Found: C, 76.78; H, 5.86.

Upon dry distillation of this acid, carbon dioxide was evolved and there appeared in the distillate a neutral, yellow oil, which could not be obtained in the crystalline state even when seeded with a crystal of retene ketone.

When the combined benzene mother liquors from the above operations was evaporated to dryness and the residue boiled with 10% sodium carbonate solution, there remained a small amount of undissolved material. This neutral body, which was also insoluble in hot dilute caustic alkali, appeared as small, yellow leaflets from 95% ethanol, m. p. 194–195° (corr.). Its structure has not yet been determined. Upon acidification of the carbonate filtrate, the mixture of acids was reprecipitated. Attempts to isolate the isomeric acid (IV) from such a mixture were unsuccessful.

Methyl Ester.—The dry potassium salt (1 g.) of the keto acid (III) was boiled with 5 g. of dimethyl sulfate for fifteen minutes, cooled and the excess dimethyl sulfate destroyed by pouring the reaction mixture into water. The resulting suspension was extracted with ether, the ethereal solution washed with 10% sodium carbonate solution, water and

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(4) Bogert and Hasselstrom, THIS JOURNAL, **56**, 983 (1934).

(5) Bamberger and Hooker, *Ann.*, **229**, 135 (1885).

(6) Komppa and Fogelberg, THIS JOURNAL, **54**, 2900 (1932).

(7) Fittig and Obermeyer, *Ber.*, **5**, 933 (1872); *Ann.*, **166**, 372 (1873).

(8) Huntress, Hershberg and Cliff, THIS JOURNAL, **53**, 2720 (1931).

finally dried over anhydrous magnesium sulfate. Evaporation of the solvent, followed by recrystallization of the residual yellow solid (0.7 g.) from methanol, yielded tiny glistening flakes, m. p. 86.5–87.5° (corr.).

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.51; H, 6.17. Found: C, 77.37; H, 5.91.

Oxime of the Methyl Ester.—A suspension of 0.6 g. of the above methyl ester, 1 g. of hydroxylamine hydrochloride and 1.5 g. of anhydrous barium carbonate in 20 cc. of absolute methanol was refluxed for eight hours, filtered and the filtrate diluted with water. This precipitated the oxime in nearly theoretical yield. Recrystallized from dilute ethanol, it appeared as short, pale yellow needles, m. p. 173–174° (corr.).

Anal. Calcd. for $C_{19}H_{19}O_3N$: C, 73.75; H, 6.20. Found: C, 73.86; H, 5.92.

The oxime of the free acid, prepared similarly, appeared as short, cream-colored needles from dilute ethanol which darkened slightly over 250° and melted with decomposition at 268–269° (corr.).

Anal. Calcd. for $C_{18}H_{17}O_3N$: C, 73.19; H, 5.81. Found: C, 73.19; H, 6.09.

1 - Methyl - 7 - isopropylfluorenone - 5 - carboxylic Acid (IV).—Retenediphenic acid (2.5 g.) was dissolved in 10 cc. of 95% sulfuric acid at room temperature and, after twenty-four hours, the clear solution was poured onto cracked ice. The yellow precipitate thus formed was filtered, washed with water and recrystallized from 90% formic acid, from which it appeared as broad, yellow leaflets, m. p. 200.5–201° (corr.); yield 1.0 g.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.11; H, 5.76. Found: C, 76.62; H, 5.94.

When retenediphenic acid was heated with 95% sulfuric acid at 60° for twenty minutes and the reaction mixture worked up as described for the above keto acid (III), a mixture of products resulted which could not be separated by fractional crystallization. At 175° complete sulfonation resulted even when heat was applied for only two minutes.

Methyl Ester.—This was prepared from the potassium salt of the keto acid (IV) in a manner similar to the synthesis described above for the isomeric methyl ester. Recrystallized from methanol, it appeared in tufts of short, bright yellow needles, m. p. 104–104.5° (corr.).

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.51; H, 6.17. Found: C, 77.31; H, 6.27.

Two grams of the acid methyl ester (V) was dissolved in 8 cc. of 95% sulfuric acid at room temperature and, after a day, the crimson solution was poured into water, a yellow precipitate forming. This was dissolved in ether, the ethereal solution was washed with 10% sodium carbonate solution, water and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the keto methyl ester in practically quantitative yield; recrystallized from methanol, it appeared as tufts of short, bright yellow needles, m. p. 104–104.5° (corr.). Mixed with a sample of the above methyl ester of m. p. 104–104.5° (corr.), it gave no depression.

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.51; H, 6.17. Found: C, 77.34; H, 6.45.

The oxime of the methyl ester, prepared similarly to the isomeric oxime described above and crystallized from dilute ethanol, appeared as clusters of long, cream-colored needles, m. p. 151.5–152° (corr.).

Anal. Calcd. for $C_{19}H_{19}O_3N$: C, 73.75; H, 6.20. Found: C, 73.72; H, 6.52.

The oxime of the keto acid (IV), prepared similarly, crystallized from dilute ethanol in short, pale yellow needles which melted with decomposition at 249–250° (corr.).

Anal. Calcd. for $C_{18}H_{17}O_3N$: C, 73.19; H, 5.81. Found: C, 73.12; H, 5.78.

6 - Methyl - 5′ - isopropyl - 1′ - diphenamic Acid (VI).—The acid methyl ester (V) was dissolved in concentrated ammonium hydroxide and allowed to stand with occasional shaking for a week. Dilution of the solution followed by acidification yielded a white precipitate which appeared as colorless, hard prisms (yield 25%) from 95% ethanol, m. p. 197–198° (corr.). Mixed with an authentic specimen of the amic acid (VI) of m. p. 201–202° (corr.), it melted at 200–201° (corr.).

8-Methyl-2-isopropylphenanthridone (VII).—To a solution of 3.5 g. of the amic acid (VI) in 30 cc. of 10% potassium hydroxide, there was added slowly a solution of 3 g. of bromine in 30 cc. of 10% potassium hydroxide. The clear solution was cooled in an ice-bath for thirty minutes, heated at 60–65° for another thirty minutes, cooled, 1 g. of sodium bisulfite added and the resulting solution acidified with concentrated hydrochloric acid. The voluminous white precipitate was boiled with 50 cc. of 5% potassium hydroxide solution, filtered, washed with water, dried at 110°, and recrystallized from benzene, 95% ethanol and finally from benzene, from which it appeared as long, silky white needles, m. p. 230–231° (corr.). A mixture of this and an authentic specimen of 1-methyl-7-isopropylphenanthridone[4] (VIII) of m. p. 221–222.5° (corr.) melted at 187–188° (corr.).

Anal. Calcd. for $C_{17}H_{17}ON$: C, 81.23; H, 6.82. (Calcd. for the amino carboxylic acid, $C_{17}H_{19}O_2N$: C, 75.79; H, 7.12). Found: C, 81.17; H, 7.10.

Two grams of the above phenanthridone was dissolved in 7 cc. of 95% sulfuric acid and the solution poured into 150 cc. of water. The finely-divided suspension was made alkaline with 10% potassium hydroxide, diluted to a volume of 400 cc., 17 g. of potassium permanganate added and the mixture was stirred and refluxed for twenty hours. The solution was filtered, the colorless filtrate evaporated to a small volume, cooled, extracted with 350 cc. of ether and the latter dried with anhydrous magnesium sulfate. Evaporation of the ether yielded 0.7 g. of a white solid which appeared as white tablets from an ether–petroleum ether mixture. After drying at 110° it melted at 188–189° (corr.), with decomposition. Upon cooling, the fused material solidified and melted at 196–197° (corr.). The recorded melting points for hemimellitic acid and hemimellitic anhydride[9] are 190 and 196°, respectively. The acid gave an excellent fluorescein test on fusion with resorcinol and sulfuric acid. Upon treating an aqueous solution of the acid with a concentrated potassium chloride solution, there resulted tiny, glistening flakes which are characteristic of the mono-potassium salt of hemimellitic acid.[9]

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[9] Graebe and Leonhardt, *Ann.*, **290**, 220 (1896).

Anal. Calcd. for $C_9H_6O_6$: C, 51.42; H, 2.88. Found: C, 51.36; H, 2.97.

Retene Ketone (1-Methyl-7-isopropylfluorenone).—Two grams of retenediphenic anhydride was dry distilled, yellow vapors coming over accompanied by carbon dioxide. The distillate soon solidified to a yellow, crystalline material; yield, 1.5 g. (90%). From 95% ethanol it appeared as long, flat, sulfur-yellow prisms, m. p. 89–90° (corr.). Mixed with an equal amount of an authentic specimen of retene ketone of m. p. 88–89° (corr.), it melted at 89–90° (corr.).

When retenediphenic acid or an intimate mixture of its anhydride and soda lime were distilled, retene ketone also resulted. In these cases, however, losses due to charring were appreciable and the yields lower.

Summary

1. Dehydration of retenediphenic acid with 95% sulfuric acid yields two isomeric methylisopropylfluorenone carboxylic acids.

2. These keto acids have been characterized by their oximes, methyl esters and the oximes of the latter.

3. Ammonia converts methyl acid retenediphenate into the previously reported retenediphenamic acid which undergoes the Hofmann degradation to yield 8-methyl-2-isopropylphenanthridone. Oxidation of the latter yields hemimellitic acid, thus establishing the structures of the compounds concerned.

4. Treatment of methyl acid retenediphenate with 95% sulfuric acid at room temperature yields the methyl ester of 1-methyl-7-isopropylfluorenone-5-carboxylic acid. The isomeric acid is therefore 6-methyl-2-isopropylfluorenone-5-carboxylic acid.

5. Pyrolysis of retenediphenic anhydride gives retene ketone in 90% yield.

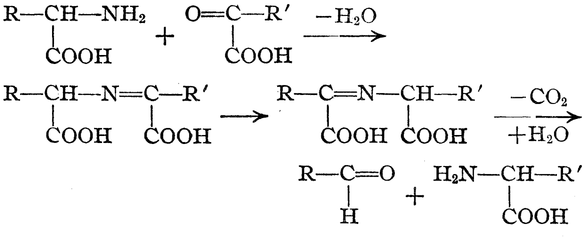
NEW YORK, N. Y. RECEIVED AUGUST 4, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLUMBIA UNIVERSITY]

The Reaction between α-Ketonic Acids and α-Amino Acids

BY ROBERT M. HERBST

In a previous paper[1] it was shown that a reaction takes place between certain α-ketonic acids and α-amino acids. The first step in the reaction was assumed to be interaction between the carbonyl and the amino groups to form a Schiff base. The second step involved the migration of a hydrogen atom from the α-carbon of the amino acid to the α-carbon of the ketonic acid residue, and the third the elimination of carbon dioxide from the intermediate and the addition of water resulting in fission with the formation of an aldehyde and an amino acid.



$$\underset{\text{COOH}}{\text{R—CH}}\text{—NH}_2 + \text{O=}\underset{\text{COOH}}{\text{C}}\text{—R}' \xrightarrow{-\text{H}_2\text{O}}$$

$$\text{R—}\underset{\text{COOH}}{\text{CH}}\text{—N=}\underset{\text{COOH}}{\text{C}}\text{—R}' \longrightarrow \text{R—}\underset{\text{COOH}}{\text{C}}\text{=N—}\underset{\text{COOH}}{\text{CH}}\text{—R}' \xrightarrow[+\text{H}_2\text{O}]{-\text{CO}_2}$$

$$\text{R—}\underset{\text{H}}{\text{C}}\text{=O} + \text{H}_2\text{N—}\underset{\text{COOH}}{\text{CH}}\text{—R}'$$

Certain results reported in the previous paper made it desirable to continue the investigation in order to gain greater insight into the mechanism of the reaction. In experiments with *l*-cystine and pyruvic acid acetaldehyde was always obtained in appreciable amounts. In the absence of any product, other than carbon dioxide, which could be attributed to the cystine molecule, it was concluded that the acetaldehyde was derived in some way from this source. This view has now been shown to be incorrect, for in the reaction between cystine and both phenylpyruvic and benzoylformic acids *no* acetaldehyde could be found. Moreover, small amounts of acetaldehyde have been isolated from the products of the reaction of pyruvic acid with *p*-methoxyphenylalanine, α-amino-*p*-methoxyphenylacetic acid, ethylcysteine, benzylcysteine and phenylcysteine, while with α-aminophenylacetic acid *no* acetaldehyde could be detected. These results point to pyruvic acid or some intermediate formed with the above amino acids as the principal source of acetaldehyde. The possibility remains that acetaldehyde could be formed by the secondary interaction of pyruvic acid with alanine formed during the primary reaction. In a separate experiment with this pair acetaldehyde was formed, but too slowly to account for its rapid formation in the reaction of pyruvic acid with cystine, S-phenylcysteine and S-benzylcysteine. The conclusion is therefore unescapable that the formation of acetaldehyde is largely a direct result of the primary reaction of pyruvic acid with the above amino acids.

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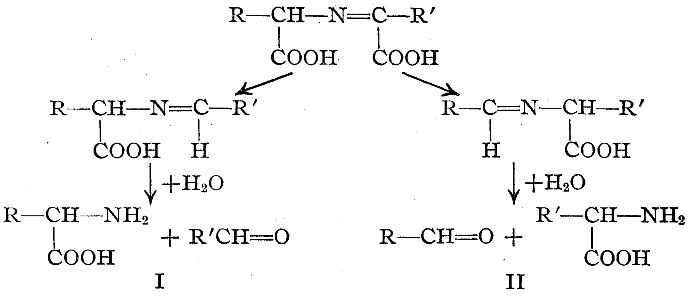
(1) Herbst and Engel, *J. Biol. Chem.*, **107**, 505 (1934).

To determine the probable fate of the cystine structure, the reaction of several S-substituted cysteine derivatives with pyruvic acid was studied. Of these, ethylcysteine gave the clearest results since it was possible to demonstrate the formation of considerable quantities of ethylthioglycolic aldehyde as well as acetaldehyde. The analogous aldehydes from phenylcysteine and benzylcysteine, which were not found in the usual experiments, could be obtained only by continuous distillation of the volatile products from the reaction flask, and then only in small yield. In both cases considerable decomposition took place with the formation of thiophenol and diphenyl disulfide in the first, and of benzyl mercaptan in the second. No analogous aldehyde could be obtained from cystine even in distillation experiments.

The results outlined above make it desirable to formulate a more labile mechanism for the reaction than the rather static mechanism given above.[2] It is now suggested that decarboxylation takes place while the molecule is momentarily in an unbalanced state during the shift of the double bond. The nature of the substituents R and R′ will influence the extent of decarboxylation in the direction of either Scheme I or II.



$$\mathrm{R{-}\underset{COOH}{CH}{-}N{=}\underset{COOH}{C}{-}R'}$$

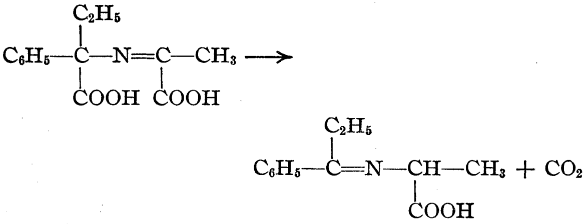
$$\mathrm{R{-}\underset{COOH}{CH}{-}N{=}\underset{H}{C}{-}R'} \xrightarrow{+H_2O} \mathrm{R{-}\underset{COOH}{CH}{-}NH_2 + R'CH{=}O} \quad \mathrm{I}$$

$$\mathrm{R{-}\underset{H}{C}{=}N{-}\underset{COOH}{CH}{-}R'} \xrightarrow{+H_2O} \mathrm{R{-}CH{=}O + R'{-}\underset{COOH}{CH}{-}NH_2} \quad \mathrm{II}$$

Such a mechanism would explain the observed formation of both aldehydes RCHO and R′CHO.

Schiff bases from α-phenyl-α-amino acids undoubtedly possess a strong tendency to form conjugated systems. Thus in the reaction of α-aminophenylacetic acid with pyruvic acid, the side chain double bond of the initial Schiff base is not conjugated with the benzene ring, and the tendency to form a conjugated system may explain the completeness of the reaction in the direction of Scheme II. When a methoxyl group is introduced in the para-position in aminophenylacetic acid, the tendency to form a conjugated system is possibly less strong, for the reaction proceeds partly in the direction of Scheme I.

Of particular interest are the results obtained in the reaction between α-amino-α-phenylbutyric acid and pyruvic acid, whereby propiophenone is produced in considerable quantity, together with mere traces of acetaldehyde. Here the tendency for the double bond to shift to the conjugated position is great, but this shift can occur only with simultaneous decarboxylation of the amino acid structure



$$\mathrm{C_6H_5{-}\overset{C_2H_5}{\underset{COOH}{C}}{-}N{=}\underset{COOH}{C}{-}CH_3 \longrightarrow C_6H_5{-}\overset{C_2H_5}{C}{=}N{-}\underset{COOH}{CH}{-}CH_3 + CO_2}$$

Contrary to a previous statement[1] it has now been found that α-aminoisobutyric acid also reacts (though very slowly) with pyruvic acid. In this case a minute amount of acetaldehyde is formed, but *no* acetone could be detected. Clarke, Gillespie and Weisshaus[3] have observed a similar difference in the action of formaldehyde in formic acid on this pair of amino acids.

Further support for the view that decarboxylation occurs exclusively during tautomeric shift is the almost complete absence of decarboxylation on treating alanine with benzoylformic acid. The Schiff base formed by this pair is conjugated, hence there is no tendency for the double bond to shift; practically no carbon dioxide is eliminated, and only a trace of benzaldehyde is formed. That this result probably is not due to failure of benzoylformic acid to form a Schiff base is shown by the fact that it reacts with α-amino-*p*-methoxyphenylacetic acid, cystine and ethylcysteine.

Experimental

The experiments were carried on in the apparatus previously employed,[1] modified to permit gravimetric estimation of carbon dioxide. The gas coming from the reaction flask was passed through a series of wash bottles containing, respectively, 5% sodium bisulfite, 2% potassium per-

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[2] Ingold and his co-workers [*J. Chem. Soc.*, 1778 (1935)] in a study of methyleneazomethine (C=N—C) systems from a kinetic point of view have found no evidence in support of an intermediate between tautomeric forms of simple Schiff bases. However, none of the systems considered involved carboxyl groups on the carbon atoms adjacent to the nitrogen [*cf.* also, Baker, Nathan and Shoppee, *ibid.*, 1847 (1935), and Turcan, *Bull. soc. chim.*, [5] **3**, 283 (1936)].

[3] Clarke, Gillespie and Weisshaus, THIS JOURNAL, **55**, 4571 (1933).

manganate in 2.5% sulfuric acid, two bottles with concentrated sulfuric acid and a Geissler absorption bulb charged with 40% potassium hydroxide. Suitable blank runs showed that only carbon dioxide was absorbed by the potash bulbs. The gas capacity of the whole train when charged was about 100 cc. Carbon dioxide was estimated periodically by changing the Geissler bulbs and weighing them. This method of estimating carbon dioxide was quicker and more convenient than that previously employed, and seemed to give more accurate results.

Pyruvic acid alone in aqueous solution slowly gives off carbon dioxide under the conditions of the experiment. The values obtained during actual experiments have been corrected, therefore, by subtraction of a suitable blank value, on the assumption that the amino acid has no effect on the rate of carbon dioxide production from pyruvic acid as such.

The reactions of pyruvic acid with α-aminophenylacetic acid and with cystine were repeated in the modified apparatus for purpose of comparison. Both experiments were in all other respects duplicates of those previously reported.

The isolation of reaction products followed in general the methods previously employed. After completion of the reaction aldehydic products were isolated as derivatives with dimedon (dimethyldihydroresorcinol) or 2,4-dinitrophenylhydrazine. Derivatives already described in the literature were identified by their melting points and mixed melting points with authentic specimens; others were identified by elementary analysis.[4] Aldehydes of low molecular weight were found in the sodium bisulfite wash bottle; less volatile aldehydes were isolated from the reaction mixture. To estimate quantitatively the amount of volatile carbonyl derivatives taken up in the bisulfite trap, the excess and bound bisulfite were titrated with standard iodine solution, as in the estimation of acetaldehyde in lactic acid determinations.[5] No acetaldehyde or other volatile carbonyl derivative is formed from pyruvic acid alone under the experimental conditions, as determined by suitable blank experiments.

Amino acids were isolated from the reaction mixture as previously described (except as noted in specific instances), either as such or in the form of derivatives with phenyl isocyanate or benzenesulfonyl chloride. Identity was established by elementary analysis, or by melting point and mixed melting point, respectively.

Mercaptans were isolated from the ether soluble portion of the reaction mixtures by vacuum distillation after removal of the solvent. Identification as 2,4-dinitrophenyl derivatives[6] rested upon melting points controlled by admixture of authentic specimens.

Reactions with Pyruvic Acid

In general 10 mml. of amino acid and 40 mml. of pyruvic acid were employed, exceptions being the reaction with α-aminophenylacetic acid where 30 mml. of pyruvic acid was employed, and the reaction with cystine where 5 mml. of the amino acid was employed. The yields of carbon dioxide and duration of the reactions are indicated by the curves in Figs. 1 and 2.

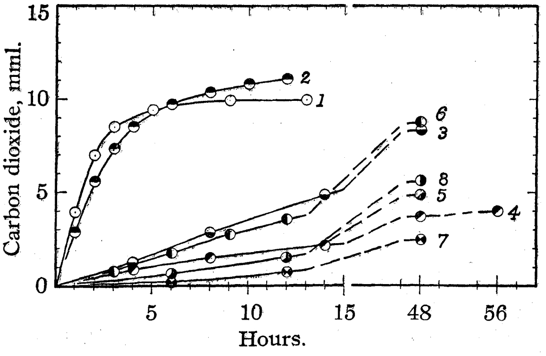

Fig. 1.—Rate of carbon dioxide evolution during reaction of pyruvic acid with: 1, α-aminophenylacetic acid; 2, α-amino-p-methoxyphenylacetic acid; 3, p-methoxyphenylalanine; 4, glutamic acid; 5, alanine; 6, leucine; 7, α-aminoisobutyric acid; 8, α-amino-α-phenylbutyric acid.

α-Aminophenylacetic Acid.—No acetaldehyde could be found. The yields of alanine (7.5 mml.) and benzaldehyde (7 mml.) were about the same as in earlier experiments.

Alanine.—Titration of the excess and bound sodium bisulfite in the trap indicated the presence of 4.4 mml. of an aldehyde, subsequently identified as acetaldehyde. Practically all of the alanine could be recovered in pure form.

Leucine.—Most of the isovaleric aldehyde was carried over into the bisulfite trap. Titration of an aliquot of the bisulfite solution indicated 12.2 mml. of aldehydes, however, since a permanent end-point in the titration was reached only after the solution began to smell strongly of isovaleric acid, much of the iodine was probably used to oxidize the aldehyde. Acetaldehyde could not be found. About 4 mml. of alanine was isolated.

α-Amino-p-methoxyphenylacetic Acid.—The high yield of carbon dioxide (11 mml.) may be explained by the formation of acetaldehyde according to Scheme I. Alanine was isolated in good yield, while anisaldehyde was obtained in 70–75% yield.

p-Methoxyphenylalanine.—Acetaldehyde was found in appreciable amounts. Alanine was isolated in small yield. p-Methoxyphenylacetaldehyde was obtained in the form of a condensation product with pyruvic acid, the lactone of α-keto-γ-hydroxy-δ-(p-methoxyphenyl)-valeric acid, which crystallized from the reaction mixture as it cooled, giving needles from hot water, m. p. 160°.[7]

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.50; OCH_3, 14.1; neut. eq., 220. Found: C, 65.66; H, 5.24; OCH_3, 13.83; neut. eq. (by back titration), 233.

With phenylhydrazine in 95% alcohol, slightly acidified by the addition of a few drops of glacial acetic acid, the phenylhydrazone is formed, m. p. 163° (dec.).

Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.65; H, 5.85; N, 9.03; OCH_3, 10.0. Found: C, 69.74; H, 5.82; N, 9.03; OCH_3, 10.29.

An attempt to prepare the 2,4-dinitrophenylhydrazone by boiling a solution of the ketolactone in 50% acetic acid with an equivalent amount of 2,4-dinitrophenylhydrazine resulted in the decomposition of the ketolactone; only

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[4] The author wishes to thank Mr. William Saschek of this department for the micro-analyses included in this report.

[5] Clausen, *J. Biol. Chem.*, **52**, 263 (1922).

[6] Bost, Turner and Norton, THIS JOURNAL, **54**, 1985 (1932).

[7] All melting points are corrected.

pyruvic acid 2,4-dinitrophenylhydrazone, m. p. 222°, could be isolated.

Glutamic Acid.—The amino acid mixture obtained by the usual procedure was treated with zinc oxide to remove glutamic acid, after which alanine could be isolated as the benzenesulfonyl derivative. No aldehydic products could be isolated.

α-Aminoisobutyric Acid.—The yield of carbon dioxide was 2.5 mml., as compared with only 0.3 mml. of aldehyde. The bisulfite solution was fractionated carefully after alkalinization with sodium bicarbonate, and the distillate caught in a trap immersed in a solid carbon dioxide–alcohol bath. Although the distillate smelled of acetaldehyde, not sufficient 2,4-dinitrophenylhydrazone for purification and identification could be obtained. As in earlier experiments the aminoisobutyric acid was recovered almost quantitatively.

α-Amino-α-phenylbutyric Acid.—From the reaction mixture 1.4 mml. of propiophenone and a small amount of alanine were isolated. The bisulfite solution contained 0.6 mml. of carbonyl compounds, of which 0.05 mml. could be identified as acetaldehyde.

Cystine.—The bisulfite trap yielded 1 mol. of acetaldehyde. The formation of 11 mml. of carbon dioxide, an excess of 1 mml. over that expected in accordance with Scheme II, together with the formation of acetaldehyde, indicates partial reaction in the sense of Scheme I. No hydrogen sulfide was formed during the reaction; the only sulfur-containing material found was a black resin from which no definite compound could be isolated.

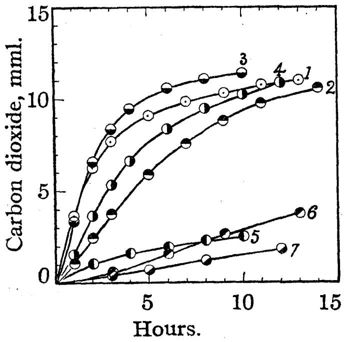

Fig. 2.—Rate of carbon dioxide evolution during the reaction of: 1, cystine with pyruvic acid; 2, S-ethylcysteine with pyruvic acid; 3, S-phenylcysteine with pyruvic acid; 4, S-benzylcysteine with pyruvic acid; 5, cystine with phenylpyruvic acid; 6, cystine with benzoylformic acid; 7, α-amino-*p*-methoxyphenylacetic acid with benzoylformic acid.

S-Ethylcysteine.—Acetaldehyde was found in the bisulfite trap together with a small amount of ethylthioglycolic aldehyde. Quantitative estimation of the aldehyde content of the trap was impossible because of secondary oxidations. Steam distillation of the reaction mixture yielded considerable quantities of an oil, the dimedon derivative (m. p. 93–94°) of which analyzed correctly as that of ethylthioglycolic aldehyde.

Anal. Calcd. for $C_{20}H_{30}O_4S$: C, 65.52; H, 8.26; S, 8.75. Found: C, 65.63; H, 8.17; S, 8.61.

Alanine was isolated in good yield. The odor of ethyl mercaptan was evident in the reaction mixture.

S-Phenylcysteine.—No aldehydic product, except acetaldehyde, of which there was 2.3 mml. in the bisulfite trap, could be found among the reaction products. Alanine was isolated in good yield. A large amount of brown oil, from which thiophenol and diphenyl disulfide were isolated, was formed during the reaction.

When the reaction was run with continuous distillation of the volatile products, instead of under reflux as was usually the case, phenylthioglycolic aldehyde was found in small amount in the distillate, and isolated as the dimedon derivative, m. p. 127–128°.

Anal. Calcd. for $C_{24}H_{30}O_4S$: C, 69.51; H, 7.30; S, 7.74. Found: C, 69.43; H, 7.34; S, 7.73.

In this case the reaction was run over a period of two to three hours, and the volume in the reaction flask was kept constant by the slow addition of water through a dropping funnel. A small amount of phenylthioglycolic aldehyde was prepared for purpose of comparison by boiling a solution of 5.5 g. of thiophenol with 7.6 g. of chloroacetal in absolute alcohol containing 1.15 g. of sodium for fifty hours, followed by hydrolysis with hydrochloric acid. The product, obtained in poor yields, was isolated as the dimedon derivative and proved to be identical with the substance obtained in the above reaction.

S-Benzylcysteine.—Acetaldehyde, 1.6 mml. by titration, was the only aldehydic product which could be isolated. Alanine was formed in good yield. A large amount of brown oil separated during the reaction, and upon careful examination yielded only a small quantity of benzyl mercaptan. By applying the technique of continuous distillation to this reaction it was possible to obtain a small amount of benzylthioglycolic aldehyde, dimedon derivative, m. p. 88–89°; and 2,4-dinitrophenylhydrazone, m. p. 156–157°.

Anal. Calcd. for $C_{25}H_{32}O_4S$: C, 70.04; H, 7.53; S, 7.49. Found: C, 70.23; H, 7.51; S, 7.69.

Anal. Calcd. for $C_{15}H_{14}N_4O_4S$: C, 51.99; H, 4.08; S, 9.26. Found: C, 51.98; H, 4.12; S, 9.28.[8]

Reaction with Phenylpyruvic Acid

Cystine.—During the reaction of cystine (2.5 mml.) with phenylpyruvic acid (10 mml.), 2.5 mml. of carbon dioxide was evolved in the course of ten hours (Fig. 2, Curve 5). The reaction was not continued over a longer period since phenylpyruvic acid gradually condenses with itself under the conditions of the experiment. No acetaldehyde nor other aldehydic products could be found among the products of the reaction. Some difficulty was encountered in separating the small amount of phenylalanine formed from traces of cystine. Analytically pure phenylalanine was obtained after decomposition of the cystine by boiling the amino acid mixture with a suspension of calcium hydroxide to which a few crystals of lead acetate had been added. After removal of the calcium and lead, phenylalanine separated upon concentrating the solution.

Reactions with Benzoylformic Acid

Usually 10 mml. of amino acid and 10 mml. of benzoylformic acid were employed in the reactions; in the case of cystine 5 mml. of the amino acid was employed. Except where specifically stated the duration of the reactions and yields of carbon dioxide are shown in Fig. 2.

Alanine.—After nine hours, only a trace of benzaldehyde (about 0.05 mml.) could be isolated, and the carbon

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[8] Micro Dumas determinations on 2,4-dinitrophenylhydrazine or derivatives thereof are not reliable.

dioxide evolved was less than could be estimated (0.1–0.2 mml.).

α-Amino-*p*-methoxyphenylacetic Acid.—From the reaction mixture an aldehyde fraction consisting of benzaldehyde and anisaldehyde was isolated as a mixture of the 2,4-dinitrophenylhydrazones, m. p. 231–233°. The corresponding derivatives of benzaldehyde and anisaldehyde melt at 242–243° and 255°, respectively. The yield of hydrazones calculated as benzaldehyde was 0.5 mml. A methoxyl determination showed 3.5% OCH_3, indicating a mixture of 64% benzaldehyde and 36% anisaldehyde. The amino acid fraction (8.0 mml.) consisted chiefly of aminomethoxyphenylacetic acid (OCH_3, 15.64; N, 7.43).

Cystine.—No benzaldehyde nor hydrogen sulfide could be detected. From the reaction mixture about 0.5 mml. of α-aminophenylacetic acid was isolated after removal of the last traces of cystine by treatment with lime and lead acetate.

S-Ethylcysteine.—During twelve hours only 0.7 mml. of carbon dioxide was formed. From the bisulfite trap a small quantity of ethylthioglycolic aldehyde was isolated. Neither benzaldehyde nor acetaldehyde could be identified as reaction products.

Summary

The investigation of the reaction between α-amino acids and α-ketonic acids has been extended in such a manner as to demonstrate more clearly the mechanism involved. The first steps in the reaction appear to lead to the formation of a Schiff base with a carboxyl group on each of the carbon atoms adjacent to the central nitrogen atom. The double bond of the methyleneazomethine system has a tendency to shift (C—N=C $\longrightarrow$ C=N—C) with the simultaneous elimination of carbon dioxide from either carboxyl group, both processes being dependent upon the nature of the other carbon substituents. In the case of α-amino-α-phenylbutyric acid this tendency is so pronounced that it takes place in spite of the necessity of forcing the displacement of the carboxyl group. Two new Schiff bases are assumed to result. Of these, one hydrolyzes to give the original amino acid and the aldehyde formed by decarboxylation of the ketonic acid; the other decomposes to form a new amino acid, derived from the ketonic acid by amination and reduction, and the aldehyde resulting from the oxidative deamination and decarboxylation of the original amino acid.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Further Observations Concerning the Crystallization of Undercooled Liquids

BY WILLIAM T. RICHARDS, EDWARD C. KIRKPATRICK AND CARL E. HUTZ

Introduction

The belief that homogeneous crystallization[1] of metastable liquids could be described successfully in statistical terms originated with the Kinetic Theory of Heat. With the writings of de Coppet, Ostwald and Tammann, which are too well known to require summary here, this belief became increasingly articulate. Recently Volmer[2] and Stranski[3] have expressed it in terms of Fluctuation Theory, and theoretical aspects of homogeneous crystallization have now advanced as far as the imperfect state of the Kinetic Theory of Liquids permits. Experiment has failed to keep pace with this development. A few cases of homogeneous crystallization, notably those described by Tammann[4] in very viscous melts, where the linear crystallization velocity is extremely small, have been reported. In general, however, a considerable body of scattered experimental work has served only to confuse the issue by the introduction of heterogeneous effects. The mechanism of heterogeneous crystal nucleus formation presents, however, certain points of interest in its own right, although the language for its description is at present less unequivocal and aesthetic than that for homogeneous crystallization. When the immense practical importance of the problem of efficiently inducing crystallization in metastable liquids, affecting, as it does, most organic preparations and many technical processes, is recalled it will be clear that any investigation concerning crystallization which contributes to the present knowledge, however imperfectly its results may be formulated, deserves attention. The object of the present communication was initially to determine the homogeneous crystallization rates of a number of liquids. It was found necessary, however, to interpret the re-

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(1) The term "homogeneous crystallization" will be used throughout to designate crystallization occurring in the free liquid, as opposed to "heterogeneous crystallization" which occurs at an interface.

(2) M. Volmer, *Z. Electrochem.*, **35**, 55 (1929).

(3) I. N. Stranski and R. Kaischew, *Z. physik. Chem.*, **B26**, 100, 317 (1934).

(4) G. Tammann, "Kristallisieren and Schmelzen," 1903.

sults in heterogeneous terms. This interpretation is incomplete in many respects but, since independent experiments from Germany have appeared during the progress of the investigation, it has been decided to report its present status, indicating in the discussion the directions in which future progress appears most probable. As an introduction a brief *résumé* of various heterogeneous effects which have been reported will be given. This review can, owing to the scattered and usually wholly independent investigations with which it deals, make no claim to completeness.

It was Tammann himself who first threw serious doubt upon the homogeneous mechanism, although he does not appear to have been willing to accept the full implications of his work. He reported that, with betol, quartz powder greatly increased the number of crystal nuclei and that powdered glass effectively prevented their formation.[5] Simultaneously Schaum reported that tubes of benzophenone showed a marked decrease in their tendency to crystallize with increasing number of meltings;[6] this phenomenon of "aging" will receive further attention below. Continuing his studies with Schoenbeck, Schaum then demonstrated that crystallization repeatedly occurred at the same spots, and that these spots could be deactivated with increased heating above the melting temperature.[6a] Similarly Jaffé showed that mechanical cleaning, such as intensive filtration, served to increase the range of temperature in which a solution could be maintained in a supersaturated condition,[7] and Füchtbauer extended these observations to undercooled liquids.[8] Both authors seem clearly to have recognized the heterogeneous character of the process of crystal nucleus formation, and Füchtbauer cites the effect of preheating noticed by Schaum and Schoenbeck, although apparently unconscious of earlier work on the subject. Young and Burke,[9] R. Marcelin,[10] Hinshelwood and Hartley[11] and Schaum and Riffert[12] independently not only of each other but of most previous work in the field, have described various aspects of the effect of preheating, and appear to agree that the crystallization center is situated on an interface of some sort. In apparent contradiction to this Orthmer[13] and Kornfeld[14] report a statistical distribution when the crystallization of a large number of samples was observed for long periods of time. Orthmer, however, admits the influence of foreign solids without attempting to account for it. It is believed that these various findings have been successfully explained by a communication from this Laboratory[15] in which it was demonstrated not only that the presence of overheatable nuclei was due to the presence of an interface but that, by the introduction of suitable solid adsorbents which had previously been infected with crystalline material, the number of crystal nuclei could be increased to almost any extent desired. A theory was given based upon the existence of two hypothetical modifications of the adsorbate which were called "crystalline"[16] and "liquid," respectively. Several consequences of the theory, especially its implication that crystal nuclei could be developed above the melting temperature, were confirmed experimentally. The subsequent publications of Biilmann and Klit[17] and Roginsky, Sena and Zeldowitsch[18] confirm this standpoint, and it does not at present appear to require modification.

Two questions remain unanswered by the work which has been summarized above. When the "crystalline adsorbate" has been destroyed by heating until all overheatable germs have disappeared, will crystallization take place in a homogeneous and consequently statistical manner? If not, is there a connection between the presence of adsorbents which contribute to the formation of overheatable germs and the process of crystallization, even when the overheatable germs themselves have been destroyed? It is believed that conclusive negative answers to both these questions may be inferred from the evidence presented below.

Experimental

The experiments were conducted with a large number of tubes, usually about a hundred, which were immersed si-

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(5) G. Tammann, *Z. physik. Chem.*, **25**, 441 (1898).

(6) K. Schaum, *ibid.*, **25**, 722 (1898).

(6a) K. Schaum and F. Schoenbeck, *Ann. Physik.*, **8**, 652 (1902).

(7) G. Jaffé, *Z. physik. Chem.*, **43**, 565 (1903).

(8) C. Füchbauer, *ibid.*, **48**, 549 (1904).

(9) S. W. Young and W. E. Burke, THIS JOURNAL, **29**, 329 (1907).

(10) R. Marcelin, *Compt. rend.*, **148**, 631 (1910).

(11) C. N. Hinshelwood and H. Hartley, *Phil. Mag.*, **43**, 78 (1922).

(12) K. Schaum and P. Riffert, *Z. anorg. allgem. Chem.*, **120**, 241 (1922).

(13) P. Orthmer, *Z. anorg. Chem.*, **91**, 209 (1915).

(14) G. Kornfeld, *Monatsh.*, **37**, 609 (1916).

(15) W. T. Richards, THIS JOURNAL, **54**, 479 (1932).

(16) The term "crystalline adsorbate" is not here intended to imply identity in structure with that of the crystal, but merely a variety of the adsorbate which yields the crystal on contact with free undercooled liquid.

(17) E. Biilmann and A. Klit, *Kgl. Danske. Videnskb. Selskab Math.-fys. Medd.*, **12**, 1 (1932).

(18) S. Roginsky, L. Sena and J. Zeldowitsch, *Phys. Z. Sov.*, **1**, 630 (1932).

multaneously in a constant temperature bath. They were then photographed on successive single frames of a 16-mm. motion picture camera at intervals of four minutes. A telechron motor, fitted with appropriate gears and contacts, provided that the bath should be stirred for three minutes and fifty seconds; the stirring was then discontinued and the illumination switched on, and, after ten seconds in which the agitation of the bath subsided, the picture automatically taken. The cycle then began anew. The apparatus was capable of functioning continuously for weeks without failure. The thermostat was a Dewar flask of about 20-liters capacity, and the tubes were held in this by a black Bakelite rack perforated to receive 100 tubes, each of which contained about 10 cc. of undercooled liquid. The photographic negative revealed clearly the difference between crystallized and uncrystallized material although it did not generally permit the location of the point at which crystallization began. Several other pertinent objects such as a clock, written information concerning the nature and conditions of the determination, etc., were also photographed. Thus, in the relatively small compass of a few feet of film, a complete record of the performances of each tube in a determination could be secured. A detailed record of this character would have been essential if statistical crystallization had been found; actually visual observation often provided sufficient evidence more conveniently.

Experiments were carried out with four substances. Salol, of the U. S. P. grade, was studied without attempt at purification. Several sources provided different samples of salol, but, in spite of minor variations in the melting point, the behavior of the various samples was uniform. Benzophenone, which had been twice distilled *in vacuo* with as little ebullition as possible, was also employed. Benzene, initially of the reagent grade, was shaken successively with sulfuric acid, dilute sodium hydroxide and water. It was then twice distilled from phosphoric anhydride. Purified carbon tetrachloride was also used, but since it was found to crystallize in too narrow a temperature range to permit differentiation in the behavior of individual samples, experiments with this substance will not be reported. The tubes were of Pyrex glass, and were steamed out for five minutes each by a jet of live steam, and dried at 110° by blowing in clean compressed air. They were evacuated and sealed after being filled with liquid. Ordinary cleanliness was maintained during their filling, but especial precautions to exclude dust were taken only in one case, which will receive individual mention below.

In reporting the experimental findings two alternatives are possible, neither of which is wholly satisfactory. Either detailed accounts of each of the various experiments may be given, or the general conclusions from a group of experiments may alone be stated. The first method would fill an immense amount of space with virtually unreadable material and, since the results are clearly not reproducible in detail, the space would largely be wasted. The second suppresses the facts and places too much emphasis on the judgment of the experimenters; details of importance may thus be lost by oversight. It has been decided to adopt the second alternative and to state the results in a series of conclusions, for which the experimental basis will be sketched only briefly. The reader is cautioned that few of these conclusions are wholly without exception; none, however, have been stated which do not represent an overwhelming majority of cases. A few specific experiments, which are not easily generalized in this way, will then be cited.

1. All samples of salol, benzophenone and benzene could be crystallized by immersing in a slush of solid carbon dioxide and acetone, and returning slowly to room temperature. (It will be apparent in the discussion why this seemingly obvious statement is included.)

2. Ten per cent. of the salol and benzophenone samples and 50% of the benzene samples could be activated by low temperature crystallization to produce crystals at relatively small undercoolings. For example 8 of 94 tubes containing benzophenone could be undercooled at −17° for twenty-four hours, and would remain apparently indefinitely at room temperature, without crystallization. After crystallization in a carbon dioxide–acetone mixture they could be heated to 100° and yet would crystallize within twenty-four hours at room temperature. A temperature of 140° was, however, sufficient to destroy this activity. Similar behavior with salol and benzene was found. Activity of this kind was destroyed with benzene, however, at about 25°, and, when present, manifested itself by permitting only two or three degrees of undercooling. This type of behavior is believed to depend on the presence or destruction of a "crystalline adsorbate."[15]

3. Crystallizations were conducted at various temperatures with each substance to determine a convenient temperature for a large number of identical determinations. Such a temperature was low enough to ensure the crystallization of at least half the tubes within forty-eight hours, and yet not so low that 15% of the tubes crystallized in the first hour. This permitted the establishment of a definite order of crystallization in the case of each substance. The temperatures were: salol −5°, benzophenone −17°, benzene −4°.

4. Repeated crystallizations at these temperatures showed, in agreement with the result which led Hinshelwood and Hartley[11] to postulate a heterogeneous mechanism, that initially the rate of

crystallization was three to ten times that reached after a few hours. A fairly constant rate was sometimes established after the first burst of activity, but it is believed that this is without significance.

5. Each sample behaved in an extremely individual and surprisingly consistent manner. For example, some six of the first ten to crystallize were almost always the same. Some 20% of the total number never crystallized at the temperature specified in the last sentence of (3) and these were also consistently the same samples. Among the intermediate cases the order of crystallization was surprisingly consistent throughout. It is believed, therefore, that a heterogeneous mechanism is responsible for crystallization in all three liquids at these temperatures.

6. No correlation could be found between the ability to form overheatable nuclei, as described in (2), and outstanding rapidity of crystallization at low temperatures. The lack of correlation between the two types of crystallization was, indeed, so striking that no doubt can remain that a different mechanism is involved in the two cases.

A few additional experiments also should be reported.

In the hope of eliminating dust, fifty tubes containing benzophenone which had been filled *in vacuo* in a mammoth all-glass apparatus from twice vacuum-distilled benzophenone were studied. Their behavior differed in no important respect from those filled in the air without special precautions.

The effect of the addition of washed powdered glass and cleaned active charcoal to salol and to benzophenone was also studied. Powdered glass served slightly to increase the tendency to crystallize, and active charcoal very greatly increased it in both cases. It should be added that these substances were added to samples which showed total inability to crystallize under ordinary conditions.

One experiment with benzene also should be cited. After 30% of the samples had crystallized at $-4°$ all tubes were placed in a bath at $+17°$ for twelve hours. On re-immersion in the bath at $-4°$ all thirty of the previous tubes plus fourteen more (44% of the total 100) had crystallized within five minutes. This appears to indicate a slow formation on the adsorbent even above the melting temperature of a form of adsorbate favorable to crystallization.

Discussion

The experiments outlined above lead inescapably to the conclusion that crystallization from undercooled liquids proceeds commonly by a heterogeneous, not by a homogeneous, mechanism. Although only three substances have been studied, two represent the unusual liquid which permits great undercooling, and one the typical symmetrical compound which can be undercooled only a few degrees. There can be little question, therefore, of the generality of the results. As a consequence it is necessary to limit the applicability of any theory describing homogeneous crystallization to very viscous liquids in which the crystal growth velocity is small enough to permit the spontaneous formation of a large number of nuclei before a few of them have grown to sizes which are comparable with the total volume of liquid. It is necessary furthermore to suppose that the "nucleation numbers" found by Tammann, which for thirty years have formed the ground-work for discussion of the subject, are not natural constants but represent only the properties of the particular combination of interfaces which happened to constitute the system which he was observing. Finally, it is indicated inescapably that investigations like the present one, where the crystallization of a large number of tubes is studied as a function of time in the hope of establishing a significant crystallization rate at a given temperature, do not give results which characterize the liquid.

It is, indeed, a questionable matter whether a liquid composed of highly unsymmetrical molecules unconfined by solid surfaces would be capable of forming the solid phase by thermal fluctuations within a reasonable time. In this connection a recent series of papers by Meyer and Pfaff[19] which greatly extend the work of Jaffé and Füchtbauer cannot receive too great attention. These investigators have shown that, by employing sintered glass filters passing particles of 1.5 μ or less, water which may be undercooled 33°, and benzophenone and salol which may be vitrified and returned to room temperature without crystallization, may be obtained. It is the stated belief of these writers that crystallization ordinarily occurs on minute dust particles of unspecified composition, and that removal of the dust precludes the possibility of crystallization.

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(19) J. Meyer and W. Pfaff, *Z. anorg. allgem. Chem.*, **217**, 257 (1934); **222**, 382 (1935); **224**, 305 (1935). A recent paper on water by G. Tammann and A. Büchner, *ibid.*, **222**, 371 (1935), expresses agreement with this standpoint.

To this point of view the investigation reported above contributes the following additional facts. The crystallization centers vary greatly in activity. They are so few in number that two 10-cc. portions of a liquid poured into separate tubes, with an effort to have all conditions identical may comport themselves wholly differently. This is doubtless also the reason for the aging effects so often described. The low-temperature crystallization centers bear no direct relation to the type of adsorption which permits the formation of overheatable nuclei, although carbon appears to be active in both respects. Finally, it is necessary to suppose that the walls themselves can assist in the formation of crystal centers, since dust-free benzophenone, obtained by distillation *in vacuo,* showed no more uniformity than that prepared without special precautions. It should be mentioned in this connection that Meyer and his associates, who were especially concerned with obtaining great undercooling, flamed their glassware intensively before introducing the liquid, whereas we merely cleaned it as described above. This may be the reason why they found no nuclei due to the presence of the containing vessel.

Attempts to account for this behavior must at present be disagreeably speculative. The crystallization centers are so small and so few in number that they defy direct study. It is natural to speak of oriented adsorption of liquid molecules at the interface, but to do so is little more than to give a resounding name to ignorance. The picture outlined in this paragraph is therefore presented in the most humble and tentative spirit, and is included merely to show that one type of adsorptive force is sufficient to account both for the retention of the "crystalline adsorbate" and for the apparently wholly unrelated activity in forming the crystallization centers at low temperatures. Let us consider a wedge-shaped crevice on the surface of the adsorbent. The adsorption forces will be strongest at the bottom of this crevice and become progressively weaker as the surface is approached, as Polanyi[20] and others have shown. Let us further suppose that the adsorbate molecules are oriented in the crevice in much the same way that fatty acid molecules are oriented by glass;[21] this assumption can scarcely meet with objection. Finally let us assume, entirely *ad hoc,* that this orientation causes the adsorbate to resemble the crystal increasingly as the orientation increases; let us suppose, in other words, that the orientation provides the greater part of the surface work, work necessary for the destruction of molecular aggregates, etc., which together may be called the "activation energy of crystallization."[22] Now the conditions are such, in the type of investigation reported above, that the entire liquid will crystallize from a single nucleus in a time much shorter than that necessary for the nucleus to become active. The portion of the adsorbate which most rapidly can project crystals into the free liquid will then cause the crystallization of the entire liquid. The lower the temperature, in the range with which we are at present concerned, the greater the instability of the undercooled liquid and the less the orientation of the adsorbate necessary to produce crystallization. But it already has been inferred from experimental evidence that the rate of rearrangement in the adsorption space is extremely slow.[15] In terms of the present over-simplified picture this involves the rearrangement of molecules bound by powerful adsorptive forces in a crevice of molecular dimensions. It is in all probability, however, exactly these molecules which form the overheatable nuclei. This may be inferred both from the high temperatures necessary to destroy them, and from the fact that weeks must sometimes elapse before they manifest their presence. If all this is granted as plausible, it is not surprising that the strongly bound molecules cannot project crystals into the free liquid with the rapidity of their more loosely bound neighbors, even though the energy conditions may favor them.

The course for future investigations is clear. There is little to be gained at present in multiplying experiments of the type which are here recorded. Rather, a detailed study should be made of the various surfaces which most effectively contribute to the formation of crystallization centers. This should embrace not only a wide variety of substances, but also as great variations in surface configuration and particle size as possible. The information so accumulated should, on the one hand, permit the elimination of heterogeneous effects in crystallization and, on the other, contribute vitally to the important practical problem of securing the crystallization of difficultly crystallizable liquids.

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(20) M. Polanyi, *Trans. Faraday Soc.*, **28**, 316 (1932).

(21) J. J. Trillat, "Les Applications des Rayons-X," 1931.

(22) M. Volmer and M. Marder, *Z. physik. Chem.*, **A154**, 97 (1931).

We are indebted to Mr. A. L. Loomis of Tuxedo Park, N. Y., for helpful advice concerning the photographic device described in the Experimental Section.

Summary

It has been shown that salol, benzophenone and benzene crystallize spontaneously by a heterogeneous mechanism even in the absence of overheatable nuclei. The tendency to form overheatable nuclei and the spontaneous tendency to crystallize, appear to be entirely unrelated, since the former may be destroyed by heating without affecting the latter. A tentative mechanism is suggested whereby one type of absorptive force might result in both forms of activity. The study has been related to previous investigations on the subject.

Princeton, N. J. Received July 7, 1936

[Contribution from the Geophysical Laboratory of the Carnegie Institution of Washington]

Phase Equilibrium Relationships in the Binary System, Sodium Oxide–Boric Oxide, with Some Measurements of the Optical Properties of the Glasses

By G. W. Morey and H. E. Merwin

The literature contains a number of observations on some of the compounds in the system, $Na_2O–B_2O_3$, which will be referred to in connection with those compounds, but there has been no systematic study of the system as a whole, except that by Ponomareff,[1] the results of which are as near correct as would be expected from his experimental method.

Most of the information relating to the phase equilibrium relations in the system was obtained by the usual quenching method. In this method a small sample of the material, usually in the form either of a homogeneous glass, or the product obtained by crystallizing such a glass, is held at constant temperature long enough for equilibrium to be attained, then cooled quickly enough to freeze that equilibrium. The quenched charge is then examined with the petrographic microscope. If it originally contained crystals and has become all glass, the temperature of heat treatment was above the liquidus; if both crystals and glass, below the liquidus. The crystals may be positively identified by their optical properties, and thus assurance given as to the crystalline phase present. The quenching method is preferred by experienced workers whenever it can be applied, but in some cases crystallization takes place so rapidly that the melt cannot be quenched. In such cases recourse must be had to the method of heating curves, and it was necessary to study the metaborate in this manner. The heating-curve method can give good results with sodium diborate, when the necessary care is exercised, as was shown by Day and Allen;[2] and it has been applied by the present authors to sodium tetraborate with satisfactory results. With intermediate mixtures, however, the heating-curve method is of doubtful assistance.

Preparation and Analysis of Materials

The raw materials used were sodium carbonate, borax ($Na_2O{\cdot}2B_2O_3{\cdot}10H_2O$) and boric acid ($H_3BO_3$). The sodium carbonate was from a specially purified stock which contained less than 0.009% $Fe_2O_3 + Al_2O_3$. The borax and boric acid were from several sources, but were purified by recrystallization before using. The mixtures were made by adding sodium carbonate or boric oxide to fused $Na_2O{\cdot}2B_2O_3$, with careful mixing, and the composition was usually known from the synthesis having been carried on under controlled conditions.

The composition of some of the mixtures was established by analysis, using a novel method. It was found that when a mixture of $Na_2O + B_2O_3$ containing an excess of boric oxide over the ratio of 1:1 was evaporated on the steam-bath with hydrofluoric acid, it was changed quantitatively to sodium borofluoride, $NaBF_4$. The properties of this compound will be discussed by us in another place. For our present purpose, it is sufficient to say that it can be dried to constant weight at 110°, and that numerous checks made by converting it to sodium sulfate established its constancy of composition. It melts, with some decomposition, at 373°. The original weight can be restored by adding a little boric acid and again evaporating with hydrofluoric acid. For example, a sample of borax, prepared by recrystallization of a commercial preparation and dehydra-

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(1) J. F. Ponomareff, *Z. anorg. allgem. Chem.*, **89**, 383 (1924); *J. Soc. Glass Techn.*, **11**, 39 (1927). The second reference apparently represents no new experimental work, contains several errors, *e. g.*, p. 43, where the compound $Na_2O{\cdot}7B_2O_3$ is claimed, probably a misprint for $Na_2O{\cdot}4B_2O_3$, and without justification claims the crystallization of B_2O_3, reproducing in support a picture of a crystal given in the earlier paper as $Na_2O{\cdot}4B_2O_3$.

(2) "The Isomorphism and Thermal Properties of the Feldspars," by Arthur L. Day and E. T. Allen, Carnegie Institution of Washington, Publ. No. 31, 1905, p. 29.

TABLE I[a]

THE CHANGE OF BETA-SODIUM DIBORATE TO ALPHA-SODIUM DIBORATE

Run	Temp., °C.	Time	Results; remarks	Run	Temp., °C.	Time	Results; remarks
Original material beta-sodium diborate				Original material a mixture of alpha- and beta-sodium diborate			
1	720	40 m	Changed to alpha				
2	660	20 m	Changed to alpha				
3	640	20 m	Changed to alpha, but still cloudy				
4	600	20 m	Cloudy; partly changed to alpha				
7	580	30 m	Traces of beta remain				
6	590	30 m	Much beta remains				
5	575	30 m	Mostly beta; trace of alpha	8	575	36 hr	All alpha
12	525	6 da	All changed to alpha	9	525	16 hr	All alpha
				10	510	48 hr	Practically all alpha
16	500	7 da	Unaltered beta; no alpha	16	500	7 da	Trace of beta remains, but has different look. Indices seem to be lowered somewhat
14	475	9 da	Unaltered beta; no alpha	11	475	16 hr	Beta is partly changed to alpha
				15	450	3 da	All grains of beta seem to have remained beta, but many of them have a different appearance from the original beta. Transformation may have begun.
13	360	5 da	Remains beta				

[a] We are indebted to our colleague, Dr. Earl Ingerson, for carrying out these experiments.

tion, gave 30.77% Na_2O by the method of evaporation with hydrofluoric acid, to be compared with the theoretical value of 30.78%. A mixture made up by controlled synthesis, with a composition calculated to be 27.91% Na_2O, gave 27.88% by the method using hydrofluoric acid. Another mixture gave 29.80% Na_2O when decomposed by hydrofluoric acid and sulfuric acid, when the Na_2O was weighed as Na_2SO_4, and 29.82% when the Na_2O was weighed as $NaBF_4$.

Temperature measurements were made with platinum *vs.* platinum + 10% rhodium thermocouples, with the cold junction in ice. Electromotive forces were measured on a White potentiometer. The thermocouples were calibrated at the following points: zinc,[3] melting point 419.4°; NaCl,[4] melting point, 800.4°; gold,[3] melting point, 1062.6°, and used with a deviation curve, as described by Adams.[3]

Properties of the Compounds

The hygroscopicity, and the existence of more than one form, of some of the compounds has caused confusion as to the identity of the material on which some of the physical properties recorded in the literature have been determined. Because of this uncertainty we have made no comments on the discrepancy between the optical properties observed by us and by others. For the same reason we have not attempted to verify the x-ray patterns given by Cole, Scholes and Amberg,[5] or by Menzel.[6]

1. Sodium Orthoborate, $2Na_2O{\cdot}B_2O_3$.—This is the only new compound found in the present study. It is easily obtained by fusing borax with sodium hydroxide or sodium carbonate in the theoretical proportions. It is remarkable for its low melting point, 625°, and the fact that in small quantities it can be obtained as glass. The system Na_2O–B_2O_3 is thus in marked contrast to the system Na_2O–SiO_2,[7] in which the (incongruent) melting point of the ortho-compound is higher than that of the meta-compound, and the tendency toward crystallization increases regularly with content of Na_2O. Sodium orthoborate is very hygroscopic, and attacks the index liquid. It is biaxial, positive: $\gamma = 1.55_0$, $\beta = 1.52_0$, $\alpha = 1.50_0$.

The eutectic between sodium orthoborate and sodium metaborate is close to the composition of the orthoborate, but its exact composition was not determined. The liquids in this composition region contain about 1% carbon dioxide, but in spite of this the orthoborate melted fairly sharply, with the first sign of sintering not more than 5° below the melting point. Mixtures intermediate between the ortho- and metaborates yield thin liquids which crystallize readily, and the presence of a small amount of metaborate makes it impossible to cool the melt to yield a glass. No liquidus

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(3) L. H. Adams, THIS JOURNAL, **36**, 65 (1914).

(4) H. S. Roberts, *Phys. Rev.*, **23**, 386 (1924).

(5) S. S. Cole, S. R. Scholes and C. R. Amberg, *J. Am. Ceram. Soc.*, **18**, 58 (1935).

(6) H. Menzel, *Z. anorg. allgem. Chem.*, **224**, 1 (1935).

(7) F. C. Kracek, *J. Phys. Chem.*, **34**, 1583 (1930).

determinations were made in this region, which is not indicated in Fig. 1.

2. **Sodium Metaborate,** $Na_2O·B_2O_3$.—A melting point for this composition was approximately determined by Burgess and Holt[8] as 930°. Van Klooster[9] found for the compound 966°, a value confirmed by Cole, Scholes and Amberg[5] (965 ±2°), and by us (966°). It crystallizes too readily to be obtained as glass. It is uniaxial, negative, $\omega = 1.568$, $\epsilon = 1.457$. It is very hygroscopic, and it slowly attacked the immersion liquid used for refractive index determination.

3. **Sodium Diborate,** $Na_2O·2B_2O_3$, **α-Form.**—This is the well-known "dehydrated borax," whose melting point was determined to be 742° by Day and Allen.[2] Other investigators have reported lower melting points. Ponomareff[1] found 732°, Cole, Taylor and Scholes,[5] 735 ± 5°, Menzel,[6] 738°. Burgess and Holt[8] found roughly 791°, but considered that this was not a true compound, but a eutectic mixture. This higher melting point is difficult to explain, but the lower ones are accounted for by the ease with which the compound takes up water from moist air. This is illustrated by the following observations, made to determine the suitability of the compound for the standardization of thermocouples.

A sample of borax was purified by recrystallization, dehydrated carefully, melted and crystallized, and the melting point of this product determined by the quenching method. It was found to melt sharply; at 741° it was not sintered, at 742° there was a very little sintering, while at 742.7° it was completely melted. The melting point is inferred to be 742.5°. The sample was then left in a screw-topped vial over the summer, when it showed a melting point of 736°. On remelting a part of the stock and recrystallizing, a melting point of 741.2° was obtained. A study of the rate of drying of some of the stock exposed over the summer showed a loss, from 10 g., at 115°, of 26 mg. in three hours, followed by 1.3 mg. in eighteen hours; subsequent heating at 300° gave an initial loss of 32.5 mg., in twenty-four hours, but on further heating the sample gained 2.1 mg. in weight. This was during a period of very humid weather, and it was found that during such weather not only would the crystalline material take up water at 300°, but the melt itself would take up water. For example, a 10-g. crystalline sample, dried at 700° (at which temperature the whole of the water was lost), on melting increased in weight 5.6 mg. The melt had been cooled quickly, so that it remained glassy; on heating to just below the melting point until it crystallized, a matter of about two hours, the crucible had returned to within 0.3 mg. of the previous weight. Quenching experiments gave a liquidus only slightly lower than the original material. There was some formation of glass at 736°, indicating a small range of melting. It is evident that during humid weather crystalline anhydrous sodium diborate will take up enough water to lower its melting point appreciably; that some water is taken up even at 300°; that the water can be entirely driven off from the crystalline compound at 700°; and that the just molten glass can take up some water. It is not a favorable material for the standardization of thermocouples.

Another sample of 4 g. on heating at 700° showed, in eighteen hours, a loss of 2.4 mg.; further twelve hours, no change in weight; twenty-two hours, loss of 0.5 mg. It is evident that the rate of evaporation from molten borax near its melting point is small. At 1200° in twenty-two hours the same sample lost 0.7215 g.; further heating for twenty hours showed a loss of 0.5235 g. The total loss was 1.2479 g., and analysis showed the composition to be 25.30% Na_2O. The original pure diborate contained 30.81% Na_2O, hence this indicates that more sodium oxide than boric oxide had evaporated, and calculation shows the average composition of the vapor to be 43% Na_2O. Experience has shown that while boric oxide passes into the vapor phase readily in the presence of water, anhydrous boric oxide, which can be obtained from the hydrous crystals only by prolonged heating at temperatures above 1200°, is not especially volatile even at 1200°.

The above discussion has referred to the form of crystalline sodium diborate ordinarily obtained, which should be called α-sodium diborate. The granular crystals have two or more good cleavages, and are biaxial, positive, $\alpha = 1.471$, $\beta = 1.493$, $\gamma = 1.528$.

Another form of crystalline sodium diborate is sometimes obtained when a borax glass is crystallized. We have obtained it in pure form only once, and it has occasionally been observed mixed with the α-form. That it is probably monotropic

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(8) C. H. Burgess and A. Holt, *Proc. Roy. Soc.* (London), **74**, 285 (1904).

(9) H. S. Van Klooster, *Z. anorg. Chem.*, **69**, 135 (1911).

is shown by the experiments of Table I. Above 600° it changes to the α-form in twenty minutes. At lower temperatures the change is slower, but is accelerated by the presence of the α-form. At low temperatures the change is very slow, or does not take place within a few days, but in no case was the transformation from the α-form to the β-form observed.

TABLE II

EXPERIMENTAL RESULTS IN THE SYSTEM Na_2O–B_2O_3

Weight fraction Na_2O	Weight fraction B_2O_3	Liquidus temp., °C.	Solid phases
0.4721	(0.5279)[a]	966[b]	$Na_2O\cdot B_2O_3$
.3664	(.6336)	839	$Na_2O\cdot B_2O_3$
.325	.675	744	$Na_2O\cdot B_2O_3$
.3077	(.6923)	742	$Na_2O\cdot 2B_2O_3$
.3001	(.6999)	739	$Na_2O\cdot 2B_2O_3$
.2982	(.7018)	737	$Na_2O\cdot 2B_2O_3$
.2788	(.7212)	723	$Na_2O\cdot 2B_2O_3$
.2746	(.7254	725	$Na_2O\cdot 3B_2O_3$
		719	$Na_2O\cdot 2B_2O_3 + Na_2O\cdot 3B_2O_3$. No glass
.2688	(.7312)	736	$Na_2O\cdot 3B_2O_3$
.2507	(.7493)	759	$Na_2O\cdot 3B_2O_3$
.2476	(.7524)	761	$Na_2O\cdot 3B_2O_3$
.2360	(.7640)	766	$Na_2O\cdot 3B_2O_3 + Na_2O\cdot 4B_2O_3$ + liquid
		769	$Na_2O\cdot 4B_2O_3$
.2308	.7692	766	$Na_2O\cdot 3B_2O_3 + Na_2O\cdot 4B_2O_3$ + liquid
		776	$Na_2O\cdot 4B_2O_3$
.2274	(.7726)	766	$Na_2O.3B_2O_3 + Na_2O\cdot 4B_2O_3$ + liquid
		777	$Na_2O\cdot 4B_2O_3$
.2168	.7832	792	$Na_2O\cdot 4B_2O_3$
.2009	.7991	803	$Na_2O\cdot 4B_2O_3$
.1862	.8138	814	$Na_2O\cdot 4B_2O_3$
.1820	.8180	815	$Na_2O\cdot 4B_2O_3$
.1778	.8222	814	$Na_2O\cdot 4B_2O_3$
.155	.845	800	$Na_2O\cdot 4B_2O_3$
.1175	(.8825)	753	$Na_2O\cdot 4B_2O_3$
.0701	(.9299)	661 ± 3	$Na_2O\cdot 4B_2O_3$
.0524	(.9476)	620 ± 3	$Na_2O\cdot 4B_2O_3$
.0299	.9701	585 ± 5	$Na_2O\cdot 4B_2O_3$
.01	.99	560 ± 10	$Na_2O\cdot 4B_2O_3$

[a] The weight fraction B_2O_3 in parentheses indicates that the Na_2O was determined by analysis, B_2O_3 by difference. The other compositions represent controlled syntheses.

[b] Determined by heating-curve method.

A careful search for an enantiotropic inversion was made from below 500° to the melting point, using a differential thermocouple and a neutral body. No indication of an inversion was obtained.

Beta-sodium diborate forms granular crystals, $\alpha = 1.50$, $\beta = 1.52$–3, $\gamma = 1.555$.

A third form of sodium diborate, γ-, was obtained under conditions which cannot be specified precisely. A stock of the crystalline material was prepared as usual by recrystallizing commercial borax, dehydrating, melting and crystallizing. This was to be used in making some other mixtures; and because the weather at the time was humid it was kept in a covered beaker on a hot plate, at about 300°. Some of this material was left for two and a half years, after which it was found to have the following optical properties: positive, with large axial angle, $\alpha = 1.526$, $\beta = 1.544$, $\gamma = 1.576$. It has one fair cleavage.

Analysis gave 30.84% Na_2O, which indicates that the composition had not changed. On heating at 700° for fifteen minutes the material was unaltered; but in four hours it contained both the α-form and unaltered material. Heated for fifteen minutes at 725° it was entirely changed to the ordinary form. In both cases in which alteration was observed there were indications that fusion had preceded recrystallization. Since the material remained largely in discrete grains, the fusion was probably local with immediate crystallization.

In one experiment sodium metaborate crystallized from a melt of the composition of sodium diborate.[10] There was, of course, much glass, but no other crystals. An attempt to determine the metastable liquidus of sodium metaborate at this composition failed, because of formation of sodium diborate.

4. Sodium Triborate, $Na_2O\cdot 3B_2O_3$.—Ponomareff gave 694° for the melting point of this compound, while Cole, Taylor and Scholes found 720 ± 5°. We have found that it has an incongruent melting point at 766°, decomposing at that temperature into crystals of sodium tetraborate and a liquid containing 76% B_2O_3. It is biaxial, negative, $\alpha = 1.453$, $\beta = 1.525$, $\gamma = 1.551$.

5. Sodium Tetraborate, $Na_2O\cdot 4B_2O_3$.—This compound was first obtained by Le Chatelier.[11] Burgess and Holt gave for it a melting point of 858°, and Cole, Taylor and Scholes gave 810 ± 5°; our determination is 816 ± 0.5°. The form which separates from the melt at high temperatures is biaxial, positive, $\alpha = 1.499$, $\beta = 1.525$, $\gamma = 1.582$. This same compound was usually obtained on crystallizing all mixtures containing

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(10) H. Menzel, *Z. anorg. allgem. Chem.*, **224**, 1 (1935), claimed to have obtained two new allotropic forms of sodium diborate, which melted at 710 and 663°, respectively. One of these may have been the above β-sodium diborate, the other, sodium metaborate, but the information as to their properties is so meager that identification is not possible.

(11) H. Le Chatelier, *Bull. soc. chim.*, **21**, 34 (1899).

up to 99% B_2O_3; but in some cases a second form was obtained, which crystallized in thin blades, $\alpha = 1.52$, $\beta = 1.54$, $\gamma = 1.56$. It was at first thought that this might be a higher borate, but when a mixture containing 98% B_2O_3 was held for ten months at a little below 300°, boric oxide evaporated, leaving crystals which had these properties, together with a little glass. Analysis gave 14% Na_2O, 86% B_2O_3, near the composition of the tetraborate. On heating for two hours at 630° the crystals were unaltered, but the glass was more evident; at 685° the crystals were about one-half altered to the high-temperature form of the tetraborate; while in thirty minutes at 770° it was more than three-quarters glass, and the crystals were all the high form of the tetraborate. The most probable conclusion is that these two crystals are an allotropic form of the tetraborate. Thus the form appearing at low temperatures is either monotropic, or it is enantiotropic, with a slow rate of inversion.

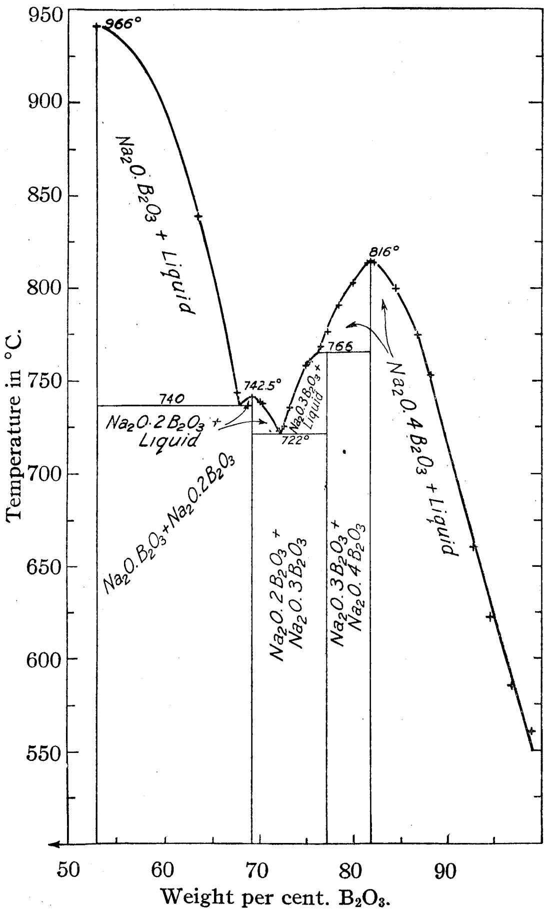

Fig. 1.—Phase equilibrium relations in the binary system, Na_2O–B_2O_3.

A careful search for an enantiotropic inversion was made from below 500° to the melting point, using a differential thermocouple and a neutral body. No indication of an inversion was obtained.

The Phase Equilibrium Diagram

The phase equilibrium relations between the various crystalline compounds and liquids are shown in Fig. 1, and the experimental results on which that figure is based are assembled in Table II.

The lowest melting compound is the orthoborate, and the eutectic between it and metaborate is close to the composition of the orthoborate. The liquid in this part of the diagram contains about 1% of carbon dioxide, but in spite of this the orthoborate melted fairly sharply, with the first sign of sintering not more than 5° below the melting point, so that its melting point is fairly accurate. Mixtures intermediate between ortho- and metaborate yield thin liquids which crystallize readily, and the presence of but a small amount of metaborate makes it impossible to cool the melt to form a glass.

The metaborate, $Na_2O \cdot B_2O_3$, has the highest melting point of any of the compounds, and it crystallizes so readily that it is not possible to obtain it as glass. The eutectic between it and sodium diborate is at 740° 68 weight per cent. B_2O_3. The melting point then rises to that of sodium diborate, 742.5°; then falls to the eutectic between diborate and triborate, at 722°, 72.3% B_2O_3. Sodium triborate melts incongruently at 766°, giving crystals of sodium tetraborate, $Na_2O \cdot 4B_2O_3$, and a liquid containing 76% B_2O_3. From this incongruent melting point the liquidus rises to the melting point of the tetraborate, at 816°. This compound remains the primary phase up to 99% B_2O_3, but below 700° a second sort of crystals, probably of the same composition, sometimes appears. In all the mixtures whose liquidus temperatures were determined, however, the crystalline phase which was present was the high-temperature form.

The phase equilibrium diagram shows the melting point curve of sodium tetraborate extending to within about 1% of the B_2O_3 side. Whether or not the lower part of this curve is metastable cannot be stated because boric oxide has not been crystallized from these melts. If the above curve is not metastable and the melting point of boric oxide and the eutectic between $Na_2O{\cdot}4B_2O_3$ and B_2O_3 lies at a temperature considerably lower than 500°, then the melting point curve must be nearly vertical at the eutectic. This is to be expected from thermodynamic considerations. As the liquid phase approaches one of the components in composition, while the crystalline phase contains a finite amount of the other component, the slope of the T–X curve must approach infinity.

All our attempts to crystallize boric oxide have failed. They include long heating of the anhydrous material at many temperatures. In one series of experiments, boric oxide glass was heated from a month to six weeks at a series of temperatures differing not more than 10°, and covering the range from 700 to 200°. In other experiments boric oxide glass was heated on a hot-plate, whose temperature ranged from 260 to 285°, for a year and a half. The material was in a covered crucible, and this in turn was in a covered glass dish. Under these conditions the glass took up some water during the humid summer months but no indication of crystallization was observed. It is elsewhere mentioned that under the same conditions a glass rich in boric oxide lost enough of this component to attain practically the composition of the crystalline tetraborate. It is probable that this loss in boric oxide was caused by the presence of moisture in the atmosphere. A glass containing 99% B_2O_3 grew beautifully formed crystals of $Na_2O{\cdot}4B_2O_3$ in three months at 525°; and, when heated for a year at a little below 300° in a sealed tube, crystals of the low-temperature form of $Na_2O{\cdot}4B_2O_3$ were formed. If these heatings had been below the melting point of boric oxide, certainly it might have been expected to crystallize, especially since the tetraborate did grow.

Other experiments include attempts to condense it from the vapor phase. In all work with anhydrous boric oxide emphasis must be placed on its extremely hygroscopic character. In making microscopical examination of the various products the material is usually crushed to a powder in an oil. In determining the properties of anhydrous boric oxide it is necessary to take the most extreme precautions to prevent the contamination by water, and that such contamination had not taken place should be proved. It was found that molecular distillation methods in which proper precautions were taken to exclude moisture gave only glassy boric oxide.

Other methods were tried. One was a prolonged pounding in a heated mortar, with exclusion of air, but this was a failure. Temperatures ranged from 80 to 250°, and at the highest temperature the glass was pounded into a cake, almost clear glass. Attempts were made to find "mineralizers" other than water. These included toluene, which was boiled for six weeks with the anhydrous glass, under a reflux condenser, provided with a guard tube, without result except for a slight film of boric acid. Other organic solvents were tried in bombs, usually at 200°, but no crystalline boric oxide could be found.

These experiments overlapped the temperature range in which Taylor and Cole believed they had crystallized boric oxide. The procedure described by them was tried several times, but crystalline boric oxide was not obtained. In our opinion, the crystallization of boric oxide is yet to be proved.

Refractive Dispersions of Glasses

The only Na_2O–B_2O_3 glasses for which refractive dispersions (C, D, F) are recorded[12] are B_2O_3 and $Na_2O{\cdot}2B_2O_3$. Three sets of these dispersions are fairly close to ones we have made. Errors of copying seem to appear in the other two, but values for n_D seem unaffected: for B_2O_3 1.463 +, and for "borax glass" 1.515+. Corresponding densities are 1.850 + and 2.370. The density of boric oxide glass is greatly affected by annealing.[13]

TABLE III

REFRACTIVE DISPERSIONS OF BORIC OXIDE AND BORATE GLASSES

	$\times 10^{-4}$		
	B_2O_3	$Na_2O{\cdot}4B_2O_3$	$Na_2O{\cdot}2B_2O_3$
4046 Hg	169+	173+	179
4340 (G′)	137	140+	145
4358 Hg	135	138+	143
4861 (F)	93+	95+	98+
4916 Hg	89+	91+	94+
5461 Hg	58	59	61
5876 He	39+	40	41
5893 (D)	38+	39	40
6563 (C)	15	15	15
6678 He	11	11	11
7065 He	0	0	0
7682 (A′)	−14+	...	...
n_D	1.458	1.501	1.516

C, D, F, G′ are interpolated.

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[12] P. P. Bedson and Carleton Williams, *Ber.*, **14B**, 2549 (1881).

[13] Arnold Cousen and W. E. S. Turner [*J. Soc. Glass Tech.*, **12**, 169 (1928)] found for chilled droplets <1.81, which was raised to >1.84 by annealing. Very recent work by P. Wulff and S. K. Majumdar [*Z. physik. Chem.*, **31B**, 319 (1936)] records a range of 1.778–1.838 for d, and 1.4502–1.4633 for n_D. Further study is required to show the effect of annealing and of small content of water on the specific refraction.

The measurements of Table III were made on prisms, from a few grams of glass cooled in air from fusion. The boric oxide prisms were protected from filming by oil and cover glasses.

Summary

A study of the phase equilibrium relationships in the system Na_2O–B_2O_3 has shown the existence of the compounds: sodium orthoborate, $2Na_2O \cdot B_2O_3$, with a congruent melting point at 625°; sodium metaborate, $Na_2O \cdot B_2O_3$, with a congruent melting point at 966°; sodium diborate, $Na_2O \cdot 2B_2O_3$, with a congruent melting point at 742°; sodium triborate, $Na_2O \cdot 3B_2O_3$, with an incongruent melting point at 766°, 76 weight per cent. B_2O_3; and sodium tetraborate, $Na_2O \cdot 4B_2O_3$, with a congruent melting point at 816°. The orthoborate, which is a newly discovered compound, can be cooled to a glass, as can mixtures containing more boric oxide than the diborate. The metaborate and compositions near it crystallize too readily to be quenched to a glass. In addition to the forms stable at the liquidus, sodium diborate may occur in two, and the tetraborate in one, additional form which are probably monotropic. Attempts to prepare crystalline boric oxide were not successful, and doubt is expressed as to previous claims to its crystallization. Refractive dispersions were measured for boric oxide, sodium tetraborate and sodium diborate glasses.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Heat Content and Heat Capacity of Aqueous Sodium Chloride Solutions

BY T. F. YOUNG AND J. S. MACHIN

Computations of activity coefficients from cryoscopic and thermal data have been greatly limited by a lack of adequate measurements.[1] This investigation was undertaken primarily to supply the heats of dilution required for a reliable determination of relative activities of sodium chloride in aqueous solutions. Because electromotive force methods[2,3] have been employed extensively in thermodynamic investigations of that electrolyte, sodium chloride is especially suitable for a critical comparison of the cryoscopic and electrical methods of evaluating activity coefficients.

The calorimetric data presented are of further interest because they furnish information concerning the variation with composition of apparent and partial molal heat capacities, and consequently have an important bearing upon the validity of the Debye–Hückel theory.[4]

The advantages of the chord-area method for the precise evaluation of partial molal properties from heats of dilution have been discussed by Young and Vogel.[5] The procedure they employed depends upon the determination of the derivative, S, of the apparent molal heat content with respect to the square root of the molality, m. Each heat of dilution experiment furnishes one average value of S which may be represented on a derivative plot by the ordinate of a horizontal line (called a "chord") extending between limits representing the initial and final values of $\sqrt{m}$, *i. e.*, $\sqrt{m_1}$ and $\sqrt{m_2}$. A special procedure was suggested by Young and Vogel[5] (p. 3037) to facilitate the drawing of a derivative curve so as to balance appropriate areas accurately. That procedure depends upon the drawing of a preliminary S curve, and the evaluation (by successive approximations, if necessary) of S', the first derivative, and S'', the second derivative of S. The final S curve is drawn in accordance with a series of points which have been plotted a distance, $P_i - \overline{P}_i$, above the center of each chord, computed from the equation

$$P_i - \overline{P}_i = -S'' (\Delta\sqrt{m})^2/24 \qquad (1)$$

where P_i represents the ordinate of a point on the derivative curve above the center of the ith chord, and $\overline{P}_i$ is the ordinate of the chord. For an application of this method it was desirable to produce chords so short that the uncertainties in values of $P - \overline{P}$ would not be large in comparison with the probable errors in the experimentally determined values of $\overline{P}$. For experiments with concentrated solutions, a dilution vessel having a volume about 0.03 that of the final diluted solution was used; for experiments with relatively dilute solutions, a larger vessel having a volume about 0.085 that of the final diluted solution was employed.

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[1] Young, *Chem. Rev.*, **13**, 103 (1933).

[2] Harned and Nims, THIS JOURNAL, **54**, 423 (1932).

[3] Brown and MacInnes, *ibid.*, **57**, 1356 (1935).

[4] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[5] Young and Vogel, THIS JOURNAL, **54**, 3030 (1932).

Experimental Procedure

The apparatus and procedures were similar to those described by Young and Vogel. The more important changes are described below.

Instead of the thin glass containers used in the earlier work, two silver capsules were employed. The smaller one, of about 25-cc. capacity, was used for the dilution of the more concentrated solutions. It consisted of a pure silver tube which could be closed with two spun silver caps, each provided with two small tabs for the attachment of wires. The tube was supported by a glass rod to which it was held by clamps and screws of pure silver. The larger vessel, of about 75-cc. capacity, was constructed of silver sheet and "silver solder" (largely copper and silver). Its cross section was a flattened ellipse. Rounded shoulders at the top and bottom terminated in vertical necks whose cross sections were similar in shape to, but smaller than, that of the body of the vessel. These were closed by soldered silver caps, to which wires were attached. After each experiment with this capsule the residual solution was tested with ammonium sulfide. No trace of copper was ever detected.

The covers were sealed to the body of the capsules with paraffin. For work at low temperatures the paraffin was covered with petroleum jelly to prevent leaks through small cracks produced in the paraffin. A gentle pull on a rod projecting through the calorimeter cover and attached by wires to the caps, detached first one and then the other. When blank experiments (*i. e.*, experiments with water both inside and outside the capsules) were made, no heats of opening were perceptible. To avoid errors due to lagging of the temperature of the contents of the dilution vessel, the caps were not removed for a dilution experiment until the temperature variation within the calorimeter had been reduced to less than 0.03 microvolt per minute.

The calorimeter was equipped with three tantalum propellers mounted on a single shaft. The submerged portion of the shaft was a tantalum tube on which the propellers were mounted. It was cemented to an upper portion made of glass tubing. A small synchronous motor geared directly to the stirrer rotated it at 450 revolutions per minute.

The calorimeter heater was similar to that used by Young and Vogel. Its flattened case was of platinum sealed with gold. Its leads were encased in a long thin tube of platinum-iridium, which projected through one of the openings of the calorimeter top. The tube extended to the bottom of the calorimeter where it terminated in a short U-shaped portion sealed to the bottom of the vertical case. The heater current was controlled by a semi-automatic set of switches. A manually operated switch caused the seconds pendulum of a weight driven clock, upon its next passage through a pool of mercury, to actuate an automatic switch which closed the heater circuit. Another manual switch was then closed to provide a by-pass for the current while two of the three leads to the automatic switch were interchanged. After a selected interval the pendulum, operating the automatic switch as before, opened the circuit.

Following each dilution there were usually two heating periods of three minutes each, from which the heat required for a temperature change of one microvolt was determined. The average deviation of 104 measurements from 52 respective means is 0.024%.

For work near 12.5° the thermostat was cooled by water pumped from an ice-water mixture through the copper coils immersed in the thermostat fluid (either water or an alcohol-water mixture), and returned to the source. For the measurements near 0°, brine was pumped through the coils. Temperature regulation was maintained by electrical heating and a large mercury regulator.

Materials.—The objectives of this investigation require a knowledge of the variation of the derivative, S, with temperature. It was desirable, therefore, to determine S at each of the three temperatures for solutions of as nearly the same composition as possible. Consequently, large quantities of the solutions were prepared and in general, two dilutions of each were made at each temperature. (An accident caused the omission of one duplicate at 25°.) Since the ratio of the volume of the solution in the calorimeter to the volume of the diluting water varied slightly, the centers of the chords derived from each stock solution were not quite the same. Corrections for these differences were computed and applied, as described below, but were extremely small. In some ranges of composition, analytical errors may introduce large errors into the chords[5] (p. 3036). In general, the use of the same solutions at all three temperatures reduced the effects of such errors upon the determinations of the variations of S with temperature, since partial cancellation ensued.

All solutions were prepared from distilled water and C. P. sodium chloride. All but the two most dilute were analyzed by the residue method of Richards and Hall.[6] Those two were prepared by weight dilution from more concentrated solutions. The quantities of solution (usually about 0.8 liter) and water introduced into the calorimeter were determined with weight burets.

Results

The experimental data are in Table I: $\Delta\phi H$ represents the heat absorbed in fifteen degree calories per gram formula weight of sodium chloride, t is the temperature of the solution and diluting water just before mixing; and $\sqrt{m_1}$ and $\sqrt{m_2}$ are the square roots of the initial and final molalities, respectively. The numbers of significant figures in the $\sqrt{m}$ columns were determined by the necessity for a precise computation of the difference, $\sqrt{m_2} - \sqrt{m_1}$. Because the second solution was produced by the dilution of the first, the difference, $\sqrt{m_2} - \sqrt{m_1}$, was determined to more decimal places than either $\sqrt{m}$.

Since the measurements were not performed at exactly the selected temperatures, it was necessary to apply a small correction to each determination to obtain $\overline{P}$ for one of the three temperatures, 0, 12.5 and 25°. The procedure was facilitated by the facts that solutions of the same composition were diluted in each of these temperature regions

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[6] Richards and Hall, THIS JOURNAL, **51**, 709 (1929).

and that the compositions of the respective solutions formed in each temperature range were nearly the same. For each dilution range, for example, the dilution of the 1.5742 molal solution ($\sqrt{m}$ = 1.2547) to solutions approximately 1.432 molal, the average value of the derivative $d\bar{P}/dt$ between 0 and 12.5 and the average value of $d\bar{P}/dt$ between 12.5 and 25° were computed from the data in column 4 of Table I. The two chords so obtained were plotted as ordinates with temperatures as abscissas and the $d\bar{P}/dt$ curve was drawn in accordance with the chord-area principle. From the straight line so obtained, a value of $d\bar{P}/dt$ was determined, for example, for the interval between 12.50 and 12.58°, the actual temperature of one of the observations. This value of the temperature coefficient multiplied by the difference, 12.50–12.58°, was added to the $\bar{P}$ observed at 12.58 to yield $\bar{P}$ at 12.50°. No correction at 25 or 12.5° amounted to more than two units and none at 0° to more than five units. Consequently the inaccuracy introduced by the treatment of $d\bar{P}/dt$ as a linear function of temperature is very small.

Table I

$\sqrt{m_1}$	$\sqrt{m_2}$	t	$\Delta(\phi H)$	$\bar{P}_{0.0}$
2.46569	2.42189	0.19	17.865	−410.7
	2.42229	.22	17.697	−411.0
2.35009	2.30872	.18	20.152	−490.0
	2.30840	.16	20.339	−490.4
2.12964	2.09288	.16	22.650	−618.9
	2.09281	.16	22.692	−618.9
1.89025	1.85832	.19	23.290	−733.2
	1.85801	.20	23.537	−733.9
1.57834	1.55201	.15	21.833	−832.6
	1.55243	.14	21.503	−833.1
1.25467	1.19683	.20	49.593	−862.4
	1.19682	.19	49.532	−860.9
0.90208	0.86122	.17	31.21	−768.5
	.86113	.19	31.24	−767.9
.72157	.68904	.18	20.78	−643.3
	.68891	.17	20.91	−644.3
.45192	.43164	.18	7.40	−369
	.43158	.20	7.27	−362
.31608	.30184	.20	2.28	−164
	.30187	.22	2.89	−207
	.30187	.21	1.97	−142
				$\bar{P}_{12.5}$
2.46569	2.42229	12.63	10.104	−234.5
	2.42244	12.60	10.056	−233.8
2.35009	2.30921	12.63	12.354	−304.0
	2.30920	12.64	12.376	−304.6
2.12964	2.09343	12.61	15.065	−417.7
	2.09333	12.61	15.107	−417.7
1.89025	1.85873	12.56	16.055	−510.3
	1.85883	12.58	16.014	−510.0
1.57834	1.55249	12.56	14.874	−576.4
	1.55252	12.56	14.844	−576.0
1.25467	1.19651	12.58	33.721	−581.3
	1.19667	12.57	33.519	−579.3
0.90208	0.86099	12.57	19.62	−478.8
	.86112	12.56	19.59	−459.5
.72157	.68893	12.55	12.19	−374.5
	.68879	12.55	12.37	−378.2
.45192	.43158	12.55	3.10	−153
	.43159	12.55	3.03	−150
				$\bar{P}_{25.0}$
2.46569	2.42241	25.02	3.4684	− 80.34
	2.42246	25.02	3.4699	− 80.48
2.35009	2.30936	25.03	5.861	−144.3
	2.30933	25.02	5.919	−145.4
2.12964	2.09343	25.01	9.028	−249.4
	2.09343	25.01	9.033	−249.6
1.89025	1.85891	25.01	10.439	−333.2
	1.85875	25.01	10.447	−331.8
1.57834	1.55258	25.06	9.998	−388.9
	1.55239	25.06	10.082	−389.2
1.25467	1.19674	25.03	21.983	−379.9
	1.19678	25.03	21.993	−380.2
0.90208	0.86089	25.02	11.77	−286.0
.72157	.68888	25.04	6.49	−199.1
	.68890	25.06	6.46	−198.4
.45192	.43156	25.05	0.47	− 23
	.43154	25.04	.28	− 14

The $\bar{P}$ values are given in the last column of Table I, and are plotted as chords on Fig. 1, the curves of which represent the derivative $S = d(\phi H)/d\sqrt{m}$ as a function of $\sqrt{m}$. The results of duplicate experiments with concentrated solutions differed so little that they are not distinguishable on the plot. Individual chords are discernible however in the dilute solution region. Measurements of the heats of dilution at 0° of the most dilute solution represented in Table I are relatively inaccurate because the temperature changes produced were very small (equivalent to galvanometer deflections of about 2 mm.). Corresponding data for 12.5 and 25° have been omitted entirely because of the availability of the equations recently derived by Young and Groenier[7] from the data obtained by Gulbransen and Robinson[8] with their calorimeter designed specially for very small thermal effects. The circles represent values calculated for 25° from Young and Groenier's equation 8 and for 12.5° from the fol-

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(7) Young and Groenier, This Journal, **58**, 187 (1936).

(8) Gulbransen and Robinson, *ibid.*, **56**, 2637 (1934).

lowing equation which is the mean of their equations 10 and 11

$$S = 385 - 1591\sqrt{m} + 758\,m \qquad (2)$$

The accuracy of this equation is restricted, especially for relatively large molalities, by the excessive length of Gulbransen and Robinson's chords, and is further limited by the necessity for interpolation. Nevertheless, because of the superior precision of Gulbransen and Robinson's apparatus for the measurement of very small thermal effects, equation 2 was given greater weight in the drawing of the 12.5° curve near $\sqrt{m} = 0.44$ than was given to the data of Table I. If the small discrepancy apparent in this region be entirely due to errors in the observed galvanometer deflections produced by the dilution of the 0.204 molal solution ($\sqrt{m} = 0.452$), the mean error is less than 0.75 mm. In the same concentration range, the 25° data of the two investigations merge, somewhat fortuitously, with no significant discrepancy.

The final curves as shown in Fig. 1 were drawn with reference to *points* calculated, by means of equation 1, from values of S' and S'' determined from preliminary plots. The sizes of the dilution vessels had been so chosen that the average value of $P - \bar{P}$ was less than 0.04, and the largest was but 0.15, which is less than the precision of measurement. The experimental dilutions were nearly equivalent, therefore, to direct determination of the derivative, S.

For calculations involving a large scale reproduction of Fig. 1, the original data in Table I are not convenient. The dilution of the 1.5742 molal solution, for example, leads to values of S which correspond to six slightly different molalities. Each datum corresponds to a $\sqrt{m}$ which is the mean of $\sqrt{m_1}$ and $\sqrt{m_2}$ of the dilution experiment from which it was derived. Let X_j denote this mean $\sqrt{m}$ of the jth dilution. The mean of the six X_j values is 1.2257. For the small interval between each X_j and 1.2257, S' was determined from curves previously mentioned. This value of S', multiplied by $(1.2257 - X_j)$, was added to S previously computed for X_j. The sum is the derivative, S, which corresponds exactly to $\sqrt{m} = 1.2257$. All six experiments thus yielded derivatives for this same value of $\sqrt{m}$. The experiments had been so designed that all of the increments were insignificant: the largest was but 0.21.

Table II contains the resulting values of the derivative, S, corrected as described for temperature, curvature (by equation 1), and composition. These are not data read from smooth curves but

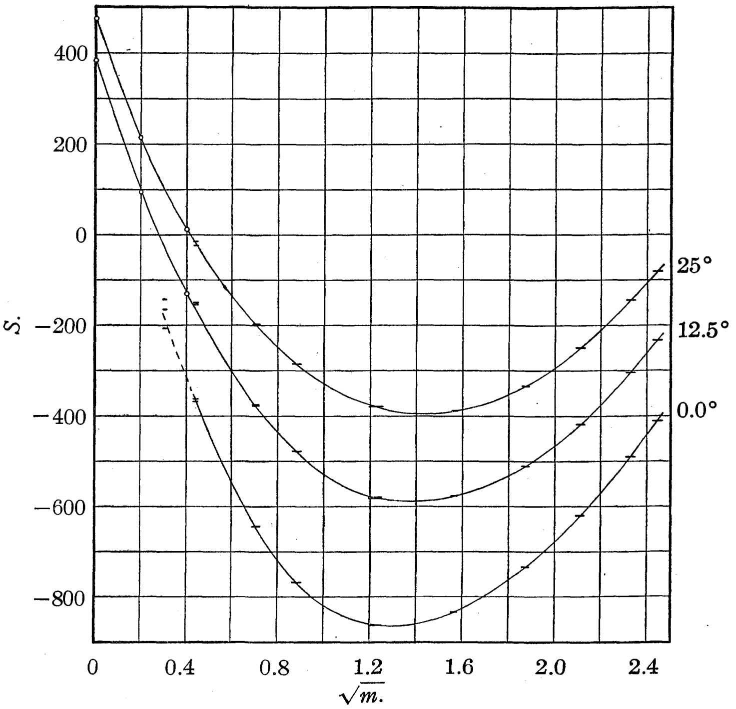

Fig. 1.

TABLE II

$\sqrt{m}$	S 0.0	S 12.5	S 25.0
2.4440	−410.5	−234.6	− 80.41
	−411.0	−233.9	− 80.57
2.3296	−489.9	−304.1	−144.4
	−490.2	−304.7	−145.5
2.1114	−618.8	−417.8	−249.5
	−618.8	−417.7	−249.7
1.8744	−733.1	−510.4	−333.3
	−733.8	−510.1	−331.8
1.5654	−832.6	−576.4	−388.9
	−833.1	−576.0	−389.3
1.2257	−862.5	−581.4	−380.0
	−861.1	−579.4	−380.3
0.8816	−768.6	−478.9	−286.1
	−767.9	−479.5	.....
.7052	−643.3	−374.5	−199.1
	−644.4	−378.3	−198.5
.4418	−369	−153	− 23
	−362	−150	− 14
.3090	−164		
	−207		
	−142		

are the original experimental quantities plus very small, usually insignificant, increments derived from smooth curves. For activity coefficient calculations a few values of S derived from the curves of Fig. 1 for round values of m are shown in Table III.

TABLE III

$\sqrt{m}$	S 0.0	S 12.5	S 25.0
0.3162	−196	− 39	91
.3500	−243	− 77	59
.4000	−311	−128	13
.4500	−376	−177	− 28
.5000	−435	−220	− 66
.6000	−545	−302	−136

Table II is suitable for a test of the precision of the calorimetric measurements. The average fractional discrepancy between duplicate measurements of heats of dilution of solutions more concentrated than 0.6 molal is about 0.2%, *i. e.*, the average deviation from the mean is 0.1%. The discrepancies in the data for the three most dilute solutions, *i. e.*, those producing very small temperature changes, are better expressed in terms of either equivalent temperature differences or galvanometer deflections. The average deviation from the mean of those data is equivalent to a deflection of about 0.2 mm.

Discussion

Three general methods have been used to test the validity of the Debye–Hückel theory for infinitely dilute solutions. Experimentally determined activity coefficients, heats of dilution and heat capacities have been compared with theoretical predictions. Many uni-univalent electrolytes in aqueous solution have been shown to meet the first two tests. The activity coefficients of sodium chloride have been compared by Brown and MacInnes,[3] and the heats of dilution by Young and Groenier[7] with the theoretical equations for extremely great dilutions.

From precise determinations of ϕC, the apparent molal heat capacity, Randall and Rossini[9] have calculated limiting values of the derivative, $d(\phi C)/d\sqrt{m}$, as m approaches 0. Though the dielectric constant of water has not been determined with sufficient precision to permit an accurate theoretical calculation of the limiting slope, Randall and Rossini demonstrated that their estimates were of the "proper order of magnitude" and that they showed "about the right" variations with changes of valence type. Their estimates depended upon extrapolations based upon the assumption that ϕC is *approximately* a linear function of $\sqrt{m}$. In a subsequent examination of various published data for 19 uni-univalent electrolytes, Rossini[10] concluded that ϕC "can be represented within the accuracy of the best experimental data, as a linear function of $\sqrt{m}$, from the lowest measured concentration to about 2.5 molal." Employing strictly linear extrapolations, he derived new values of the limiting slopes which are very similar to those of Randall and Rossini. Gucker and Schminke[11] also investigated several electrolytes of the 1–1 valence type, and found linear relationships between ϕC and $\sqrt{m}$ to represent their very precise measurements throughout wide ranges of concentration. For three of their solutes they found the linear relationship valid over the whole range investigated, and by extrapolation estimated the respective limiting derivatives. The largest of their values is over three times the smallest. A similar variation exists in the limiting slopes tabulated by Rossini. Randall and Rossini did not investigate the electrolytes whose limiting slopes were found in the later investigations to be the smallest. Nevertheless, the largest limiting value in their table is 65% larger than the smallest. If these differences are significant, the data are in conflict with the Debye–Hückel theory, which demands that the limiting slopes be the same for all strong electrolytes of a given valence type. It is important, therefore, to investigate the validity of the linear relationship upon which the various extrapolations were based. Gucker[12] has pointed out the difficulty of obtaining the precision necessary for this purpose from direct heat capacity measurements. The heat of dilution data, however, may be used.

If, at each temperature between 12.5 and 25°, $d(\phi C)/d\sqrt{m}$ is independent of molality, the vertical distance between the two upper curves of Fig. 1 must be constant. In Fig. 2 the solid line exhibits the difference between the two smooth S curves divided by 12.5; it therefore represents for each molality, the average value of $d(\phi C)/d\sqrt{m}$ throughout the temperature range between 12.5 and 25°. The open circles show, for comparison, data calculated directly from values of P in Table II, and the filled circles denote cor-

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[9] Randall and Rossini, THIS JOURNAL, **51**, 323 (1929).

[10] Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

[11] Gucker and Schminke, THIS JOURNAL, **54**, 1358 (1932); **55**, 1013 (1933).

[12] Gucker, *Chem. Rev.*, **13**, 111 (1933).

responding data derived from Young and Groenier's equations. The dashed line represents the constant value 14.4 which Rossini found to be valid for the various sodium chloride data at, and somewhat below, 25°. The measurements reported here and represented by the open circles, are in themselves evidence of the failure of the linear relationship,[13] but the smallness of the thermal effects observed made corroboration desirable. This has now been supplied by the measurements of Gulbransen and Robinson which reveal similar evidence of the variation of $d(\phi C)/d\sqrt{m}$ with composition. The variation observed within the concentration range of either investigation alone might not seem conclusive, because it might be ascribed to experimental error. A single horizontal line drawn through both sets of points, however, would imply the existence of very large and improbable errors, and would be untenable. Manifestly, the derivative $d(\phi C)/d\sqrt{m}$ does vary with composition.

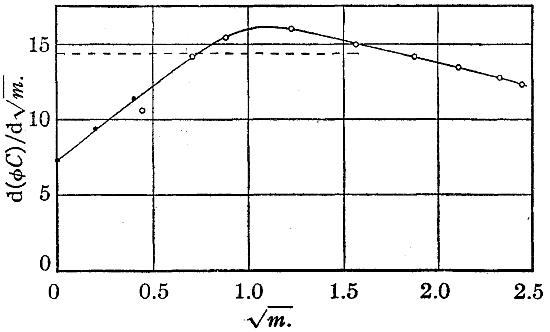

Fig. 2.

On Fig. 3 is plotted $\phi C - \phi C^\circ$ *vs.* $\sqrt{m}$. The dashed line represents Rossini's equation for temperatures between 18 and 25°; the solid line represents the integration of the solid curve of Fig. 2, *i. e.*, the average value of $\phi C - \phi C^\circ$ throughout the range between 12.5 and 25°. Because of the temperature difference the two curves should not correspond exactly. It is to be observed that their shapes are similar throughout the range between $\sqrt{m} = 0.2$ and $\sqrt{m} = 1.6$, *i. e.*, the range investigated experimentally by Randall and Rossini. Within this limited region the integrated (solid) curve is, in fact, approximately straight and its average slope does not differ greatly from that of the dashed line. Since there is some difference between the temperatures to which the two lines correspond, the agreement within the concentration range between $\sqrt{m} = 0.2$ and $\sqrt{m} = 1.6$ is quite satisfactory. There is, therefore, no conflict between Randall and Rossini's precise measurements[14] and the heats of dilution.

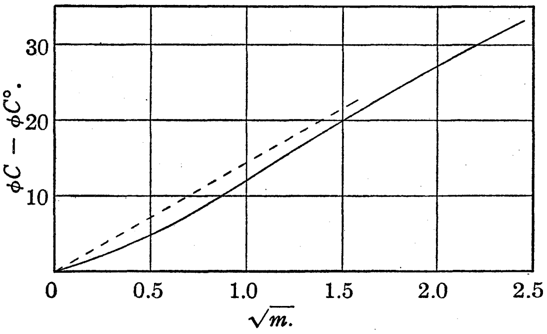

Fig. 3.

The slope of the ϕC *vs.* $\sqrt{m}$ curve for sodium chloride varies so rapidly near the origin that the limiting slope determined by linear extrapolation of apparent molal heat capacities is much larger (about twice as large) than the value derived from heats of dilution. Yet the heat capacity measurements for sodium chloride—especially those at 25°—are among the best in existence. The differences found between the limiting slopes of the various salts are, therefore, not significant and constitute no evidence of failure of the Debye–Hückel theory. That the theoretical limiting law is valid for sodium chloride at least is indicated by other data; the activity coefficients determined by Brown and MacInnes and the apparent molal heat content equations of Young and Groenier. More investigations of the latter type are desirable to supply further information concerning the variation with concentration of the heat capacities of electrolytic solutions.

These heat of dilution data have already been utilized[1] for a preliminary computation of activity coefficients from available freezing point tables. The computation revealed errors in older activity

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(13) This was pointed out at the meeting of the American Chemical Society in March, 1933; *cf.* Young, ref. 1. The purpose of Rossini's investigation of existing heat capacity data was to collect and arrange them conveniently for various thermochemical calculations. He did not discuss the relation of his equations to the Debye–Hückel theory. The influence upon his calculations of the differences between the two curves of Fig. 2 (and the corresponding curves of Fig. 3) are small and probably quite negligible.

(14) It is interesting that three of the four actual measurements (not average values) corresponding to Randall and Rossini's two smallest concentrations indicate a curvature in the expected direction. The fourth measurement yields a point which is well below even the straight line drawn by Rossini. Randall and Rossini did actually put some curvature into the line drawn to represent their measurements, but the heat capacity data were not capable of determining the change of slope quantitatively. Indeed, Rossini later represented the same data by a linear equation.

coefficient calculations introduced by the use of inaccurate and inadequate thermal data. A subsequent communication will describe the application of these dilution measurements to some freezing point determinations recently made in this Laboratory.

Summary

Differential heats of dilution to be used with cryoscopic data for the evaluation of activity coefficients of sodium chloride in aqueous solution have been obtained (by the chord-area method) from appropriate calorimetric measurements at 0, 12.5 and 25°.

These dilution data have been combined with those of Gulbransen and Robinson (extrapolated to infinite dilution by the method of Young and Groenier) to demonstrate that the apparent molal heat capacity of sodium chloride in aqueous solution is not a linear function of the square root of the molality. Many of the discrepancies between various precise measurements of the heat capacities of electrolytes, and the limiting law derived from the Debye–Hückel theory arose from linear extrapolations. Others are probably due to extrapolations which are too nearly linear. The theory is in agreement with measurements of the heats of dilution of aqueous sodium chloride solutions.

CHICAGO, ILL. RECEIVED SEPTEMBER 8, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 374]

The Normal Vapor Pressure of Crystalline Iodine[1]

BY LOUIS J. GILLESPIE AND LEWIS H. D. FRASER

The normal vapor pressure of iodine is the pressure of the pure vapor in equilibrium with pure solid or liquid iodine when this is subjected to the pressure only of the pure vapor. But few attempts have been made to measure it directly. Ramsay and Young[2] appear to have determined the pressure of air necessary to stop the sublimation of iodine at various temperatures from 58 to 113°. Haber and Kerschbaum[3] used a vibrating quartz fiber as manometer below 0 to $-48°$. They report some data by Naumann[4] from 19 to $-40°$. The precision of none of this work is within the theoretical uncertainties of the better indirect methods.

These uncertainties are due to the assumption, necessary in the indirect methods as ordinarily practiced, that iodine vapor behaves as an ideal gas—more particularly, that a mixture of iodine vapor and a permanent gas behaves as an ideal gas mixture. Gerry and Gillespie[5] showed how the uncertainties may be removed by applying thermodynamic corrections. They derived the corrections from the extensive data of Braune and Strassmann[6] and applied them to the precise indirect results of Baxter and co-workers.[7] They applied to these corrected results the rational equation of Giauque,[8] which has only one adjustable constant—the coefficient of the reciprocal temperature—and found the following equation to fit the corrected results very well

$$\log p = -3512.8/T - 2.013 \log T + 13.3740 \quad (1)$$

where p is the vapor pressure of the solid iodine in atmospheres, log is to the base 10 and $T = 273.1 + t°$.

The present paper deals with some direct measurements of the normal vapor pressure of solid iodine, of relatively high precision, made by means of a flexible metallic diaphragm to restrain the iodine vapor and devices for measuring precisely the low pressures of dry air on the opposite side of the diaphragm when the position of a pointer on the diaphragm, observed with a microscope, indicates a state of balance.

Apparatus

Corrosion experiments showed that platinum is not attacked by iodine, and gold becomes slightly tarnished, but the tarnish disappears on standing in air. These metals and glass were used to contain the iodine.

Figure 1 shows the diaphragm A, a disk of platinum-rhodium foil (4% Rh) 0.01 mm. thick with an effective diameter of 5.7 cm. It is mounted between two brass

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[1] From a thesis submitted by Mr. L. H. D. Fraser in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Ramsay and Young, *J. Chem. Soc.*, **49**, 453 (1886).

[3] Haber and Kerschbaum, *Z. Elektrochem.*, **20**, 296 (1914).

[4] Naumann, Dissertation, Berlin, 1907.

[5] Gerry and Gillespie, *Phys. Rev.*, **40**, 269 (1932).

[6] Braune and Strassmann, *Z. physik. Chem.*, **A143**, 225 (1929).

[7] Baxter, Hickey and Holmes, THIS JOURNAL, **29**, 127 (1907); Baxter and Gross, *ibid.*, **37**, 1061 (1915).

[8] Giauque, *ibid.*, **53**, 507 (1931).

rings B and B′. Through six holes in these rings screws pass into the block C. By tightening these screws the diaphragm is stretched over the curved surface of C like a drumhead and free from wrinkles. All brass surfaces against which iodine vapor may come are gold-plated. The tube D is of glass. It is ground well to the gold-plated conical hole in C, and the annular space at the bottom is tightly packed with gold dental moss and sealed with deKhotinsky cement, protected in turn with several coats of shellac.

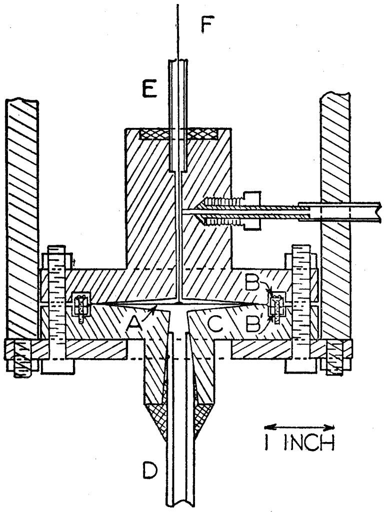

Fig. 1.—Diaphragm pressure balance.

The pointer F is a very light fiber of blue glass cemented to the diaphragm. The pointer and the tube E extend well up out of the thermostat. The top of the pointer is cut off square and is observed through the flattened wall of the top of the tube E through a microscope with the aid of a scale in the ocular.

The sensitivity of the diaphragm has been from 0.001 to 0.004 mm. of mercury pressure, depending on the initial stretch given the foil.

The portion of the apparatus shown in Fig. 1 is well immersed in the oil of the thermostat.

Figure 2 shows a manometer used by Professor F. G. Keyes in unpublished research and kindly lent to us. The arms A and B are 3.2 cm. in diameter. A vacuum is maintained over the mercury in B. The pointer P is operated by a 12.7-cm. dial D through a mercury-protected packing gland G. This can be tightened at any time by means of a special wrench. The periphery of the dial has 200 equal divisions; the thread of the screw is about 1 mm. in pitch, and the position of the screw can easily be estimated to 0.001 mm.

The manometer and the compression chamber C are in an air-bath. By means of the compression chamber the pressure of the dry air can be multiplied about 7 times before measurement with the manometer.

Experience showed that the zero reading of the dial (for equal pressures on both sides) varies with time, particularly because of necessary retightening of the packing. Hence in many cases it was preferred to find the pressure without the zero reading, by measuring in turn the dial reading for the original pressure and for the pressure after compression in the chamber C, and dividing the difference of the two dial readings by a number equal to the compression ratio diminished by unity. The pitch of the screw has been carefully calibrated by means of a good cathetometer with invar scale and found to be uniform. From the temperature of the air-bath and the value of gravity at Cambridge, pressures in international millimeters of mercury were calculated from the dial readings. These pressures are those of the dry air in the apparatus. When the vapor pressure of mercury is added we obtain the total pressure which balances the iodine pressure across the diaphragm.

A portion (not shown) of the tube D in Fig. 1 is bent to give elasticity and communicates through two special stopcocks either to a tube containing the supply of pure iodine or to the vacuum line, which includes condensing trap, gage and mercury and oil pumps. The stopcocks are operated under the oil of the thermostat but are protected by shields so that no oil can touch the plugs. By means of these cocks the tube D can be evacuated for a null-point determination of the diaphragm or connected with the iodine reservoir for a vapor pressure measurement. These cocks are lubricated with a mixture of meta- and pyrophosphoric acids obtained by heating two parts by weight of 85% ortho- with one part of metaphosphoric acid to various temperatures and for different lengths of time.[9] The mixtures used are very viscous and the cocks readily freeze if not turned frequently. The volume of the tubing D and its ratio to the volume of the system including the McLeod gage are known, so that any permanent gas present with the iodine after an experiment can be determined.

The pressure of the air used to balance the vapor pressure is steadied by means of a large bulb in the thermostat.

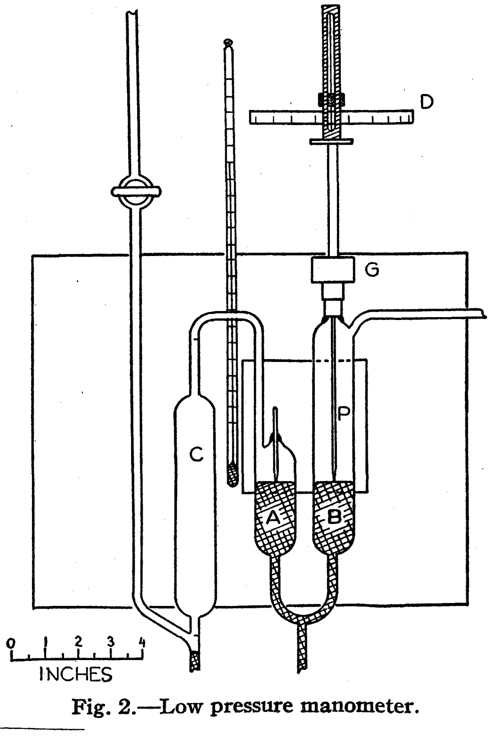

Fig. 2.—Low pressure manometer.

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[9] Stephens, THIS JOURNAL, 52, 635 (1930).

The stirrer of the thermostat and its motor are hung on a separate support to avoid vibration.

The Experiments

The iodine used was purified and dried by subliming it *in vacuo* from a mixture of resublimed iodine, anhydrous potassium iodide and phosphorus pentoxide. Sublimation was between temperatures of about 45 and −78° and required about three days. The bulb containing the pure product was brought into communication with the rest of the apparatus by breaking a glass tip *in vacuo* by a solenoid arrangement.

Before admitting iodine vapor to the tube D of Fig. 1 for a measurement, it was necessary to find the reading of the pointer on the scale in the ocular of the microscope when equal pressures were on either side of the diaphragm. Zero pressure was chosen for this. The null-point of the diaphragm should not vary with the small pressures in question at constant temperature, because of the simple and symmetrical geometry of the strong metal apparatus.[10]

Iodine vapor was then admitted to the tube D from the reservoir, dry air being admitted to the air system on the other side of the diaphragm, and by use of a mercury injector the diaphragm was again brought to the null-point. When equilibrium had been reached the pressure of the dry air was measured as described above, and the vapor pressure of mercury at the temperature of the gage of Fig. 2 added to obtain the vapor pressure of iodine. After a series of such measurements the null-point was observed again and the results discarded if a significant change had occurred during the series.

No effort was spared to obtain the greatest precision of which the apparatus was capable. Thus twenty-four experiments involving over 500 settings of the dial were performed to determine the two compression ratios used in the multiplication of the pressure (about 7, in each case). The corrections for deviations from Boyle's law were negligible. Eighty-one vapor pressure measurements involving over 1600 settings of the dial were performed at four temperatures from 30 to 60°. Of these, 32 were discarded either because the null-point of the diaphragm had changed or because equilibrium seemed not to have arrived. At each temperature the exact value of the temperature varied slightly from run to run, and the mean reciprocal temperature was found for the mean value of the logarithm of the pressure. This calculation is slightly better than direct averaging of the pressure and temperature but gave practically the same results, because of the smallness of the temperature variation.

At the end of the experiments at 30 and 40° no partial pressure of permanent gas was found in the iodine chamber. When the pressures of permanent gas found at the end of the groups of experiments at 50 and 60° were divided by the time elapsed since the previous evacuation, the rates of air leakage appeared to be constant at each temperature, and from these rates corrections were applied to each result according to the time elapsed, Dalton's law being used for the small corrections. At 50° the correction was 0.3% of the final value of the presssure on the average, and reached about 1% in a single case. At 60° it was about 1% on the average and reached 3% toward the end of one series.

The results are shown in Table I. A thermodynamic check for consistency is given by calculating from each result the value of ΔE_0° in the following equation of Giauque

$$\Delta F^\circ = -RT \ln p_{\text{atm.}} = \Delta E_0^\circ + 429 + 4.0T \ln T - 61.186T \quad (2)$$

Table I

Vapor Pressure of Solid Iodine in Mm. and ΔE_0°

Temp., °C.	29.967	40.017	50.154	60.119
Pressure, mm.	0.46709	1.02614	2.21318	4.30723
ΔE_0°	15643.29	15645.56	15630.91	15644.50

The value of ΔE_0° at 50° is inconsistent with the others, pointing to too high a value of the vapor pressure (by about 0.045 mm.). At this temperature the same inorganic stopcock lubricant was used as for the two lowest temperatures, and it proved too fluid, finally failing altogether. We believe that this was associated with a perceptible vapor pressure of water which caused the high results. In any case, a stiffer batch of lubricant was prepared and used at 60°, and the results here are consistent with those at the lower temperatures. From the mean result for ΔE_0°, excluding the value for 50°, the latent heat of sublimation of iodine at 25° is found to be $\Delta H_{298.16} = 14880.8 \pm 0.8$ cal.$_{15}$ per gram mole. In the above calculations 273.16 was used for the ice point and 1.98690 cal.$_{15}$ for R.

The mean result for the coefficient of $1/T$ in the simple equation of Giauque for the vapor pressure is 3512.859, nearly the same as that in equation (1) above derived by Gerry and Gillespie. The following table affords a comparison between the observed vapor pressures and those calculated by equation (1) and by equation (1) but with the modified value of the coefficient (marked 0.859). All pressures are in international millimeters.

Table II

Observed and Calculated Vapor Pressures of Solid Iodine

Temperature, °C.	Observed	Calcd. Eq. 1	Calcd. 0.859
29.967	0.4671	0.4663	0.4661
40.017	1.0261	1.0284	1.0279
50.154	2.2132	2.1682	2.1673
60.119	4.3072	4.3107	4.3089

The agreement of the results with the calculated values is very good, with the exception of the data for 50°, which are excluded from all further

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[10] Mr. Joseph E. Goossens found in this Laboratory that a glass diaphragm with a flattened working surface may change in null-point as the pressure is changed on both sides at constant temperature.

averages and calculations. The average percentage deviation from equation (1) is only 0.16, the greatest deviation being 0.0035 mm. and the greatest percentage deviation being 0.22. (The excluded value at 50 differs tenfold.)

The agreement of the data with equation (1) derived from the gas-stream data of Baxter and collaborators is noteworthy. The mean deviation (observed minus calculated) taken with respect to sign is only −0.044%. Now, in the reduction of these data by Gerry and Gillespie, the values of px_1 received corrections for non-ideality of the gas of 0.58, 0.51 and 0.37% at the temperatures 30, 40 and 60°, respectively, as may be found from their Table III. The agreement is therefore within the magnitude of the correction for failure of the ideal gas laws in the gas-stream method.[11]

The average percentage deviation of the results from the equation using the modified value of the coefficient of $1/T$ is 0.14%. The improvement (over 0.16) is not great. The use of a mean value (or of either) should afford very good vapor pressure values, probably from 0 to 100° or higher. Below 0° the equations do not agree well with the data of Haber and Kerschbaum and of Naumann—thus at −48.3° the observed pressure is only 72.7% of that calculated from equation (1) (or 72.3% of that calculated from the original equation of Giauque), and the true vapor pressure is in turn estimated by Haber and Kerschbaum to be about 12% lower than that observed (at room temperature), by reason of the Knudsen effect.[12]

The equations also disagree somewhat at 90° and above with the data of Ramsay and Young, the calculated values becoming progressively greater than the observed, the difference reaching 6.4% of the observed pressure at 113.8°.

These facts suggest that equation (1) is perhaps too simple in form for such a range of temperature as from −48 to 114°.

Nevertheless, the best values at present available for the normal vapor pressure of iodine are probably those calculable from equation (1) with the value 3512.830 for the coefficient of $-1/T$, which averages the results of Baxter and collaborators and the present work. Table III gives such values for even values of the temperature.

TABLE III

NORMAL VAPOR PRESSURE OF SOLID IODINE IN INTERNATIONAL MILLIMETERS OF MERCURY

t, °C.	0	10	20	25	30	40	50	60
p, mm.	0.0307	0.0814	0.201	0.309	0.467	1.027	2.144	4.276
t, °C.	70	80	90	100	110	114.15 (m. p.)		
p, mm.	8.175	15.04	26.73	45.97	76.76	94.18		

Summary

The normal vapor pressure of solid iodine has been measured directly by means of a flexible metallic diaphragm at 30, 40 and 60° with a precision of better than 0.004 mm. of mercury, or better than 0.22%. The results agree with the equation deduced by Gerry and Gillespie from the data of Baxter and collaborators, as corrected for failure of the ideal gas laws, within the magnitude of these corrections. A table is given of vapor pressures derived from a combination of the new data with the corrected older data, as embodied in the modified equation of Giauque

$$\log_{10} p_{\text{atm.}} = -3512.830/T - 2.013 \log T + 13.37400$$

The corresponding value of ΔH for the sublimation of iodine at 25° is 14880.7 cal_{15}/mole.

CAMBRIDGE, MASS. RECEIVED AUGUST 12, 1936

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[11] Air was the inert gas in this case. The corrections depend in part on the nature of the inert gas.

[12] The calculated pressure at −48.3° is only 7.84×10^{-5} mm.; the observed, 5.7; the observed after Knudsen correction, 5.0×10^{-5} mm.

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The System Dioxane and Water

BY FRANK HOVORKA, RALPH A. SCHAEFER AND DALE DREISBACH

Introduction

There has been a considerable interest shown in the use of symmetrical dioxane (1,4) after it was recommended by Anschütz and Broeker[1] as an excellent organic solvent for molecular weight determinations. The first important workers, Herz and Lorentz,[2] unfortunately overlooked the highly hygroscopic nature and the slow decomposition with time of dioxane. These two properties were later pointed out by Roth and Meyer[3] and consequently some of the results of Herz and Lorentz are in error because of the questionable purity of their dioxane.

Since dioxane is completely miscible with water it cannot only serve as a solvent for investigating the properties of the various solutes in it, but can also be used when it is desirable to know the properties of solutes in the mixed solvents, dioxane and water. Thus in view of the importance of dioxane in its various applications it was thought desirable to determine various physical properties not only in the pure state but also in its various mixtures with water over a wide range of temperatures.

Experimental

Materials.—The dioxane was purified by a modification of the Kraus and Vingee[4] method. Commercial dioxane was refluxed over sodium hydroxide and after distillation boiled for a long period over metallic sodium, fresh metal being added from time to time. It was then crystallized several times. The final product melted at 11.78 ± 0.01°.

The water used in this investigation was prepared by repeated crystallizations from selected pieces of ice.[5] The fifth crop proved very pure. The conductivity of the liquid from this ice was 0.95×10^{-6} mhos at 25°.

Procedure.—The apparatus was cleaned and dried and allowed to stand overnight in dry air. The different concentrations were prepared by weighing the desired amounts in small glass-stoppered bottles. Transfer of liquids and all the weighings were performed in an atmosphere of purified air. The dioxane was recrystallized each time before being used.

Temperatures in all cases were kept constant to 0.01° up to 40° and ±0.02° above 40°, and were referred to a thermometer calibrated by the Bureau of Standards.

Densities were determined by the dilatometer method. The dilatometer was calibrated with purified mercury. The working volume was 7.7 to 8.7 cc. and the total height 23.3 cm. The smallest volume capable of being read was 0.0001 cc., which corresponds to an accuracy of approximately one part in fifty thousand.

The capillary rise method was used for surface tension measurements as outlined by Richards and Coombs.[6] The large tube had a diameter of 3.8 cm. and the capillary tube a radius of 0.01815 cm. as determined by careful calibration with a mercury thread. The length of the thread was measured by means of a precision micrometer.

A static method similar to the one previously described by Hovorka and Dreisbach[7] was used for measuring the vapor pressure.

For the measurements of the three properties above a cathetometer with a reproducible accuracy of ±0.01 mm. was used. All of the determinations were carried out with the apparatus sealed off *in vacuo*.

The index of refraction was determined with an Abbé refractometer accurate to ±0.0001. Measurements were carried out at 25 ± 0.05° using sodium light as a source of illumination.

The freezing point curve was investigated with the usual Beckmann apparatus. The temperature was controlled by cooling ethyl alcohol with solid carbon dioxide in a gallon (4-liter) Dewar flask and was maintained three degrees lower than the freezing point of the solution under investigation. Precautions were taken to prevent moisture from entering the freezing point tube.

Experimental Results.—The experimental results are summarized in Tables I–VI and Figs. 1–3. The temperature is in degrees centigrade and vapor pressure in mm. of mercury. The vapor pressure data, Table III, are for round values of concentration obtained by graphical interpolation.

Discussion of Results

The results obtained deviate widely from the ideal solution laws as was to be expected, since dioxane is non-polar while water is a highly polar substance. A study of the experimental data shows a pronounced difference in internal pressures of the dioxane and water. Table IV of the partial molal volumes of the 25° isotherm shows this phenomenon exceedingly well. ($\overline{V} - V^0$ is the partial molal volume of each constituent, $\overline{V}$, less the molal volume of that constituent in the pure state, V^0.) From the curves in Fig. 1 we see that the maximum change in the partial molal

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[1] Anschütz and Broeker, *Ber.*, **59**, 2844 (1926).

[2] Herz and Lorentz, *Z. physik. Chem.*, **A140**, 406 (1929).

[3] Roth and Meyer, *Z. Elektrochem.*, **39**, 35 (1933).

[4] Kraus and Vingee, THIS JOURNAL, **56**, 511 (1934).

[5] Ephraim, "Inorganic Chemistry," translated by P. C. Thorne, Gurney and Jackson, London, 1932, p. 356.

[6] Richards and Coombs, THIS JOURNAL, **37**, 1656 (1915).

[7] Hovorka and Dreisbach, *ibid.*, **56**, 1664 (1934).

TABLE I

SURFACE TENSION OF THE DIOXANE–WATER SYSTEM

Dioxane mole fr.	Temperature, °C.								
	10	20	25	30	40	50	60	70	80
0.1011	48.09	46.52	45.73	44.91	43.44	42.24	40.62	39.09	37.71
.1916	42.66	41.38	40.45	39.81	38.29	36.92	35.56	34.22	33.02
.3219	39.30	37.99	37.13	36.52	35.26	33.98	32.73	31.41	30.16
.4065	38.09	36.82	36.25	35.52	34.28	32.89	31.69	30.39	29.05
.4319	37.87	36.69	36.05	35.32	34.02	32.75	31.40	30.14	
.5251	36.94	35.77	35.31	34.63	33.21	32.08	30.58	29.43	28.11
.6091	36.55	35.38	34.74	33.96	32.72	31.34	30.08	28.86	27.42
.7417		34.62	34.06	33.31	32.45	30.60	29.20	27.78	
.8748	35.21	34.02	33.52	32.80	31.25	30.11	28.57	27.09	
1.0000		33.39	32.85	32.19	30.73	29.35	27.81	26.25	24.76

TABLE II

DENSITY OF THE DIOXANE–WATER SYSTEM

Dioxane mole fr.	Temperature, °C.								
	10	20	25	30	40	50	60	70	80
0.1011	1.03324	1.02738	1.02447	1.02136	1.01491	1.00860	1.00176	0.99439	0.98858
.1916	1.04467	1.03708	1.03314	1.02961	1.02208	1.01388	1.00553	.99669	.99006
.3219		1.02420	1.03722	1.03355	1.02468	1.01464			
.4065		1.04063	1.03634	1.03123	1.02164	1.01161	1.00140	.99091	.98054
.4319	1.05015	1.04042	1.03553	1.03063	1.02034	1.01025	1.00001	.98721	.97902
.5021		1.03785	1.03296	1.02790	1.01758	1.00690	0.99601	.98648	.97558
.6074	1.04486	1.03521	1.02995	1.02427	1.01416	1.00315	.99168	.98233	.97107
.7633	1.04379	1.03361	1.02806	1.02285	1.01094	1.00038	.98981	.97840	.96766
.8760	1.04307	1.03328	1.02788	1.02210	1.01074	0.99974		.97733	.96598
1.0000		1.03318	1.02766	1.02189	1.01045	.99948	.98781	.97693	.96486

TABLE III

VAPOR PRESSURE OF THE DIOXANE–WATER SYSTEM

(Corrected to 0°)

Dioxane mole fr.	Total pressure									Partial pressure 25°C.	
	Temperature, °C.										
	10	20	25	30	40	50	60	70	80	Dioxane	Water
0.000	9.2	17.5	23.8	31.8	55.4	92.6	149.6	233.8	355.1	0.0	23.8
.100	14.8	27.7	37.0	49.2	84.1	138.8	218.8	336.1	501.5	11.1	25.9
.200	18.0	32.9	42.8	57.6	95.7	156.8	245.4	373.7	550.0	17.7	25.1
.300	19.5	35.4	45.7	61.3	101.8	164.0	255.9	387.9	569.5	22.5	23.2
.400	20.1	36.5	47.3	62.5	104.3	165.1	257.7	390.8	575.5	26.2	21.1
.500	20.3	36.7	47.7	62.9	104.6	165.3	257.9	390.9	576.5	28.6	19.1
.600	20.4	36.8	47.7	62.9	104.6	165.3	257.9	390.7	571.0	30.1	17.6
.700	20.5	36.9	47.7	62.9	104.4	165.0	257.4	386.7	556.0	31.6	16.1
.800	20.6	36.7	47.5	62.4	103.0	163.6	252.0	374.1	526.5	33.2	14.3
.900	19.5	34.4	45.2	59.0	97.4	150.2	230.9	345.2	476.0	35.0	10.2
1.000	17.0	28.1	36.9	47.6	76.6	119.8	181.3	266.9	382.8	36.9	0.0

TABLE IV

PARTIAL MOLAL VOLUME IN CC.

Dioxane mole fr.	Water	Dioxane
0.0000	18.05	79.78
.1011	17.95	82.77
.1916	17.77	83.84
.3219	17.46	84.72
.4065	16.92	85.65
.4319	16.76	85.97
.5021	16.75	85.95
.6074	16.78	85.88
.7633	17.20	85.75
.8760	17.43	85.70
1.0000	17.48	85.69

TABLE V

REFRACTIVE INDEX

Dioxane mole fr.	Refr. index	Dioxane mole fr.	Refr. index
0.0000	1.3325	0.5021	1.4080
.0132	1.3380	.6052	1.4116
.1011	1.3670	.7417	1.4153
.1916	1.3840	.7633	1.4155
.3219	1.3980	.8760	1.4173
.4065	1.4038	1.0000	1.4198
.4319	1.4049		

volume of water is about 8%, whereas that of the dioxane is about 4%. The greatest deviation is in the region of low concentration of dioxane.

TABLE VI

FREEZING POINTS OF DIOXANE–WATER SYSTEM

Dioxane mole fr.	Freezing point, °C.	Eutectic temp., °C.
0.0000	0.0	
.0855	−10.1	−14.9
.0905	−10.8	
.1011	−11.6	−14.9
.1140	−12.7	−14.9
.1515	−14.9	−14.9
.1830	−11.1	
.2500	− 3.6	
.3219	− 0.7	
.4007	1.0	
.4285	1.5	−14.9
.5202	2.8	
.6074	3.7	
.6351	3.9	
.7296	5.0	
.7633	5.4	
.8760	7.5	−14.9
.9208	8.7	
1.0000	11.78	

The partial pressure of water, Fig. 2, is abnormally high in this neighborhood, while dioxane follows the natural course for systems having a maximum vapor pressure. There is also a decided maximum in the density curve of this system. Geddes[8] reports a maximum in the viscosity of this system as well as an inflection point in the fluidity curve. The latter is "an unusual type of behavior." It is to be noted that this point of inflection may be due entirely to the densities given by Geddes. In the region between 0 and 5% water he gives two points which are decidedly higher than his values at 0 and 5%. No such high values were found in this work nor in that of Gillis and

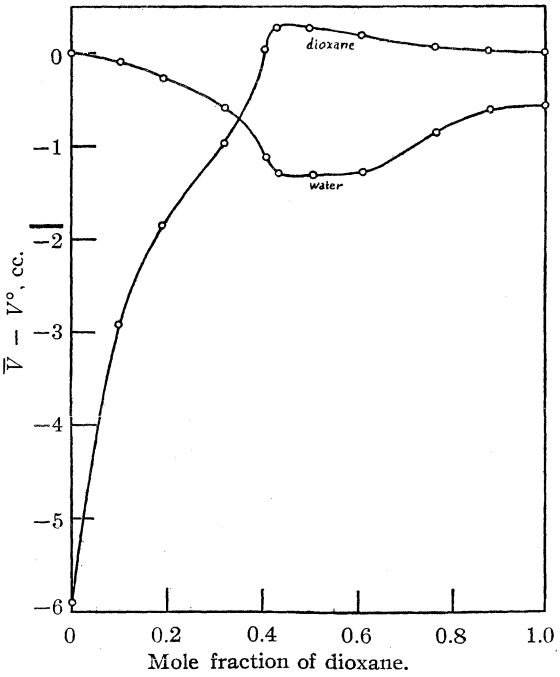

Fig. 1.—Partial molal volumes of dioxane and water.

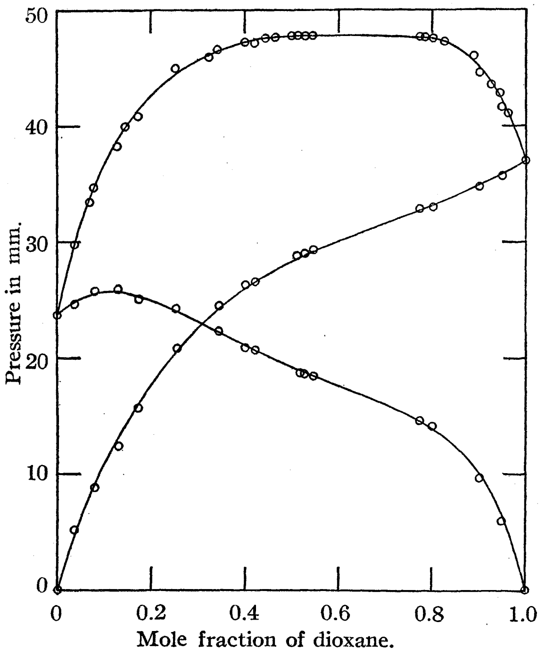

Fig. 2.—Total and partial vapor pressure curves of dioxane–water mixtures at 25°.

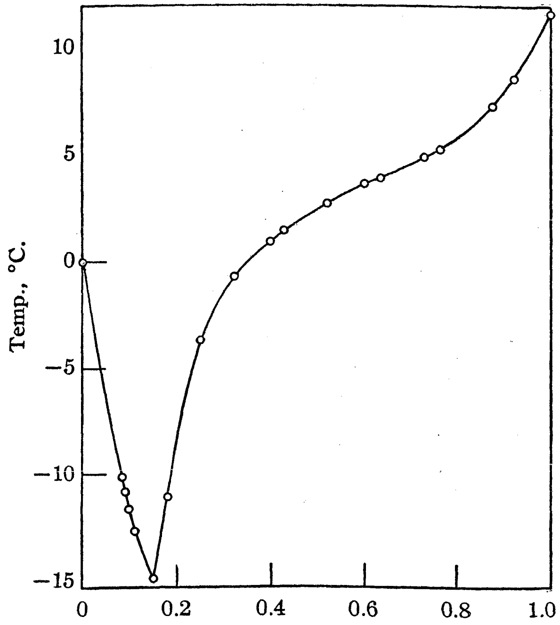

Fig. 3.—Freezing point curve of dioxane–water mixtures.

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(8) Geddes, THIS JOURNAL, 55, 4832 (1933).

Delaunois.[9] The density curve is quite normal in this region.

The refractive index does not possess a maximum but for both refractive index and surface tension the deviations from the ideal are very great.

The eutectic point at 0.152 mole fraction of dioxane and a temperature of −14.9° agrees well with that found by Gillis and Delaunois. However, these workers report a peculiar trend in the curve between 0.8 and 1.0 mole fraction dioxane. This has not been confirmed and the results obtained here are in excellent agreement with those found by Bell and Wolfenden.[10] Gillis and Delaunois in calling attention to this peculiar irregularity base their conclusions on one point only which may well be in error by 10%. Further, it is difficult to understand why they report two densities for their pure dioxane at 20°, namely, 1.0345 and 1.03215. The maximum deviation from the ideal linear freezing-point curve, Fig. 3, occurs at 0.37 mole fraction of dioxane corresponding to the maximum found in the density measurements.

Values for the vapor pressure of pure dioxane, Table III, are higher at low temperatures and lower at higher temperatures than the corresponding values given by Herz and Lorentz.[2] The vapor pressure may be expressed by means of the equation

$$\log_{10} P \text{ (mm.)} = -1933.8/T + 8.0588$$

with a maximum deviation of one per cent. over the temperature range 10 to 80°.

Dioxane itself is a very normal liquid. The Eötvös constant as calculated is 2.11 for the temperature range investigated. The parachor is 205.7, which agrees fairly well with the calculated value of 202.1. The molecular refraction according to the expression of Lorentz and Lorenz gives an experimental value of 21.678, which is in excellent agreement with the theoretical value of 21.690.

The authors wish to express their appreciation to Dr. J. O. Morrison, of Yale University, for furnishing the purified dioxane.

Summary

1. The density, surface tension and total vapor pressure of the dioxane–water system were investigated for the temperature range 10 to 80°.

2. The partial vapor pressure and the index of refraction for this system were determined at 25°.

3. The freezing point curve of the dioxane–water system was studied.

4. The dioxane–water system was discussed and the possible errors of other workers in the case of freezing points, density and fluidity were pointed out.

CLEVELAND, OHIO RECEIVED SEPTEMBER 4, 1936

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(9) Gillis and Delaunois, *Rec. trav. chim.*, **53**, 186 (1934).

(10) Bell and Wolfenden, *J. Chem. Soc.*, 822 (1935).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

The Reaction of 2,3-Epoxybutane with the Grignard Reagent

BY D. L. COTTLE AND LEO S. POWELL

The rearrangement of certain ethylene oxides in Grignard reactions is well known. Among the simple alkyl or aryl substituted ethylene oxides, 2,3-epoxybutane,[1] 1,2-epoxy-2-methylpropane,[2] 1,2-epoxy-2-methylbutane,[3] 1,2-epoxy-2-phenylpropane,[4] and styrene oxide,[5] have been reported to rearrange in Grignard reactions to produce one alcohol, while 1,2-epoxypropane[6–8] and 1,2-epoxybutane[8] have been reported not to rearrange.

In order to explain the rearrangement of cyclohexene oxide in a methylmagnesium iodide reaction reported by Bedos, Bartlett and Berry[9] adopted the Blaise[10] structure for the primary intermediate.[11,12]

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(1) L. Henry, *Compt. rend.*, **145**, 406 (1907).

(2) L. Henry, *ibid.*, **145**, 21 (1907).

(3) Fourneau and Tiffeneau, *ibid.*, **145**, 438 (1907).

(4) Tiffeneau, *ibid.*, **140**, 1460 (1905).

(5) Fourneau and Tiffeneau, *ibid.*, **146**, 698 (1908).

(6) Hess, *Ber.*, **46**, 3117 (1913).

(7) Levene and Walti, *J. Biol. Chem.*, **90**, 81 (1931).

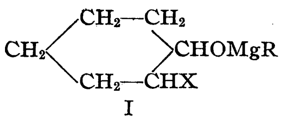
(8) Levene and Walti, *ibid.*, **94**, 367 (1931).

(9) Bartlett and Berry, THIS JOURNAL, **56**, 2683 (1934).

(10) Blaise, *Compt. rend.*, **134**, 552 (1902).

(11) This theory was criticized by Grignard [*Bull. soc. chim.*, [3] **29**, 944 (1903)] who preferred to depict the oxide ring as breaking at much higher temperatures. Boord and Summerbell readvanced the Blaise theory (Columbus, Ohio, meeting of The American Chemical Society, May, 1929) and Ribas and Tapia placed it on a more secure basis as a result of extensive experiments with ethylene oxide, epichlorohydrin and 3-methoxy-1,2-epoxypropane [*Anal. soc. españ. fís. quím.*, **30**, 778 (1932); **30**, 944 (1932)].

(12) Boord and Summerbell and Ribas and Tapia suggested as likewise possible the structures BrMgOCH$_2$CH$_2$Br and Mg(OCH$_2$CH$_2$Br)$_2$ for ethylene oxide intermediates.



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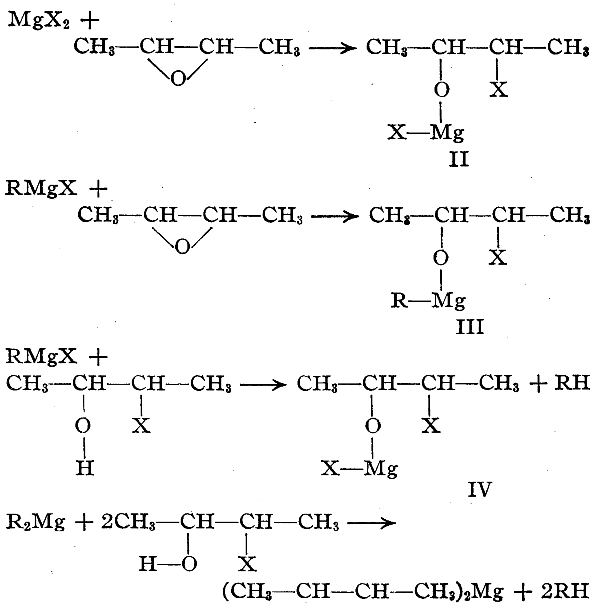
These workers further assumed that I rearranged to cyclopentylformaldehyde instead of reacting through replacement of the halogen by the methyl group. These assumptions were based on experimental work by Bedos[13,14] who found that the alkoxide formed from cyclohexene chlorohydrin and ethylmagnesium bromide gave a 40% yield of cyclopentylformaldehyde when the ether was evaporated from its mixture with magnesium bromide. The oxide treated similarly with magnesium bromide etherate gave a 34% yield of aldehyde. These magnesium bromide reaction mixtures, both chlorohydrin and oxide, reacted vigorously with methylmagnesium iodide to form methylcyclopentylcarbinol.

If the reaction path outlined by Bartlett and Berry is applicable to 2,3-epoxybutane, 3-bromo-2-butanol should react with a Grignard reagent and yield a tertiary alcohol since Henry[1] obtained tertiary amyl alcohol when methylmagnesium bromide reacted with the oxide. The intermediates, II and III, would have structures similar or identical to IV and V.



$$MgX_2 + CH_3-\underset{\diagdown O \diagup}{CH-CH}-CH_3 \longrightarrow CH_3-\underset{\underset{X-Mg}{|}}{\underset{O}{|}}{CH}-\underset{X}{\underset{|}{CH}}-CH_3 \quad \text{II}$$

$$RMgX + CH_3-\underset{\diagdown O \diagup}{CH-CH}-CH_3 \longrightarrow CH_3-\underset{\underset{R-Mg}{|}}{\underset{O}{|}}{CH}-\underset{X}{\underset{|}{CH}}-CH_3 \quad \text{III}$$

$$RMgX + CH_3-\underset{\underset{H}{|}}{\underset{O}{|}}{CH}-\underset{X}{\underset{|}{CH}}-CH_3 \longrightarrow CH_3-\underset{\underset{X-Mg}{|}}{\underset{O}{|}}{CH}-\underset{X}{\underset{|}{CH}}-CH_3 + RH \quad \text{IV}$$

$$R_2Mg + 2CH_3-\underset{H-O}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH}}-CH_3 \longrightarrow (CH_3-\underset{O}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH}}-CH_3)_2Mg + 2RH \quad \text{V}$$

We found that 3-bromo-2-butanol reacted with the second mole of ethylmagnesium bromide without application of heat, and the end-products consisted of 2-butanone, postulated by Henry as an intermediate in the oxide reaction, and 3-methyl-3-pentanol. We were unable to isolate any 3-methyl-2-pentanol, which would have resulted from a replacement of the halogen by the alkyl group of the Grignard reagent. Thus, the explanation of Berry and Bartlett applies to 2,3-epoxybutane.

The Grignard reaction of this bromohydrin without application of heat undoubtedly is due to the secondary bromine atom. Ethylene bromohydrin is well known to require higher temperatures for reaction of the bromine atom.[15] The magnesium salt of 3-bromo-2-butanol, prepared from 2,3-epoxybutane and magnesium bromide in ether benzene solution decomposed practically quantitatively at slightly above room temperature. The product was 2-butanone. Rector[16] was able to prepare 3-bromo-2-butanol in 60% yield by this method by working at 0°.

Although the Blaise theory is satisfactory in predicting the behavior of 3-bromo-2-butanol the isolation by Henry, Fourneau and Tiffeneau and others of only one alcohol in the oxide reactions which involved rearrangements is not in satisfactory agreement with known experimental data. Ribas and Tapia[11] found in treating 2 moles of ethylene oxide with one of ethylmagnesium bromide in the cold that the magnesiumalkyl bond also reacted. Later, Bartlett and Berry[9] obtained no rearrangement in the reaction of cyclohexene oxide with diethylmagnesium or dimethylmagnesium. Ribas and Tapia obtained a 5% yield of *n*-butyl alcohol when ethylene oxide was reacted with ethylmagnesium bromide in a 1 to 1 ratio in the cold. This may be assumed to represent the percentage of reaction of C_2H_5Mg bond when in competition with a similar quantity of MgBr bond. Consequently, we considered it probable that small amounts of normal products

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[13] Bedos, *Compt. rend.*, **189**, 255 (1929).

[14] Berry and Bartlett are confused in the history of this reaction for they credit Bedos with their explanation as well as with the experimental work. There is nothing in the reference[13] cited by Berry and Bartlett or in other articles by Bedos to indicate that he wished to advance the explanation credited to him. The statement by Berry and Bartlett[9] (p. 2684), "Bedos has further elucidated the mechanism of this rearrangement by showing that, as in the aliphatic series, the primary product of reaction between cyclohexene oxide and a Grignard reagent is the halohydrin derivative. . . .," is misleading in another respect inasmuch as in only one case, 1,2-epoxy-2-methylbutane, are there sufficient data in the literature to support a qualified explanation of an aliphatic ethylene oxide rearrangement. Moreover, no reference is given to the work of Ribas and Tapia of 1932 which is the only successful attempt to refute the unsatisfactory theory advanced by Grignard in 1903.

[15] Grignard, *Bull. soc. chim.*, [3] **34**, 918 (1905); Conant and Kirner, THIS JOURNAL, **46**, 240 (1924).

[16] Rector, Master of Science Thesis, Rutgers University, 1933.

in the rearrangements cited were overlooked by the early workers.

2,3-Epoxybutane was selected for investigation of this and related points for the following reasons: the recent description[17] of a source of pure 2-butene made its preparation in larger than usual quantities feasible; 3-bromo-2-butanol is the only bromohydrin that it can form; and the difference in boiling points of the possible alcohols produced by the Grignard reagent is greater than if a higher molecular weight oxide were used.

In the present work 2,3-epoxybutane was found to react with diethylmagnesium and dimethylmagnesium to yield secondary alcohols. These results are in complete agreement with the predictions of Bartlett and Berry[9] and have been reported by other investigators.[18] Secondary alcohols were also isolated in 2,3-epoxybutane reactions with ethylmagnesium chloride and bromide and methylmagnesium bromide. A trace of secondary alcohol probably was present in an ethylmagnesium iodide experiment. A tertiary alcohol also was produced in each of these reactions. That the formation of the secondary alcohol was due to a direct reaction of the alkylmagnesium bond with the oxide was demonstrated by the absence of the secondary alcohol in the 3-bromo-2-butanol reaction with ethylmagnesium bromide. The formation of appreciable yields of the tertiary alcohol (see Table I) without heating of the bromide and iodide reactions was predicted on the basis of the results obtained with 3-bromo-2-butanol.

TABLE I

Expt.	RMgX	Yield, % Secondary alcohol	Yield, % Tertiary alcohol
1	C_2H_5MgCl	27[a]	30[a]
2	C_2H_5MgBr	2	31
3	C_2H_5MgI	Trace	27
4	CH_3MgBr	7[a]	44[a]

[a] Based on refractive index of the mixture.

In view of the discovery by Brönsted and coworkers[19] that of the aqueous potassium halides, iodide adds faster than bromide and bromide faster than chloride to glycid and epichlorohydrin it is not surprising that of the three ethyl Grignard reagents, the iodide gave the least alkylmagnesium reaction. However, several factors need evaluation before a valid conclusion can be drawn.

The discovery by Schlenk and Schlenk[20] that the dioxane precipitate from a Grignard solution behaved like a Grignard reagent with esters and ketones caused us to treat 2,3-epoxybutane with the precipitate from an ethylmagnesium bromide solution. The precipitate contained a larger amount of magnesium halide bond compared with magnesiumalkyl than the original Grignard and a tertiary alcohol with very little if any of the secondary was expected. However, the precipitate was apparently too insoluble for reaction and dissociated to form soluble diethylmagnesium for only the secondary alcohol was formed.

In the reaction of 3-bromo-2-butanol there was obtained, besides 2-butanone, a small amount of liquid which boiled around 155–165°. From the boiling point, reduction of permanganate and the formation of a solid with semicarbazide solution this product contained an octenone. Pariselle and Simon[21] obtained a similar product in the reaction of isopropylmagnesium bromide with 2-butanone and analogous observations have been made by many other workers although generally with Grignard reagents with more complex alkyls than ethyl. In the present work similar material was obtained from the reaction of 2,3-epoxybutane with ethylmagnesium iodide and of 2-butanone with diethylmagnesium. In the latter reaction the yield of alcohol was only 8%.

Experimental

The Preparation of Crude 3-Bromo-2-butanol.—Bromine water was treated with 2-butene by the method given by Read and Williams[22] for ethylene bromohydrin. 2-Butene, generated by heating 4 moles of 2-butanol with 60% sulfuric acid,[17] was passed into the bottom of a well stirred, 5-liter, 3-necked flask which contained 4 liters of water. At the same time, air, regulated by a needle valve, carried bromine into the reaction vessel at such a rate as to give the solution a faint yellow color. The air and butene bubbles were broken up by Jena G-4 gas distribution tubes. In order to prevent the dibromide from extracting the butene and bromine from the water the flask was fitted with a siphon for the intermittent removal of the by-product.

At the end of the reaction the remaining dibromide was separated and the water layer saturated with salt and extracted with ether. After drying over sodium sulfate the ether was expelled on a water-bath. The residue, in 7 preparations, averaged 164 g. or 27% of the theoretical based on the 2-butanol used.

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[17] Young and Lucas, THIS JOURNAL, **52**, 1964 (1930); *cf.* Komarewsky, Johnstone and Yoder, *ibid.*, **56**, 2705 (1934), and Young and Winstein, *ibid.*, **58**, 102 (1936).

[18] Norton and Hass, *ibid.*, **58**, 2147 (1936).

[19] Brönsted, Kilpatrick and Kilpatrick, *ibid.*, **51**, 443 (1929).

[20] Schlenk and Schlenk, *Ber.*, **62B**, 920 (1929).

[21] Pariselle and Simon, *Compt. rend.*, **173**, 88 (1921).

[22] Read and Williams, *J. Chem. Soc.*, **117**, 359 (1920).

The Preparation of 2,3-Epoxybutane.—Crude 3-bromo-2-butanol (360 g.) was added drop by drop to a well-stirred solution of 450 g. of sodium hydroxide in 1050 cc. of water in a 2-liter, 3-necked flask heated on a water-bath. The oxide and some water distilled over at 50–60°. After drying over potassium carbonate it was fractionated with a 3-bulb Snyder column and gave a 75% yield of oxide, b. p. 55–59°, $n^{20}{}_{D}$ 1.3765, $d^{20}{}_{20}$ 0.8144.

The Preparation of Pure 3-Bromo-2-butanol.—The method of Thayer, Marvel and Hiers[23] for the preparation of ethylene bromohydrin was used. 2,3-Epoxybutane (66 g.) was added to 172 cc. of 48% hydrobromic acid kept at 0–2°. The yield was 123 g. or 88% of the theoretical of 3-bromo-2-butanol, b. p. 46–50° (8 mm.); $n^{20}{}_{D}$ 1.4780, $d^{20}{}_{20}$ 1.4500.

Anal. Calcd. for C_4H_9OBr: Br, 52.24. Found: Br, 52.2, 52.3.

This compound has been prepared previously.[24]

The Preparation of Reference Compounds.—In order to facilitate the identification of the various alcohols obtained in the experiments described below it was necessary to prepare some new urethans.

3-Methyl-3-pentanol was prepared from ethylmagnesium bromide and 2-butanone. The α-naphthyl urethan was prepared by heating 1 g. of the alcohol with 1.7 g. of α-naphthyl isocyanate for three hours. It melted at 83.5°.

Anal. Calcd. for $C_{17}H_{21}O_2N$: N, 5.17. Found: N, 5.05, 4.85.

The phenylurethan, similarly prepared, melted at 43.5°.

Anal. Calcd. for $C_{13}H_{19}O_2N$: N, 6.33. Found: N, 6.37, 6.32.

3-Methyl-2-pentanol was prepared from *s*-butylmagnesium bromide and acetaldehyde by an adaptation of the method for 3-methyl-2-butanol.[25]

The α-naphthylurethan melted at 72°.

Anal. Calcd. for $C_{17}H_{21}O_2N$: N, 5.17. Found: N, 5.21, 4.98.

3-Methyl-2-butanol was prepared according to the directions of Drake and Cooke.[25] The α-naphthylurethan melted at 108–109°.

Anal. Calcd. for $C_{16}H_{19}O_2N$: N, 5.45. Found: N, 5.39, 5.24.

The phenylurethan melted at 68°.

Anal. Calcd. for $C_{12}H_{17}O_2N$: N, 6.76. Found: N, 6.67, 6.87.

These derivatives and the α-naphthylurethan of 2-methyl-2-pentanol, described by Neuberg and Kansky,[26] were used in mixed melting point determinations with urethans prepared from the products of the experiments described below.

The Reaction of 3-Bromo-2-butanol with Ethylmagnesium Bromide.—The bromohydrin (0.65 mole), prepared from the oxide and hydrobromic acid, was added drop by drop to 480 cc. of an ice-cooled ether solution containing 1.3 moles of ethylmagnesium bromide. A precipitate gradually formed which filled half of the solution. Soon after removal of the ice-bath the reaction mixture refluxed violently for an hour. After standing overnight it was hydrolyzed, the ether extract dried over sodium sulfate and the ether removed on the water-bath. The residue was treated with 30% sodium hydroxide in order to remove unchanged bromohydrin. After extracting with ether and drying over potassium carbonate distillation was made through a 6-bulb Snyder column.

A portion of a 1.0-g. fraction boiling at 65–78° gave a semicarbazone which melted at 138–139°. A mixed melting point with an authentic semicarbazone of 2-butanone did not vary.

The fraction distilling at 121–122° weighed 17.4 g. which corresponds to a 26% yield of alcohol. It was identified as 2-methyl-2-pentanol. The 122–131° fraction weighed 0.9 g. and the material boiling from 131–136°, 0.6 g. The latter gave an α-naphthylurethan melting at 81.5°. A mixture with the α-naphthylurethan of 3-methyl-3-pentanol melted at 82.5°. When a mixture of equal quantities of 3-methyl-3-pentanol and 3-methyl-2-pentanol was reacted with α-naphthyl isocyanate no derivative melting above 52° could be obtained.

A residue of 1.0 cc. was investigated and is reported below.

The Reaction of 2,3-Epoxybutane with Magnesium Bromide.—One mole of oxide was added drop by drop to 1 mole of magnesium bromide, prepared in 300 cc. of ether by the method of Zelinsky[27] and diluted with 300 cc. of benzene. The original object of this experiment was the preparation of 3-bromo-2-butanol but cooling was inefficient and the hydrolysis product consisted of 16 g. of uninvestigated liquid which did not volatilize on the steam-bath. 2-Butanone was extracted from the ether and benzene distillate with sodium bisulfite and identified by the melting point of its semicarbazone and a mixed melting point determination. The oxide dissolved in ether and benzene did not give a precipitate with sodium bisulfite.

The Reaction of 2,3-Epoxybutane with Diethylmagnesium and Dimethylmagnesium.—The oxide was added drop by drop to the dialkylmagnesium in ether in an atmosphere of tank nitrogen using ordinary Grignard technique.

To 0.105 mole of dimethylmagnesium, prepared according to the method of Gilman and Schulze,[28] in 200 cc. of ether was added 0.20 mole of oxide. After addition of the oxide the reaction mixture was refluxed for a short time. A crude yield of 6.1 g. or 35% of the theoretical of alcohol identified as 3-methyl-2-butanol was obtained.

Diethylmagnesium, in 1 liter of ether (0.62 mole), was prepared from ethylmagnesium bromide by filtering off the dioxane precipitate. The oxide (0.62 mole) was added and the solution concentrated by distillation to 200 cc. of clear solution. On hydrolysis it gave a 50 g. or 79% yield of alcohol, b. p. 132–34°. In a similar experiment in which part of the alcohol was dehydrated during distillation, the alcohol was identified as 3-methyl-2-pentanol.

The Reaction of 2,3-Epoxybutane with the Grignard Reagents.—In each of the four experiments reported in Table I the ratio of Grignard reagent to solution was approximately 1 mole to 300 cc. The amount of the reagent

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[23] Thayer, Marvel and Hiers, *Organic Syntheses*, **6**, 12–14 (1926).

[24] Fourneau and Puyal, *Bull. soc. chim.*, [4] **31**, 427 (1922); Likhosherstov and Alekseev, *C. A.*, **28**, 3054 (1934).

[25] Drake and Cooke, *Organic Syntheses*, **12**, 48–50 (1932).

[26] Neuberg and Kansky, *Biochem. Z.*, **20**, 448 (1909).

[27] Zelinsky, *Chem. Zentr.*, **74**, **II**, 277 (1903).

[28] Gilman and Schulze, THIS JOURNAL, **49**, 2329 (1927).

was determined by the titration method of Gilman and coworkers.[29] The oxide was added drop by drop to the reagent cooled in ice and the mixture allowed to come to room temperature. On warming up to room temperature a reaction set in which refluxed the ether violently for about an hour in each case. With the exception of the methylmagnesium bromide experiment, which stood overnight, the reaction mixtures were hydrolyzed at the end of this spontaneous reaction and worked up as described under the 3-bromo-2-butanol experiment.

The results were obtained with the following quantities of oxide and Grignard reagent: no. 1, 0.68 mole; no. 2, 0.30 mole; no. 3, 0.86 mole; no. 4, 1.0 mole. The yields of tertiary alcohol in expts. 2 and 3 were calculated on the basis of the product boiling at 121–122°. In expt. 2, the secondary alcohol boiled at 132–140°. The yields of secondary and tertiary alcohol in expts. 1 and 4 were determined from the refractive indices of the alcohol mixtures which were previously separated by distillation from low and high boiling substances. These mixtures then were fractionated until sufficient quantities of pure alcohols were obtained for the formation of a sharp melting α-naphthyl or phenylurethan. These derivatives were identified further by mixed melting point determinations with authentic samples. Experiment 3 produced 1 g. boiling at 131–140°, which gave an α-naphthylurethan melting at 56–66° after many recrystallizations. The experience with this material was similar to that recorded in the 3-bromo-2-butanol experiment for synthetic mixtures of the two possible alcohols. Experiment 3 also produced a residue of 4 g., the investigation of which is reported below.

The Reaction of 2,3-Epoxybutane with a Dioxane Precipitate from Ethylmagnesium Bromide.—The dioxane precipitate from a diethylmagnesium preparation by calculation contained 0.80 mole of active ethylmagnesium bromide. Enough ether was added to facilitate stirring and 0.80 mole of oxide added. At the end of nine to ten hours of refluxing the reaction mixture gave a negative Gilman and Schulze[30] test for R–Mg bond. The hydrolysis product was treated in the same manner as that in the 3-bromo-2-butanol experiment. Fractionation showed 0.6 g. boiling at 110–120°, 0.3 g. at 120–125°, 1.6 g. at 125–130° and 7.6 g. at 130–135°. The first two and last fractions gave sharp-melting α-naphthylurethans of 3-methyl-2-pentanol. The yield of alcohol based on the fractions boiling from 125–135° was 11% of the theoretical.

The Reaction of 2-Butanone with Diethylmagnesium.—2-Butanone (0.46 mole) was added to 0.195 mole of diethylmagnesium in 300 cc. of ether. The reaction mixture set to a gelatinous mass after standing overnight. At this time it gave a positive Gilman and Schulze color test. It was hydrolyzed and treated in the usual manner and 7.9 g. or a yield of 8% of 3-methyl-3-pentanol, b. p. 118–124°, and some unreacted ketone were obtained. There also was obtained 10.1 g. of some higher boiling material the investigation of which is reported below.

Examination of the Residues.—The major portion of the residues collected from the 3-bromo-2-butanol, ethylmagnesium iodide and diethylmagnesium experiments distilled at 155–165°. All three of these small fractions gave a test for unsaturation with potassium permanganate, evolved hydrogen bromide when treated with bromine in carbon tetrachloride and gave a small yield of crystals when treated with an excess of semicarbazide solution. After thorough washing with water, alcohol and chloroform, in all of which they were quite insoluble, they melted with decomposition at 250.5–251.5°, corr. The melting point varied with the rate of heating.

2-Butanone was treated with ethoxymagnesium bromide and the product, b. p. 170–173°, gave a good yield of crystals with semicarbazide solution which melted at the same temperature. This appears to be a new derivative of a 2-butanone condensation product.[31]

Anal. Calcd. for $C_9H_{17}N_3O$: N, 22.95. Found: N, 22.79, 22.76.

Mixtures of the latter with the crystals from the three residues mentioned above did not cause a change in melting point behavior.

Summary

1. The reaction of 3-bromo-2-butanol with ethylmagnesium bromide produced only the tertiary alcohol.

2. In complete agreement with the prediction of Berry and Bartlett, secondary alcohols were obtained from the reaction of 2,3-epoxybutane with diethylmagnesium and dimethylmagnesium.

3. The reaction of 2,3-epoxybutane with ethylmagnesium chloride and bromide and methylmagnesium bromide produced both secondary and tertiary alcohols. Henry obtained only the tertiary alcohol in the latter case.

4. The formation of tertiary alcohols in the Grignard reactions is interpreted as the result of a rearrangement of the halohydrin derivatives, *i. e.*, the Blaise intermediate, formed from the reaction of the magnesium halide bond with the oxide.

5. 2,3-Epoxybutane and magnesium bromide in ether and benzene solution produced 2-butanone. The same ketone was isolated in the reaction of 3-bromo-2-butanol with ethylmagnesium bromide.

6. 3-Bromo-2-butanol and 2,3-epoxybutane gave appreciable yields of alcohols when treated with Grignard reagents without the application of heat.

7. The reaction of 2,3-epoxybutane with ethylmagnesium iodide, of 2-butanone with diethylmagnesium and of 3-bromo-2-butanol with ethylmagnesium bromide produced, in addition to 3-methyl-3-pentanol, condensation products of 2-butanone.

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[29] Gilman, Wilkinsno, Fishel, and Meyers THIS JOURNAL, **45**, 156 (1923).

[30] Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

[31] Colonge, *Bull. soc. chim.*, [4] **49**, 432 (1931). This paper summarizes the data on semicarbazones of the octenones from 2-butanone. All of the semicarbazones listed melt below the melting point of our derivative.

8. 3-Methyl-2-pentanol was the only alcohol obtained from the reaction of 2,3-epoxybutane with a dioxane precipitate from ethylmagnesium bromide.

9. Some new urethans of 3-methyl-2-pentanol, 3-methyl-3-pentanol and 3-methyl-2-butanol were described.

NEW BRUNSWICK, N. J. RECEIVED AUGUST 25, 1936

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Isolation of 1,2-Diketones from the Ozonization of Disubstituted Acetylenes

BY THOMAS L. JACOBS

In a recent paper, Hurd and Christ[1] have discussed the course of the ozonization of acetylenes. They formulate the reaction as proceeding through a 1,2-diketone which is assumed to be oxidized by the hydrogen peroxide produced from the decomposition of the ozonide. From the six acetylenes ozonized, they isolated only acids in yields of 42–61%. The isolation of glyoxal in 81% yield from the ozonization of acetylene[2] is the only instance in which a 1,2-dicarbonyl compound actually has been obtained.

I have ozonized diphenylacetylene and benzylphenylacetylene[3] under carefully controlled conditions, and have isolated benzil and benzylphenyl diketone. At −78° the action of ozone on diphenylacetylene produced an unstable ozonide which decomposed to a black tar shortly after the solvent was removed. When the ozonization was carried out in petroleum ether at 5–15°, the product was a yellow oil which on hydrolysis gave benzoic acid in 65% and benzil in 5% yield. The unstable ozonide apparently produced the same yellow oil as an intermediate when treated with water. When benzylphenylacetylene ozonide, prepared at −30 to −40°, was decomposed with water, the sole products were a mixture of acids and tar. From the acid mixture were isolated benzoic acid in 60% and phenylacetic acid in 10% of the theoretical yield.

$$C_6H_5C{\equiv}CCH_2C_6H_5 \xrightarrow[H_2O]{O_3} C_6H_5COOH + C_6H_5CH_2COOH$$

When the product of ozonization was decomposed with neutral potassium iodide solution, benzylphenyl diketone was isolated in 25% yield. In addition, a small amount of acidic material and much tar were obtained. One attempt was also made to decompose the ozonide by distillation under reduced pressure. A mixture of acid and neutral material resulted, from which a low yield of a mixture of acids was obtained. The neutral portion was accidentally lost.

Ozone was never absorbed completely by any of the acetylenes investigated. The rate of absorption was nearly constant until one mole of ozone had been taken up for each mole of acetylene treated, and then began to fall off rapidly. In one experiment in which the ozonization was continued beyond this point, the initial absorption was 83% and dropped to 25%, but decreased only slowly from this point. The residual absorption probably represents attack of the benzene rings.

The isolation of 1,2-diketones does not prove that such compounds are always intermediates in the production of acids by the ozonization of acetylenes, but the brilliant yellow color of the oil which appears during the preparation or decomposition of the ozonides does suggest that this is the case. In this connection it should be noted that benzil is not attacked by ozone under the conditions of the experiments. The detailed mechanism postulated for the reaction by Hurd and Christ[1] assumes the formation of only monomolecular species, and this appears subject to some question. The amorphous character of the unstable product of ozonization at low temperatures indicates that it is probably polymeric.

An extension of the investigation has been temporarily interrupted, and a report of experiments already completed is made at this time in consideration of the publication of Hurd and Christ.[1]

Experimental

An ozonizer of the Henne[4] type yielding 6.5 to 8% of ozone when oxygen was supplied at 18 to 14 liters per hour was used. Ozone concentrations were determined by the

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(1) Hurd and Christ, *J. Org. Chem.*, **1**, 141 (1936).

(2) Briner and Wunenburger, *Helv. Chim. Acta*, **12**, 786 (1929).

(3) The synthesis, properties and reactions of this compound and related acetylenes will be described in a paper by Johnson, Schwartz and Jacobs. See also Schwartz, Cornell Thesis, 1931; Jacobs, Cornell Thesis, 1935.

(4) Henne, THIS JOURNAL, **51**, 2676 (1929).

potassium iodide method of Smith.[5] The amount of ozone used was easily found by successive determinations on the oxygen stream first as it came from the ozonizer and second after it had passed through the solution of the acetylene. Dry oxygen was used. In experiments below 0°, the stream of ozonized oxygen was passed through a glass coil immersed in solid carbon dioxide–acetone before entering the reaction flask.

The Ozonization of Diphenylacetylene

Diphenylacetylene was prepared from benzil by the method of Schlenk, Bergmann and Rodloff[6] or by the action of alcoholic potassium hydroxide on stilbene dibromide.

The Isolation of Benzil.—A solution of 35.6 g. (0.2 mole) of diphenylacetylene in 350 cc. of purified petroleum ether was ozonized at 5–15°. The solvent was attacked almost as rapidly as the compound, but impurities thus introduced were volatile with steam. The ozonized solution, which contained a heavy, yellow, insoluble oil, was steam distilled, and the residue extracted with hot water. The oil remaining was dissolved in ether and extracted with 2% sodium hydroxide. The total benzoic acid obtained was 31.9 g. (65.5% yield). The ether solution gave 8.4 g. of neutral material from which 2.3 g. (5.5% yield) of benzil was obtained, m. p. 94–95°, mixed m. p. the same. The quinoxaline derivative was prepared, m. p. and mixed m. p. 124.5–125°. The residual neutral material was a mixture from which a very little more benzil was obtained by distillation.

Ozonization at −78°.—A solution of 5.2 g. of diphenylacetylene in 100 g. of methyl chloride was ozonized at −78°. The resulting mixture was opaque, and contained an amorphous white precipitate. The solvent was allowed to evaporate and the product was a pasty, yellowish, almost odorless mass, which after remaining at room temperature for about fifteen minutes decomposed suddenly with a considerable heat effect and the evolution of acrid white fumes. Benzoic acid was isolated in poor yield from the black tar remaining. The unstable ozonide was found to ignite with a puff and much liberation of carbon when heated on a platinum foil; it liberated iodine from neutral potassium iodide solution, reacted violently with concentrated sulfuric acid, and on heating in water was converted into a brilliant yellow oil, apparently the same as that obtained directly by ozonization at the higher temperature.

The Ozonization of Benzylphenylacetylene

All experiments with this compound were carried out in purified ethyl chloride at −30 to −40°.

Decomposition of the Ozonide with Potassium Iodide.—By ozonization of 5 g. (0.027 mole) of benzylphenylacetylene and evaporation of the solvent was obtained 5 cc. of a yellow oil containing considerable solid material. This product was decomposed by standing for fifteen hours with dilute, slightly acid potassium iodide solution; titration with thiosulfate (19.2 cc. of 0.4177 *N* required) gave the iodine liberated as 0.004 mole, equivalent to about one-seventh of the acetylene taken. The solution was extracted with ether and this extract washed with water and 10% sodium carbonate solution and dried over anhydrous potassium carbonate. Distillation gave 1.5 g. of a yellow oil, b. p. 161° (4 mm.). The product gave a quinoxaline derivative, m. p. 97–98°. Kohler and Barnes[7] report the boiling point of benzylphenyl diketone as 175° (8 mm.), and the melting point of the quinoxaline derivative as 97–98°. A mixed melting point of the quinoxaline derivative with that prepared by Kohler and Barnes showed no depression.

Decomposition of the Ozonide with Water.—The material from the ozonization of 19.2 g. (0.1 mole) of benzylphenylacetylene was extracted several times with hot water. Impure benzoic acid resulted on cooling and the acid was purified by crystallization from water. All aqueous residues were then extracted with ether in a continuous extractor for two hours. A total of 3.13 g. of mixed acids resulted; in order to effect a separation, the mixture was esterified in ether with diazomethane, and the mixture of esters distilled through a small, simplified Podbielniak-type column[8] (35 cm. long, 3 mm. internal diameter, containing a spiral of No. 28 platinum wire). This gave 0.94 g. of methyl benzoate, b. p. 72–73° (8 mm.), and 1.57 g. of methyl phenylacetate, b. p. 90–90.5° (8 mm.). Known methyl phenylacetate distilled through the same column at 89–90° (7.5 mm.). The recovery of pure, separated esters from the mixture of acids was 90%. The methyl phenylacetate from the ozonization had a refractive index of $n^{16}\text{D}$ 1.5102, compared with $n^{16}\text{D}$ 1.5100 for the sample prepared by standard methods (lit., $n^{16}\text{D}$ 1.5091). Both of these samples were converted to phenylacetamide by reaction with concentrated ammonium hydroxide. The melting point and mixed melting point was 159–160°. The total benzoic acid (including methyl benzoate) isolated from this ozonization was 7.3 g. (0.06 mole), a yield of 60%, assuming complete conversion of the acetylene to one mole of each acid. The phenylacetic acid recovered amounted to 0.01 mole (10% yield). The oily residue from the water extraction was not further examined.

Summary

From the decomposition of the products of ozonization of diphenylacetylene and benzylphenylacetylene, the corresponding 1,2-diketones have been isolated, as well as the expected acids.

HARVARD CHEMICAL LABORATORY
CAMBRIDGE, MASS.
RECEIVED AUGUST 18, 1936

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[5] Smith, THIS JOURNAL, **47**, 1844 (1925).

[6] Schlenk, Bergmann and Rodloff, *Ann.*, **463**, 76 (1928).

[7] Kohler and Barnes, THIS JOURNAL, **56**, 211 (1934).

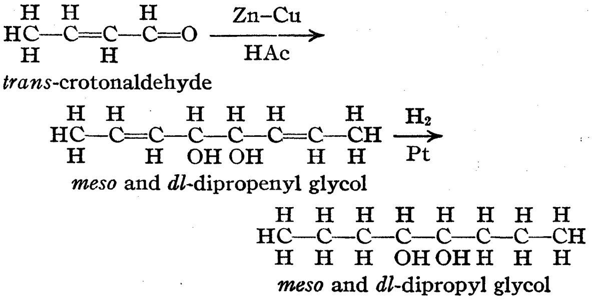
[8] Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931); **5**, 119 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Investigations on the Stereoisomerism of Unsaturated Compounds. II. The Composition of Dipropenyl Glycol[1]

BY WILLIAM G. YOUNG, LEO LEVANAS AND ZENE JASAITIS

In continuing the study of methods of synthesis of pure isomers of the aliphatic polyene hydrocarbons of known configuration[2] it was important to know the composition of dipropenyl glycol. Since Kuhn and Rebel[3] reported that only one of the expected isomeric glycols was formed during the pinacolic reduction of aldehydes, we would expect that the reduction of *trans*-crotonaldehyde would produce only *dl*, *trans-trans*-dipropenyl glycol. However, if this were the case it would be difficult to explain the formation of two tetrabromides[4] or of two dimethylhexatrienes[5] from dipropenyl glycol. Since Kuhn and Rebel's method of oxidizing the dipropenyl glycol to racemic tartaric acid (by several steps) resulted in poor yields, they were not justified in concluding that only one stereoisomeric form was present in the original glycol. Accordingly, we reinvestigated the composition of dipropenyl glycol prepared by the pinacolic reduction of crotonaldehyde and reported[6] the formation and isolation of both *meso* and *dl*-dipropyl glycols from the catalytic reduction of dipropenyl glycol. The reactions involved were as follows



$$\underset{\text{H}}{\overset{\text{H}}{\text{HC}}}-\overset{\text{H}}{\text{C}}=\underset{\text{H}}{\text{C}}-\overset{\text{H}}{\text{C}}=\text{O}\xrightarrow[\text{HAc}]{\text{Zn–Cu}}$$

trans-crotonaldehyde

$$\underset{\text{H}}{\overset{\text{H}}{\text{HC}}}-\overset{\text{H}}{\text{C}}=\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{OH}}{\overset{\text{H}}{\text{C}}}-\underset{\text{OH}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\text{C}}=\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\text{CH}\xrightarrow[\text{Pt}]{\text{H}_2}$$

meso and *dl*-dipropenyl glycol

$$\underset{\text{H}}{\overset{\text{H}}{\text{HC}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{OH}}{\overset{\text{H}}{\text{C}}}-\underset{\text{OH}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\text{CH}$$

meso and *dl*-dipropyl glycol

Contrary to the opinion expressed by Kuhn and Rebel,[3] several other investigators have clearly demonstrated that both *meso* and *dl* forms are produced by the pinacolic reduction of aldehydes. The duality of divinyl glycol has been established by separation into the *meso* and *dl* forms,[7] by hydrogenation to *meso* and *dl*-diethyl glycols[8] and by conversion into *dl*-mannitol[9] and allodulcitol.[10] The duality of dipropenyl glycol has also been conclusively established since our oral report[6] was made. Wiemann[11] treated the glycol with phenyl isocyanate and isolated a solid phenylurethan from which he recovered on hydrolysis *meso*-dipropenyl glycol, m. p. 48°. By catalytic reduction[12] of his dipropenyl glycol he obtained both the solid *meso*- and the liquid *dl*-dipropyl glycols which had been prepared from butyroin by Bouveault and Locquin[13] and identified by Veibel.[14]

Although the above-mentioned workers have established the fact that the pinacolic reduction of aldehydes gives both *meso*- and *dl*-glycols, they have not answered the important question which originally prompted the work on this subject. Kuhn and Rebel[3] had suggested that, from purely geometrical grounds, in such reactions there should be formed 25% each of the *d*- and *l*- and 50% of the *meso*-glycol. It is the purpose of this paper to show that in the case of the pinacolic reduction of crotonaldehyde, at least, the *meso*- and *dl*-glycols actually are formed in equal quan-

TABLE I

MELTING POINTS OF BI-3,5-DINITROBENZOATES FROM KNOWN MIXTURES OF DIPROPYL GLYCOLS

% *meso*-dipropyl glycol	M. p., °C. of dinitrobenzoate
0	125 –125.3
3	124.3–126.5
5	124.8–131
7	124.1–135
10	124.2–143
50	123.7–182
100	200.3–200.4
Eutectic	124 –128
Original mixture	123 –181

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(1) This work was started in 1930 by the senior author during the tenure of a National Research Council Fellowship at Stanford University. The authors are indebted to Colorado College for the use of library and stenographic facilities during the preparation of this manuscript.

(2) Young, THIS JOURNAL, **54**, 2498 (1932).

(3) Kuhn and Rebel, *Ber.*, **60B**, 1565 (1927).

(4) Charon, *Ann. chim. phys.*, [7] **17**, 260 (1899).

(5) Urion, *Compt. rend.*, **196**, 353 (1933); *Ann. chim.*, [11] **1**, 5 (1934).

(6) A preliminary report of this work was presented before the Organic Division at the Denver meeting of the American Chemical Society, August, 1932.

(7) Van Romberg and Van Hasselt, *Proc. Acad. Sci. Amsterdam*, **35**, 40 (1932).

(8) Farmer, Laroia, Swift and Thorpe, *J. Chem. Soc.*, 2937 (1927).

(9) Lespieau and Wiemann, *Compt. rend.*, **194**, 1946 (1932).

(10) Lespieau and Wiemann, *ibid.*, **195**, 886 (1932).

(11) Wiemann, *ibid.*, **197**, 1654 (1933).

(12) Wiemann, *ibid.*, **196**, 118 (1933).

(13) Bouveault and Locquin, *ibid.*, **140**, 1699 (1905).

(14) Veibel, *Biochem. Z.*, **239**, 456 (1931).

tities. This has been accomplished by determining the phase relationships existing between the *meso-* and *dl*-dipropyl glycols (Fig. 1) prepared from the dipropenyl glycol and by comparing the melting points of the bi-3,5-dinitrobenzoates prepared from the pure *meso-* and *dl*-dipropyl glycols and from various mixtures of these glycols (Table I). In this work the *dl*-dipropyl glycol, m. p. 28°, was obtained in a pure form for the first time.

Experimental Part

The Preparation of Dipropenyl Glycol.—Several kilograms of dipropenyl glycol were prepared by the reduction of 200-g. portions of *trans*-crotonaldehyde[2] in a dilute solution of acetic acid according to Charon's method.[4] Special care was exercised to prepare an active zinc–copper couple[15] and to keep the temperature of the reaction mixture between −5 and −10° during the reduction. After the reaction mixture was filtered to remove the zinc–copper residue, it was extracted 7–8 times with 250-ml. portions of ether to assure the removal of the constituents which absorb bromine. It was also advantageous to neutralize the ether extract with potassium carbonate before removing the solvent. A fractional distillation of the product through a 90-cm. Claisen-head column filled with glass rings and equipped with a Hopkins condenser gave the two main fractions: crotyl alcohol, b. p. 117–120° (15% of theoretical), and dipropenyl glycol b. p. (9 mm.) 113.4–114.4° (67%). These yields are similar to those reported by Charon[4] but contrary to those reported by Kuhn and Rebel.[3]

Fractional Distillation of Dipropenyl Glycol.—Several distillations of dipropenyl glycol, b. p. (9 mm.) 113.4–114.4°, d^{20}_4 0.9744, through the fractionating column described above, failed to produce any evidence of separation into *meso-* and *dl*-isomers. The failure to separate the isomers by distillation is not surprising, since Van Romberg and Van Hasselt[7] have shown that in the case of the closely related *meso-* and *dl*-divinyl glycols the isomers possess the same boiling point.

Catalytic Hydrogenation of Dipropenyl Glycol and the Isolation of *meso-* and *dl*-Dipropyl Glycols.—Freshly distilled dipropenyl glycol (72 g.) was reduced with the aid of a platinum catalyst[16] in 200 ml. of 95% ethanol. The solvent was removed through a Hempel column and the mushy residue, m. p. 20–90°, was filtered. The solid portion after recrystallization from petroleum ether was found to be *meso*-dipropyl glycol, m. p. 123.5–124.5°.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.69; H, 12.42. Found: C, 65.67; H, 12.41.

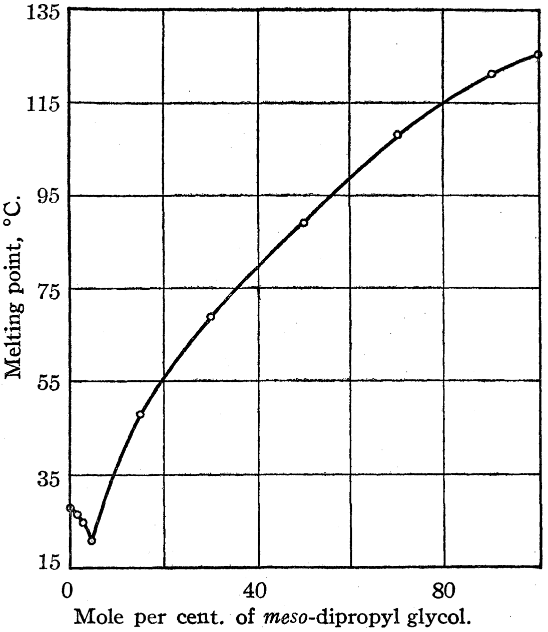

Fig. 1.—The melting point diagram of the system *meso-dl*-dipropyl glycols.

The filtrate was then fractionally distilled several times through the column described above. A fraction (1), b. p. (9.5 mm.) 110–111°, was obtained which was thought to be the pure *dl*-isomer. When a cooling curve was made the liquid supercooled easily due to its high viscosity but when seeded it solidified at 20.0–20.5°. The temperature remained constant for several hours when the bath temperature was held slightly above or below 20°, the only difference being in the quantity of crystals present in the mixture. However, when some of this fraction was converted into the bi-3,5-dinitrobenzoate, the product melted over a range indicating that the glycol fraction might not be a pure product, as suggested by the melting point. Consequently, a cooling curve was made using another fraction (3) which had some solid *meso*-glycol present even at 43°. As the mixture was cooled the quantity of solid increased until the temperature reached 15°. At this point a sudden evolution of heat occurred, the temperature rose to 20.0–20.5°, and the mixture solidified completely. The most likely explanation of this result is that 20.0–20.5° is the eutectic temperature for the system *dl-* and *meso*-dipropyl glycol. The *dl*-component failed to form when the eutectic temperature was reached, causing a metastable condition to exist, but as soon as some of the *dl*-component was formed an equilibrium was established immediately at the eutectic temperature. Fraction 1 was therefore subjected to several more fractional distillations until the main fraction had the same melting point after two consecutive distillations. This fraction was *dl*-dipropyl glycol, b. p. (9 mm.) 109.8–110°, m. p. 28°.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.67; H, 12.42. Found: C, 65.59; H, 12.43; $n^{24.5}_D$ 1.4419.

In a series of experiments the yield of *meso*-glycol was approximately 95% of that expected if the dipropenyl glycol contained equal quantities of *meso-* and *dl*-forms. The

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(15) The zinc–copper couple was prepared by the method of Gladstone and Tribe, *J. Chem. Soc.*, **31**, 561 (1877), except that the copper sulfate solution was added to 80-mesh zinc in smaller portions and the reaction mixture was allowed to become decolorized completely before another portion was added. Although the yields of glycol decreased 10–15% if the sulfate solution were added in too large portions, nevertheless, we never obtained yields as low as those reported by Kuhn and Rebel.[3]

(16) Adams, Voorhees and Shriner, "Organic Syntheses," John Wiley and Sons, Inc., New York City, Vol. VIII, 1928, p. 92.

yield of *dl*-isomer was about 10% lower than the *meso*-form due to unavoidable losses during the many fractionations.

Analysis of Mixtures of the Dipropyl Glycols by Conversion into 3,5-Dinitrobenzoates.—In order to follow the degree of separation of the dipropyl glycols during the fractional distillation of large batches of material, it was desirable to have a convenient method of analysis. The preparation of the bi-3,5-dinitrobenzoates proved satisfactory for this purpose. It was found that 3,5-dinitrobenzoic acid, its acid chloride and the mono-ester of the glycols were all fairly soluble in a mixture of alcohol and nitrobenzene, while the di-esters of both glycols were insoluble. It was therefore possible to recrystallize the di-esters made from glycol mixtures without changing their composition. The crude esters were prepared from 0.3 g. of the glycol, 6 ml. of dry pyridine, and 1.2 g. of 3,5-dinitrobenzoyl chloride in the usual manner. The crude product thus obtained was dissolved in 4–5 ml. of warm nitrobenzene and then 40–50 ml. of alcohol was very slowly added to ensure the formation of crystals instead of oil. The product was finally filtered, washed with cold alcohol and dried in a vacuum desiccator; yield, 90–95% of theoretical based on the di-ester. Bi-3,5-dinitrobenzoate from *meso*-dipropyl glycol, m. p. 200.3–200.4°.

Anal. Calcd. for $C_{22}H_{22}O_{12}N_4$: C, 49.42; H, 4.15; N, 10.49; mol. wt., 530. Found: C, 49.40; H, 4.10; N, 10.69; mol. wt., 540 (in nitrobenzene). Bi-3,5-dinitrobenzoate from *dl*-dipropyl glycol, m. p. 125–125.3°. *Anal.* Found: C, 49.58; H, 4.21; N, 10.59; mol. wt. 538 (in nitrobenzene). The melting points of esters made from known mixtures and from the original mixture of dipropyl glycols are given in Table I. It will be seen that the eutectic mixture contains about 4.5% *meso*-glycol and the original mixture 50% *meso*-glycol.

The Melting Point Diagram for the System *meso-dl*-Dipropyl Glycol.—In view of the fact that distillation methods did not give a satisfactory estimate of the composition of the dipropyl glycol mixture obtained from the catalytic reduction of dipropenyl glycol, it was necessary to construct a melting point diagram for the system *meso-dl*-dipropyl glycol. The eutectic temperature for mixtures of *meso* and *dl*-dipropyl glycols was determined by the Beckmann method on ten different mixtures of glycols. The average value for these runs was 20.7 ± 0.5°. Due to the extreme viscosity of the glycol mixtures and since the Beckmann method is subject to more or less error,[17] the remaining data were obtained by the melting point method. Known mixtures of *dl*- and *meso*-dipropyl glycols were sealed in small tubes which were heated slowly in a water-bath under constant agitation. The temperature at which the last particle of solid disappeared was recorded as the melting point. The temperature of the bath was raised slowly (never faster than 1° in five to ten minutes) and all melting points were duplicated with at least two different tubes. In all mixtures richer in *meso* than the eutectic, the solid phase in equilibrium with the liquid was found to be the *meso*-isomer. The results are recorded in Fig. 1. The composition of the eutectic mixture was found to be about 5% *meso*- and 95% *dl*-dipropyl glycol. The composition of the crude glycol mixture obtained from the reduction of dipropenyl glycol proved to be 50% *meso* and 50% *dl* since the final melting point of this mixture was 90°. It may therefore be concluded that the pinacolic reduction of crotonaldehyde gives equal quantities of *meso*- and *dl*-dipropenyl glycol.

The authors are indebted to Mr. Harold Milner, of the Division of Plant Biology of the Carnegie Institution of Washington, for the micro-analysis of *meso*-dipropyl glycol and to Drs. G. Ross Robertson and J. B. Ramsey for their helpful suggestions.

Summary

Dipropenyl glycol obtained from the pinacolic reduction of crotonaldehyde has been found to contain equal quantities of the *meso*- and *dl*-glycols.

Pure *dl*-dipropyl glycol and the bi-3,5-dinitrobenzoates of both *meso*- and *dl*-dipropyl glycols have been prepared for the first time.

The melting point diagram of the system *meso-dl*-dipropyl glycol is given.

LOS ANGELES, CALIF. RECEIVED JULY 13, 1936

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[17] Skau and Rowe, THIS JOURNAL, **57**, 2437 (1935).

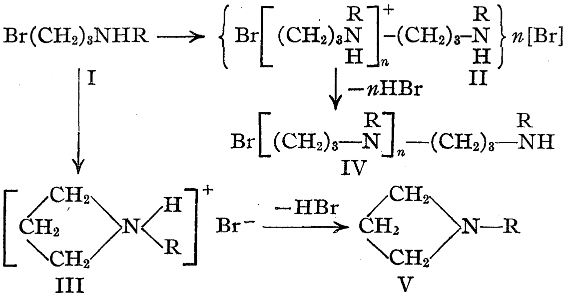
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Ammonium Salts from Bromopropylamines. VI. Salts of Polymeric Tertiary Amines[1]

BY JOHN CHARLES COWAN AND C. S. MARVEL

Previous work in this Laboratory has shown that halogenated tertiary amines of the type $Br(CH_2)_nNR_2$ undergo self-condensation intermolecularly or intramolecularly to give polymeric or cyclic quaternary ammonium salts, depending on the numerical value of n and the nature of the R group. The work described in this communication was undertaken in order to learn whether linear polymeric or cyclic tertiary amines would be obtained by a similar self-condensation of halogenated secondary amines.

It should be noted that halogenated secondary amines may be expected to give far more complex products than were obtained from related halogenated tertiary amines. For, whereas the latter give stable quaternary ammonium salts, the former give tertiary amine salts which may react further with unchanged bromoamine. On the basis of our earlier work, bromopropylalkylamines (I) would be expected to condense intermolecularly to give long-chain polymeric compounds (II), or with certain R groups to form monomeric cyclic salts (III) containing a four-membered ring. In the presence of an excess of the bromoalkylamine, these products might be expected to undergo double decomposition reactions to yield the hydrobromide salt of the simple bromoamine and the free polymeric (IV) or cyclic (V) tertiary amine, which then would react further with the bromoalkylamine to give quaternary ammonium salts of very complex type.



Our experiments have shown that when a free bromoalkylamine of type I in which R is methyl, ethyl, n-propyl, n-butyl or isobutyl is allowed to stand at room temperature in concentrated solution, the polymerization reaction occurs fairly smoothly, and is accompanied by few side reactions. However, in dilute solution, the products become very complex, due to the occurrence of secondary reactions, the exact nature of which has not as yet been elucidated. This observation is in accordance with the views which Salomon[2] has recently expressed in connection with rates of reactions of primary amines containing a haloalkyl group.

The polymers which are formed by the intermolecular condensation reactions vary greatly in size, depending on the size of the R group. In Table I are given the calculated values for the number of monomeric units in and the molecular weights of the various polymeric tertiary amine salts which have been prepared. The values for the number of monomeric units ($n + 1$) in the polymers were calculated from the formula

$$\frac{n}{n+1} = \frac{\%\text{ ionic halogen}}{\%\text{ total halogen}}.$$

Since in a few cases the percentage of total halogen which we found in a polymer was lower than the theoretical value, we have used the theoretical value for total halogen in our calculations. It seems probable that any loss of halogen must be from the alkyl halide end-group, and not from the ionic fraction of the halogen.

TABLE I

MOLECULAR WEIGHTS OF POLYMERIC TERTIARY AMINE SALTS

$Br\{[(CH_2)_3NRH]_n{}^+(CH_2)_3NHR\}n[Br]^-$

R	$n + 1$	Approximate mol. wt.
CH_3	71–100	10800–15200
C_2H_5	22–23	3650–3820
n-C_3H_7	16–17	2880–3060
n-C_4H_9	20–21	3900–4100
i-C_4H_9	7–8	1350–1550

The polymeric salt from bromopropylmethylamine was treated with silver oxide to give the free base, which proved to be a viscous, semisolid, hygroscopic material. In 0.1 N solution, it gave a pH of approximately 9.3, indicating that it is a tertiary amine, and that it does not contain quaternary ammonium groups.

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[1] For the fifth paper in this series, see THIS JOURNAL, **57**, 1137 (1935).

[2] Salomon, *Helv. Chim. Acta*, **17**, 851 (1934); *Trans. Faraday Soc.*, **32**, 153 (1936).

TABLE II

γ-PHENOXYPROPYLALKYLAMINES

$C_6H_5OCH_2CH_2CH_2NHR$

R =	Yield of amine, %	B. p., °C.	B. p., Mm.	n^{20}_D	d^{20}_4	M. p. of hydrobromide, °C.	Br analyses, % Calcd.	Br analyses, % Found
CH_3	60.5	133–138	23	1.5255	1.002	150–151	17.60[a]	17.65[a]
C_2H_5	66	147–148	26	1.5127	0.981	154–155	30.77	30.71
n-C_3H_7	66	154–155	25	1.5098	.971	160–161	29.20	29.27
n-C_4H_9	56.5	134–135	5	1.5060	.958	170–171	27.78	27.83
i-C_4H_9	79.8	153–156	20	1.5038	.955	174–175	27.78	27.65

[a] Chlorine in the hydrochloride was determined in this case. The hydrochloride melted at 155–156°.

The bromoalkylamines were prepared from phenoxypropylalkylamines by cleavage with hydrobromic acid by the general methods which have been described previously[3] for related compounds.

Experimental Part

γ-Phenoxypropylalkylamines.—The phenoxypropylamines were prepared by adding four times the theoretical amount of an alcoholic solution of the appropriate primary amine to γ-phenoxypropyl bromide and allowing the solution to stand for about twenty-four hours until reaction was complete. The alcohol and excess amine were removed by distillation from a steam-bath, and the residue was treated with a 25% aqueous solution of sodium hydroxide. The phenoxypropylamine was collected in ether, the ether removed and the amine distilled under reduced pressure. For analysis, the amines were converted to the hydrobromides, and ionic halogen was determined by direct titration with silver nitrate. The amines thus prepared are described in Table II.

γ-Bromopropylalkylamine Hydrobromides.—The γ-phenoxypropylamines were cleaved with hot 48% hydrobromic acid solution by the procedure used in previous work.[3] The best results were obtained when these cleavage reactions were carried out in an oil-bath held at 137–142°. The distillate was tested with bromine water from time to time, and when no phenol was distilling, the reaction was complete. The reaction mixture was diluted with water and evaporated under reduced pressure. The residue was again dissolved in water and evaporated under reduced pressure to remove the excess hydrogen bromide. If the distillate at this point was not neutral to methyl orange, this process was repeated. The dry residue, free from excess hydrogen bromide, was dissolved in absolute alcohol (dried with magnesium methylate[4]) and treated with Norite until the filtered solution was pale amber or yellow. After removal of the Norite, a part of the alcohol was distilled off under reduced pressure and a large excess of dry ether was added to the remaining solution. In some cases, the bromoamine hydrobromides precipitated at once; in other cases, the salts came out on standing. For analysis the salts were recrystallized by taking up in alcohol and precipitating with ether until no change in melting point was observed on repeating the purification. Less highly purified salts were used for conversion into polymers. The properties of the bromoamine hydrobromides are listed in Table III.

TABLE III

γ-BROMOPROPYLALKYLAMINE HYDROBROMIDES

$[BrCH_2CH_2CH_2NH_2R]^+Br^-$

R =	M. p., °C.	Analysis Ionic Bromine, % Calcd.	Analysis Ionic Bromine, % Found
CH_3	64–66	34.33	34.25
C_2H_5	144–146	32.38	31.77
n-C_3H_7	225–226	30.65	30.65
n-C_4H_9	253–255[a]	29.09	29.15
i-C_4H_9	255–257[a]	29.09	29.59

[a] Bloc Maquenne.

Polymeric Tertiary Amine Salts.—Each of the free γ-bromopropylalkylamines in which the alkyl group was methyl, ethyl and n-propyl, respectively, was obtained by treating the crude hydrobromide with 50% sodium hydroxide solution and then distilling the free bromoamine from the reaction mixture under reduced pressure. The amines thus obtained contained some water, and they were allowed to polymerize without drying. The n-butyl and isobutyl derivatives polymerized very rapidly at the temperatures at which they distilled. Hence, in these cases the free amines were obtained by treating the salts with 25% sodium hydroxide solution at about 0°, and then extracting the amine with ether. About 15 cc. of 95% alcohol was added to the ether extract and then the solution was evaporated to 10–15 cc. Titration indicated that this gave 1.5–2 molal solutions of the bromoamine. On standing for two or three days, these bromoamines polymerized.

All of the polymeric amine salts were colorless to light amber, sticky, hygroscopic solids. The experiments are summarized in Table IV.

In dilute solution the products of polymerization were complex, and the nature of the physical properties precluded the possibility of crystallizing and separating the substances which were formed. A solution of 5 g. of γ-bromopropylethylamine was treated with an excess of cold (0°) 25% sodium hydroxide solution, and the free amine was taken up in ether and diluted to 145 cc. Titration with standard acid showed that this ether solution was 0.14 molar. This dilute solution was allowed to stand for three days at room temperature. Then the ether was removed and the residue dried over phosphorus pentoxide at 100° under reduced pressure. This crude mixture contained 51.66% bromine, but the bromide ion was only 45.45%. When this product was taken up in absolute alcohol and

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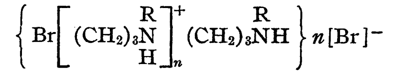
(3) Littmann and Marvel, THIS JOURNAL, **52**, 287 (1930).

(4) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, New York, 1932, p. 244.

TABLE IV

POLYMERIC SALTS FROM γ-BROMOPROPYLALKYLAMINES



$$\left\{ Br\left[(CH_2)_3\overset{R}{\underset{H}{N}}\right]^+_n (CH_2)_3\overset{R}{N}H \right\} n[Br]^-$$

R =	Amine salt, g.	B. p., Bromoamine, °C.	Mm.	Yield, amine, g.	M. p. of polymers, °C.	Formula	Calcd. total	Analyses, Br % Found Total	Ionic
CH_3	10	29–30	4	2.5	205–210 dec.	$(C_4H_{10}NBr)_n$	52.63	52.56	51.89–52.10
C_2H_5	10	31–32	2	7.0	195–199	$(C_5H_{12}NBr)_n$	48.19	47.00	46.04
n-C_3H_7	8	37–38	3	1	.....	$(C_6H_{14}NBr)_n$	44.44	43.31	41.74
n-C_4H_9	5.2	...	..	3.6	100–120	$(C_6H_{16}NBr)_n$	41.23	41.33	39.16
i-C_4H_9	6.4	...	..	4.4	.....	$(C_7H_{16}NBr)_n$	41.23	41.30	35.23

precipitated with dry ether, the total bromine remained approximately constant at 51.96%, but the bromide ion fell to 43.38%. Further attempts to purify the mixture did not lead to any definite product.

A sample of the free polymeric tertiary amine was prepared from the polymeric salt obtained from γ-bromopropylmethylamine. The salt used in this experiment contained 50.3% bromine, and 49.07% bromide ion. A solution of 5 g. of this salt in water was treated with an excess of silver oxide, and then the solution was filtered. The filtrate was again treated with silver oxide to ensure complete removal of bromide ion. The mixture was centrifuged and the liquid filtered. The water was then removed under reduced pressure at room temperature (about 25°). The residue was an amber-colored, viscous, sticky, hygroscopic solid. This material still contained bromine which would react slowly with alcoholic silver nitrate. The water solution of the free polymer was tested with thymolphthalein, and showed a *p*H of about 9.3. This is slightly less basic than an aqueous solution of trimethylamine, showing that the polymer did not carry quaternary ammonium hydroxide groups. The polymeric amine could not be purified by reprecipitation, and the analysis was not especially significant.

Anal. Calcd. for $(C_4H_{10}N)_x$: N, 19.44. Found: N, 15.98.

Summary

γ-Bromopropylalkylamines in concentrated solution react intermolecularly to produce polymeric tertiary amine salts. The molecular weight of the linear polymeric salt is dependent on the alkyl group attached to the nitrogen atom, being about 10,000–15,200 when R is methyl, and falling to about 1350–1550 when R is isobutyl.

URBANA, ILLINOIS RECEIVED AUGUST 31, 1936

The Extraction of Europium from Monazite Residues and the Preparation of Pure Europium Compounds

BY HERBERT N. MCCOY

The method of separation of europium from other rare earths by reduction with zinc and precipitation as europous sulfate has been described in a preliminary note.[1] An account of further studies of some of the properties of europous salts is given in a later paper.[2]

The extraction of europium has now been carried out on a larger scale so that a more detailed description of the process of refinement can be given. In the earliest experiments, the starting material had been subjected to long-continued fractional crystallization as double magnesium nitrates in the presence of bismuth nitrate. It contained little besides samarium, europium and gadolinium. For this material, reduction in a Jones reductor two or three times repeated sufficed to give a pure product.[1]

When, later, material less rich in europium was used, it was found that modification of the process gave better recoveries of the desired element. Instead of running the rare earth solution through a reductor, it was found more expedient with low grade material to add zinc dust to the solution along with magnesium sulfate. It was also found that the addition of barium chloride as suggested by Selwood[3] for use in the electrolytic separation of europium was helpful in giving increased yields. The subsequent purification of the enriched europium concentrates so obtained was carried out in a large reductor as will be described later.

After europium had been extracted successfully from 12 to 15 lots of material varying in amounts from 20 g. to several kilograms and of varying degrees of richness, the separation of the europium

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[1] McCoy, THIS JOURNAL, **57**, 1756 (1935).

[2] McCoy, *ibid.*, **58**, 1577 (1936).

[3] Selwood, *ibid.*, **57**, 1145 (1935).

content of 386 kg. of rare earth oxalate was undertaken. This material was accumulated during several years as the residue from the technical production of La, Ce, Pr and Nd from Monazite sand from Travancore, India. The large scale operations were carried out in the works of the Lindsay Light and Chemical Co., Chicago.[4]

As the rare earths had been precipitated once as double sodium sulfates, the material doubtless contained but little ytterbium and lutecium, the compounds of which are easily soluble in a solution of sodium sulfate. The material had been freed from all but traces of cerium and thorium. Lanthanum, praseodymium and neodymium had been separated by systematic fractional crystallization of the double magnesium nitrates. The final mother liquors were precipitated with oxalic acid.

The material consisted essentially of the oxalates of Nd, Sa, Eu, Gd, Tb, Dy, Ho, Y and Er, in which the salts of Sa and Gd predominated. The europium oxalate content amounted to about 0.5%. Small amounts of thorium and lead were also present. The material was in the form of a light buff powder.

The 386 kg. of oxalates were boiled in an iron tank, fitted with a stirrer, with 210 kg. of caustic potash and about 1500 liters of water for about an hour, and filtered and washed in an iron suction filter. The hydroxides which resulted were dissolved in hydrochloric acid in a wooden tank to give 1070 liters of chloride solution of density 1.20. The solution settled clear, leaving but a very small residue which was discarded. It was but slightly acid to congo paper.

The chloride solution was reduced in 140-liter portions in a 210-liter stoneware jar, fitted with a cover and stirred vigorously by a 0.25 h. p. motor with stainless steel shaft and propeller.

In making a reduction there was added to the 140 liters of solution, 4 kg. of magnesium sulfate, 0.5 liter of glacial acetic acid and 0.65 kg. of zinc dust. The reduction began at once as was shown by the bleaching of litmus paper. To minimize reoxidation by air, the latter was displaced by a stream of carbon dioxide run into the jar. During the reduction, which required about five hours, a solution of 1 kg. of barium chloride in 20 liters of water was run in slowly. The reaction was judged to be finished when litmus was no longer bleached. The stirring was then stopped and the solution allowed to settle. The residue consisted largely of excess zinc, barium sulfate and europium sulfate, together with considerable rare earths. Usually the solution did not settle clear and had to be filtered. In such case the filter cake was returned to the jar. The reduction and filtration required the working time of one day.

To the whole of the residue left in the jar was added 140 liters of fresh rare-earth chloride solution, together with magnesium sulfate, acetic acid and zinc dust in amounts the same as for the first reduction and the process continuously repeated until, after eight runs, the whole of the solution had been worked up.

The accumulated residue was finally filtered and washed. It was a dark colored mass of high density. The wet cake weighed about 30 kg. It was returned to the jar in which it had been made, and covered with 170 liters of water, 1 kg. of sodium chlorate dissolved in a little water was added, followed by 15 liters of concentrated hydrochloric acid. A vigorous reaction took place as the remaining zinc dust dissolved. At the same time part of the europous sulfate was oxidized and passed into solution. The residue was now pure white. The solution settled clear overnight. The clear solution was drawn off and the rare earths precipitated by adding oxalic acid.[5]

The barium sulfate residue still contained much europous sulfate which was extracted by repeated treatments with hydrochloric acid and sodium chlorate in hot dilute solution. For 140 liters of water 14 liters of concentrated hydrochloric acid and 0.5 kg. of sodium chlorate were used. Each solution after it had settled was drawn off and treated with oxalic acid. A total of five extractions was made and 9 kg. of oxalic acid was used, giving 16 kg. of moist white oxalates.[6]

The oxalates so obtained were converted into hydroxides in a 175-liter glass-lined steam-jacketed kettle where they were boiled with 10 kg. of potassium hydroxide. The washed hydroxides after being dried weighed 7.2 kg. In all the large scale operations only technical grades of chemicals and ordinary water were used.

The dry hydroxides were now shipped to the laboratory for further treatment. They were still quite impure. An analysis[2] showed about 20% of the whole to be europium hydroxide. The remainder consisted of the same rare earths and other impurities as were contained in the original oxalates. The 7.2 kg. of hydroxides was dissolved in 7.5 liters of concentrated c. p. hydrochloric acid, diluted with water. The solution had a density of 1.27. It was filtered from a small residue. The chloride solution contained a small percentage of lead, which had to be removed in order to avoid trouble in the next operation. This was done by stirring with about 100 g. of amalgamated zinc. The europous salt first formed reacts with the lead chloride to give a black colloidal solution of metallic lead.

$$2EuCl_2 + PbCl_2 \longrightarrow 2EuCl_3 + Pb$$

The latter coagulates slowly, but after two days it could be filtered clear by the aid of filter-cel. The filtered solution contained but a trace of lead.

The solution was now ready for reduction. The reductor consisted of a 1-liter percolator holding 3.5 kg. of

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[4] In this plant work I enjoyed the helpful and efficient coöperation of Mr. Mark W. Eichelberger, secretary and superintendent of the Company, to whom I wish to express my warmest thanks. Mr. Sterling Nails also assisted materially.

(5) Zinc can be precipitated as oxalate, but if the solution contains sufficient acid it does not come down nearly as readily as do rare-earth oxalates. By filtering promptly a separation may be made.

(6) The difficulty in extracting the europium is due to the fact that europic sulfate is the least soluble of the rare-earth sulfates [Jackson and Reinacker, *J. Chem. Soc.*, 1687 (1930)] and is much less soluble hot than cold. Hot water was used to facilitate oxidation.

amalgamated, C. P., 10-mesh zinc. The receiving vessel was a 4-liter wide-mouthed bottle. Into it was put a liter of a hot solution containing 400 g. of magnesium sulfate and 50 ml. of 6 *N* sulfuric acid. The exit tube of the reductor (with rubber tubing connector and screw clamp) reached nearly to the bottom of the receiving bottle. The bottle was closed with a cardboard cap having a hole for the tube. In this case no carbon dioxide or barium chloride was used.

It was found that a hot acidulated magnesium sulfate solution gave rise to the β-form of europous sulfate,[2] rather than the α-form. This is desirable as the former is less soluble and much denser than the latter. Two receiving bottles were used alternately.

The charge in a receiver was sufficient for 1.5 liters of rare earth solution of density 1.27. A precipitate of europous sulfate forms as the first drop of reduced solution enters the bottle. The rate of flow of solution is such that 1.5 liters are reduced in about forty minutes. The solution settles clear in about an hour longer. The precipitated europous sulfate is very dense and occupies but a small volume. While the first run is settling another 1.5-liter lot of chloride solution is run through the reductor into the alternate receiver charged with magnesium sulfate solution and sulfuric acid as before. The process was thus continued until the whole solution was converted into europous sulfate.

The accumulated filtrates from the process were saved to be again reworked for the small amount of europium they contained. The reduction of the europium by zinc is probably complete, $2EuCl_3 + Zn \longrightarrow 2EuCl_2 + ZnCl_2$, but apparently a small amount (about 1%) is reoxidized before it reacts to form sulfate. The amount is so small that it scarcely pays to try to prevent the re-oxidation.

The europous sulfate is filtered and the cream of wet sulfate poured into a boiling solution of sodium carbonate and sodium hydroxide. The amount of europous sulfate resulting from one run of 1.5 liters of rare earth solution—about 200 g. of moist filter cake—requires 80 g. of sodium carbonate, 15 g. of sodium hydroxide and 1.5 liters of water. It quickly turns light greenish-yellow when boiled due to change into europous carbonate. After ten minutes of boiling it is washed three times by decantation, filtered and washed free of sulfate with hot water. The carbonate is granular and very dense.

When it is dissolved in hydrochloric acid, a light yellow solution of the europous chloride is formed. Considerable other rare earths, as well as thorium, aluminum and perhaps other weak bases are present. If lead is present the solution will be dark and cloudy. Its purity may be 65 to 70%. It is now oxidized at the boiling point by 8 or 10 ml. of 6 *N* nitric acid.[7]

The nearly colorless oxidized solution is next freed from weak bases by neutralizing it (to congo paper) with basic magnesium carbonate, adding 10 g. of magnesium acetate, and boiling it for a few minutes. The rather heavy precipitate (42 g. wet, in one case) containing but a trace of europium is filtered out. To remove remaining rare earths, the crude europium trichloride is again run through the reductor, precipitated as europous sulfate with 160 g. of magnesium sulfate and 8 g. of sulfuric acid, the sulfate converted into carbonate, the latter dissolved in hydrochloric acid, and the whole process repeated several times. Re-oxidation of the europous chloride solution with nitric acid before running it through the reductor is unnecessary.

After the eighth precipitation as europium sulfate no further rare earths were recoverable from the filtrate, and the solution of europium trichloride resulting showed no absorption bands of other earths. It was again reduced and precipitated as sulfate. This was washed finally with methyl alcohol. The yield was 88 g. of dry europous sulfate. Upon analysis, a portion dried in the oven at 100° and titrated with 0.04 *N* permanganate[2] showed a purity of 99.7%.

Another lot, made from 1.5 liters of chloride solution of 20% purity, was treated similarly excepting but six precipitations as sulfate were made. The product, 104 g., titrated with standard permanganate, showed a purity of 96.6%. About a week's time is sufficient to prepare approximately 100 g. of pure europous sulfate from the 1.5 liters of chloride solution resulting from 0.5 kg. of crude hydroxide of 20% purity.

Summary

1. A process is described for the extraction of europium from rare earth residues from monazite by reduction of this element to the bivalent state with zinc and subsequent separation as insoluble europous sulfate.

2. Pure europium compounds have been prepared by several repetitions of these reactions.

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RECEIVED AUGUST 3, 1936

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[7] If the solution is sufficiently acid no oxides of nitrogen are formed. It is probable that the reaction $10Eu^{++} + 10H^+ + 2HNO_3 \rightarrow 10Eu^{+++} + N_2 + 6H_2O$ occurs.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The System Nickel Oxalate, Potassium Oxalate and Water at 30°

BY W. C. VOSBURGH, KATE ISRAEL AND OLIVE G. BIRCH

A complex oxalate with the formula $K_2Ni(C_2O_4)_2 \cdot 6H_2O$ was reported by Rammelsberg,[1] and an analogous sodium salt, $Na_2Ni(C_2O_4)_2 \cdot 8H_2O$, by Dodson,[2] but no satisfactory study of the system nickel oxalate, potassium oxalate and water by the phase rule method seems to have been made. Deakin, Scott and Steele[3] made some determinations of the solubility of nickel oxalate in potassium oxalate solutions. They found the approach to equilibrium very slow, and obtained evidence of the formation of solid solutions of nickel and potassium oxalates.

Experimental.—Nickel sulfate was treated to remove cobalt by the method used by Deakin, Scott and Steele.[3] Potassium oxalate was recrystallized. Nickel oxalate was prepared by adding a solution of nickel sulfate to a solution of oxalic acid at a slow rate with mechanical stirring. Samples of the complex salt were prepared by dissolving nickel oxalate in saturated potassium oxalate solutions at an elevated temperature, filtering and allowing to crystallize at room temperature.

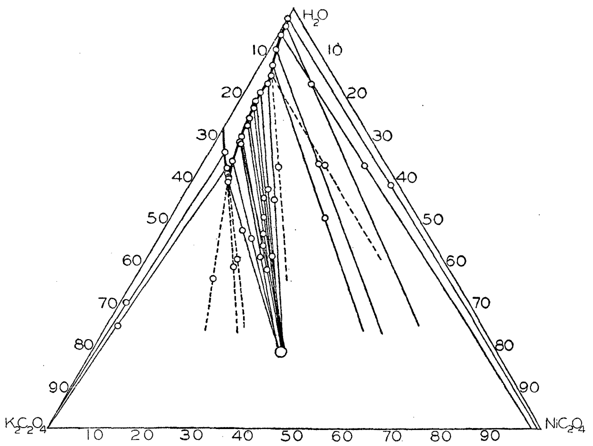

Fig. 1.—The system nickel oxalate, potassium oxalate and water at 30°. The large circle represents the theoretical composition of the compound $K_2Ni(C_2O_4)_2 \cdot 4H_2O$.

The experiments consisted in solubility determinations in which both the saturated solutions and wet solid phases were analyzed. The procedure was essentially as described in a previous paper[4] except as mentioned below. For solutions containing more than 12.4% of potassium oxalate, the samples were prepared as follows. A portion of either nickel oxalate or the complex salt was dissolved completely in a potassium oxalate solution by heating. The solution was allowed to cool in the Pyrex tube in which the sample was to be brought to equilibrium. In some of the experiments seeds were added. Seeding was found desirable, as otherwise erratic results were frequent. The excess complex salt was allowed to crystallize while the tube was rotated mechanically. The crystals were slow in forming, even after seeding. All samples were rotated for at least a week and some for much longer times. When the right solid phase was present, a week's rotation undoubtedly was sufficient, as the results were independent of the time of rotation.

For the more dilute potassium oxalate solutions (less than 12.4% potassium oxalate) the solid phase was nickel oxalate prepared either as described above or by slow addition of a nickel sulfate solution to a large excess of a potassium oxalate solution. Samples prepared by the second method were brought to equilibrium with solutions of about the same concentration as those from which they had been precipitated. The nickel oxalate was not dissolved completely and reprecipitated as in the more concentrated solutions.

The temperature was maintained at 30 ± 0.1° for at least a day previous to sampling, in either an oil-bath or an air-bath.

In the analysis of the samples,[5] the oxalate content was determined by titration with permanganate and the nickel content either by means of dimethylglyoxime or by cyanide titration.[6] Both methods for nickel were checked by the analysis of known samples to which potassium oxalate had been added. For some of the samples it was found necessary to evaporate to fumes with sulfuric acid to destroy the oxalate before titration with cyanide. The results are given in Table I and Fig. 1. In the fifth column of Table I the letter A represents solid solutions of nickel oxalate and potassium oxalate, B the complex salt, $K_2Ni(C_2O_4)_2 \cdot xH_2O$, and C potassium oxalate, possibly containing nickel oxalate in solid solution. In Fig. 1 the larger circle represents the theoretical composition of the compound $K_2Ni(C_2O_4)_2 \cdot 4H_2O$.

In the last column of Table I are given values for the percentage of water in the complex salt, calculated by algebraic extrapolation on the assumption of the formula $K_2Ni(C_2O_4)_2 \cdot xH_2O$. The theoretical value for $x = 4$ is 18.7% water and that for $x = 6$ is 25.7%. The results may be divided roughly into two groups, one indicating four and the other six molecules of water. In nearly all of the results that indicate six molecules, the percentage of nickel oxalate in solution is a little larger than that in comparable results indi-

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[1] Rammelsberg, *Ann. Physik*, **95**, 198 (1855).

[2] Dodson, *Proc. Chem. Soc.*, **27**, 260 (1911).

[3] Deakin, Scott and Steele, *Z. physik. Chem.*, **69**, 129 (1909).

[4] Vosburgh, Newlin, Puette, Peck and Dick, THIS JOURNAL, **58**, 2079 (1936).

[5] The authors are indebted to Mr. Herbert A. Pohl for making some of the analyses.

[6] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley & Sons, Inc., New York, 1929, p. 320.

TABLE I

COMPOSITION OF SATURATED SOLUTIONS AND WET SOLID PHASES

Weight per cent					
Solution		Wet solid		Solid phase	Dry solid H_2O, %
$K_2C_2O_4$	NiC_2O_4	$K_2C_2O_4$	NiC_2O_4		
2.26	0.08	1.76	40.34	A	..
3.77	.55	5.42	12.52	A	..
5.67	.57	4.42	32.84	A	..
8.40	1.38	13.48	23.26	A	..
11.08	2.55	18.82	30.95	A	..
12.44	3.53	12.45	24.79	A + B	..
12.44	3.53	21.88	15.82	A + B	..
14.22	3.80	26.79	18.81	B	20.3
16.74	3.28	26.67	16.27	B	17.6
18.77	3.48	30.41	21.68	B	28.5
18.78	3.39	34.05	24.93	B	17.6
19.95	3.84	28.46	16.57	B	20.2
20.50	3.77	29.62	17.66	B	19.3
20.62	3.87	31.71	21.98	B	25.2
22.12	4.02	30.95	18.82	B	21.6
23.24	4.55	32.94	20.78	B	18.2
25.82	4.67	36.54	25.56	B	19.4
26.83	4.93	36.21	22.74	B	14.7
26.94	5.13	35.83	25.55	B	24.5
26.98	5.13	33.53	20.07	B	24.1
27.11	5.20	34.42	21.91	B	23.8
30.55	5.85	35.87	18.69	B	16.5
34.08	7.39	36.84	16.01	B	16.8
33.03	6.64	41.24	18.19	B + C	..
33.31	6.81	47.91	15.80	B + C	..
33.57	6.37	43.00	18.44	B + C	..
31.07	3.34	68.80	1.30	C	..
32.51	5.56	73.19	2.22	C	..

cating four molecules. This suggests that the solid phases having the larger percentages of water were metastable and leads to the conclusion that the stable solid phase at 30° is the tetrahydrate. However, the variability in the calculated percentage of water could have been caused by a small variation in the ratio of nickel oxalate to potassium oxalate in the solid phase, and the conclusion as to the amount of water in the dry solid is uncertain.

In the experiments corresponding to the two tie-lines that approach the nickel oxalate corner of Fig. 1, the solid phase introduced was nickel oxalate prepared from nickel sulfate and oxalic acid. Since nickel oxalate is a hydrated salt, the direction of the lines indicates the presence of potassium oxalate in the solid phase, probably in solid solution. Other similar experiments gave similar results. The time allowed was insufficient for the establishment of equilibrium in the solid phases in these experiments.

Samples of nickel oxalate precipitated from potassium oxalate solutions were contaminated with potassium oxalate, the amount of contamination varying with the concentration of the solution. Portions of these precipitates were washed with water, dried at 110° and analyzed. The results are given in Table II.

TABLE II

COMPOSITION OF NICKEL OXALATE PRECIPITATED FROM POTASSIUM OXALATE SOLUTIONS

$K_2C_2O_4$, concn., %	[a]	3	5	7	10
Ni in ppt., %	31.83	29.37	26.74	23.44	20.26
C_2O_4 in ppt., %	46.67	47.88	49.20	50.80	51.50

[a] Precipitated from oxalic acid solution.

The conclusion of Deakin, Scott and Steele that solid solutions are formed of potassium oxalate in nickel oxalate is confirmed.

Summary

Solid solutions of nickel oxalate and potassium oxalate can exist in equilibrium at 30° with aqueous solutions containing less than 12.5% of potassium oxalate and saturated with the nickel salt. From 12.5% to saturation with potassium oxalate the stable solid phase is the complex salt $K_2Ni(C_2O_4)_2 \cdot xH_2O$ in which x is probably four.

DURHAM, N. C. RECEIVED SEPTEMBER 14, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Electrolysis of Methylmagnesium Iodide in *n*-Butyl Ether

BY WARD V. EVANS AND EDMUND FIELD

The electrolysis of the methyl Grignard reagents in ether solution has been studied[1] thoroughly for the three halides in ethyl ether using bright platinum electrodes. The products of the electrolyses in ethyl ether pointed definitely to the fact that the solvent played an important role. The ether appeared to be directly responsible for the ethylene, ethyl alcohol and isopropyl alcohol found, as a result of decomposition after the loss of a hydrogen to a free methyl radical to form methane. In order to bear this out and investigate further the mechanism involved, an electrolysis was carried out using *n*-butyl ether as the solvent.

It was also shown previously that the ratio between the methane and ethane formed depended on the current density independent of the concentration of the solution. This fact drew attention to the function of the surface of the electrode in the electrolysis. With this in view the effect of platinizing the anode where the gases evolved was determined by performing another electrolysis in ethyl ether.

Experimental

The apparatus and procedure were the same as that previously described. For the experiment with a platinized anode a platinized electrode of identical size and shape, dried by washing in anhydrous ether, was slipped over the anode.

On attempting the electrolysis of methylmagnesium iodide in butyl ether it was found necessary to introduce a new variable, that of temperature. At 40° polarization was so great that 110 volts would pass a sustained current of only 0.005 ampere. On raising the temperature to 90° polarization was still pronounced, a current of 0.2 ampere passing initially, dropping off to 0.05 ampere in one minute. The composition of the gases evolving at 90° was determined so as to enable an estimation of the effect of temperature to be made. The temperature was then raised to 143°, at which the solution refluxed gently. Polarization was almost completely absent and currents approaching 0.5 ampere could be maintained. A series of current densities was used at this temperature.

Methane and ethane predominated in the gases and small and erratic amounts of carbon dioxide were obtained just as in ethyl ether. Ethylene, formerly present, was absent; butane and butene-1 (the absence of butene-2 was not definitely proved) were new products, proved by a Podbielniak distillation of the 5 liters of gas collected during the run not used for Orsat analyses. The absence of ethyl ether vapor made the absorption analysis simple. The presence of the three saturated gases made it necessary to assume the amount of butane present before the simple combustion analysis could give the ratio of methane to ethane. The purely arbitrary assumption was made that butane was present to one-half the extent of the butene because this reduced the observed variations in the combustion values under apparently identical conditions to a minimum. The analyses are shown in Table I, where the arbitrary value for butane is given as well as the observed and corrected values for *n* in the formula C_nH_{2n+2}. The corrected value of *n*, representing the methane and ethane only, was used to calculate the fraction of methyls coupled, *Fc*, which is shown plotted as curve 1, Fig. 1.

The efficiency of the electrolysis was 43.3% based on the change in basic magnesium determined by titration. This is much lower than in ethyl ether. On the basis of the gas evolved using the corrected analysis for ethane and making use of the previously demonstrated[1] equivalency of methyls evolved to Grignard decomposed, the efficiency was 42%. The excellent agreement confirmed the assumptions made.

When the electrolysis was completed the solution was hydrolyzed in a nitrogen atmosphere and fractionally distilled through a 75-cm. vacuum jacketed spiral coil column; 2.6 cc. (0.043 equivalent per faraday) of butanol-1 was isolated (b. p. 116–116.5°, 3,5-dinitrobenzoate m. p. 63.5–64° and confirmed by a mixed melting point). A small amount of pentanol-2 was also found present, estimated at 0.2 cc. The presence of a secondary alcohol was first proved by the $ZnCl_2 \cdot HCl$ reagent; fractional crystallization of the dinitrobenzoate followed by means of mixed melting points with the known pentanol-2 deriva-

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(1) Evans and Field, THIS JOURNAL, **58**, 720 (1936).

TABLE I

ELECTROLYSIS OF METHYLMAGNESIUM IODIDE IN BUTYL ETHER WITH BRIGHT ELECTRODES

Initial concn. 1.900 *N;* final concn. 1.056; average concn. 1.422. Over-all efficiency: 0.433 equiv. decomp./faraday; 0.343 mole gas/faraday; 0.42 methyl/faraday; 0.97 methyl/equiv.

Temp., °C.	Order taken	Amp./sq. dm.	CO_2	C_4H_8	C_4H_{10}	C_2H_6	CH_4	*n*, obsd.	*n*, corr.	100*Fc*
143	11	1.60	0.2	9.5	4.8	23.1	62.4	1.41	1.27	43
	7	1.60	.4	13.5	6.8	23.0	56.3	1.51	1.29	45
	10	1.20	.7	4.2	2.1	17.7	75.3	1.25	1.19	32
	9	1.20	2.1	6.7	3.4	19.3	68.5	1.32	1.22	46
	3	0.80	0.0	4.4	2.2	19.6	73.8	1.27	1.21	35
	8	.40	.0	2.7	1.4	15.4	70.5	1.20	1.16	28
	5	.12	.0	5.2	2.6	4.6	87.6	1.13	1.05	10
	4	.12	.0	4.5	2.3	5.6	87.6	1.13	1.06	11
	6	.04	.0	3.8	1.9	5.8	88.5	1.12	1.06	11
90	2	.20	.0	1.0	0.5	23.7	74.8	1.25	1.24	39
	1	.20	.0	0.9	0.4	22.7	76.0	1.24	1.23	37

TABLE II

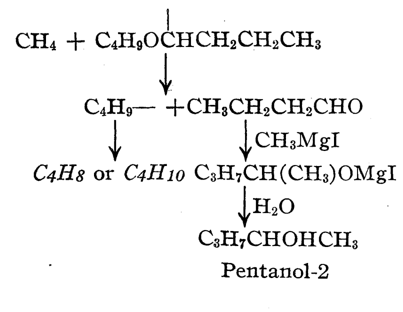
ELECTROLYSIS OF METHYLMAGNESIUM IODIDE IN ETHYL ETHER WITH PLATINIZED ANODE

Initial concn. 1.794 *N;* final concn. 0.892; average concn. 1.34. Over-all efficiency: 0.467 mole gas/faraday; 0.761 equiv. decomp./faraday; 0.772 methyl/faraday; 1.01 methyl/equiv. decomp.

Order taken	C. d. amp./sq. dm.	Gas constituents Ethane	Methane	Ethylene	Carbon dioxide	100*Fc*
4	0.060	25.7	73.0	1.1	0.2	41
3	.12	29.6	68.9	1.3	.2	46
5	.24	40.4	58.2	1.1	.3	58
2	0.40	50.4	48.7	0.9	0.0	68
9	.60	58.6	40.6	0.6	.2	74
1	.80	63.0	35.5	1.3	.2	78
8	.80	63.6	35.7	0.5	.2	78
7	1.60	72.3	26.8	.6	.3	84
6	2.40	77.3	22.3	.7	.1	88

tive proved its presence. There was also found 5 cc. of high boiling liquid products.

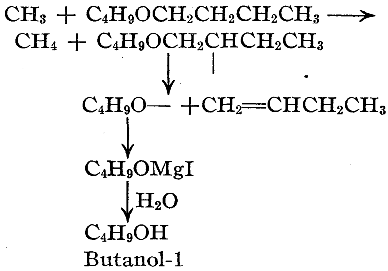
Decomposition of the Ether.—The products obtained were in excellent agreement with the mechanism proposed for the electrolysis in ethyl ether. Applied to the α- and β-hydrogens in butyl ether we have



$$\begin{array}{l} \mathrm{CH_3 + C_4H_9OCH_2CH_2CH_2CH_3 \longrightarrow} \\ \mathrm{CH_4 + C_4H_9O\overset{|}{C}HCH_2CH_2CH_3} \\ \qquad\qquad \downarrow \\ \mathrm{C_4H_9—\ + CH_3CH_2CH_2CHO} \\ \quad \downarrow \qquad\qquad \downarrow \mathrm{CH_3MgI} \\ C_4H_8 \text{ or } C_4H_{10} \ \mathrm{C_3H_7CH(CH_3)OMgI} \\ \qquad\qquad\qquad \downarrow \mathrm{H_2O} \\ \qquad\qquad \mathrm{C_3H_7CHOHCH_3} \end{array}$$

Pentanol-2

and



$$\begin{array}{l} \mathrm{CH_3 + C_4H_9OCH_2CH_2CH_2CH_3 \longrightarrow} \\ \mathrm{CH_4 + C_4H_9OCH_2\underset{|}{C}HCH_2CH_3} \\ \qquad\qquad \downarrow \\ \mathrm{C_4H_9O—\ + CH_2{=}CHCH_2CH_3} \\ \quad \downarrow \\ \mathrm{C_4H_9OMgI} \\ \quad \downarrow \mathrm{H_2O} \\ \mathrm{C_4H_9OH} \end{array}$$

Butanol-1

These two sets of reactions account for all the products identified and explain the absence of ethylene. There can be no question that the solvent furnishes the fourth hydrogen for the methane and that its subsequent decomposition is responsible for the secondary products formed.

The above mechanism applied to the other two kinds of hydrogen present in the ether molecule predicts products which were not found; this would seem to cast some doubt on the free radical mechanism and suggest another such as an ionic reaction. It is not necessary, however, to assume that these positions were not subject to attack, but merely that the intermediate radicals thus formed were stable enough to polymerize in some manner instead of breaking down, explaining the appreciable amount of high molecular weight liquid compounds obtained.

Fraction of Methyls Coupling.—The amount of coupling to form ethane was much lower in butyl ether than in ethyl ether, as is shown when curves I and II are compared with III and IV in Fig. 1. This indicates a greater rate of reaction of the butyl ether with the methyl radicals. Since this effect was obtained by changing both solvent and temperature, the individual effect of each remained to be determined. The two temperatures used showed that the coupling decreased as the temperature increased. An extrapolation down to the 40° used with ethyl ether by means of the Arrhenius equation gave a value for *Fc*, the fraction of methyls coupled, of 0.62; the observed value in ethyl ether at the same current density was 0.77. This may be interpreted to show that the loss of a hydrogen to a methyl radical takes place more readily in the case of butyl ether even at the same temperature. The slope of the line determined by the two points gave the low value of 1100 calories per mole for this reaction.

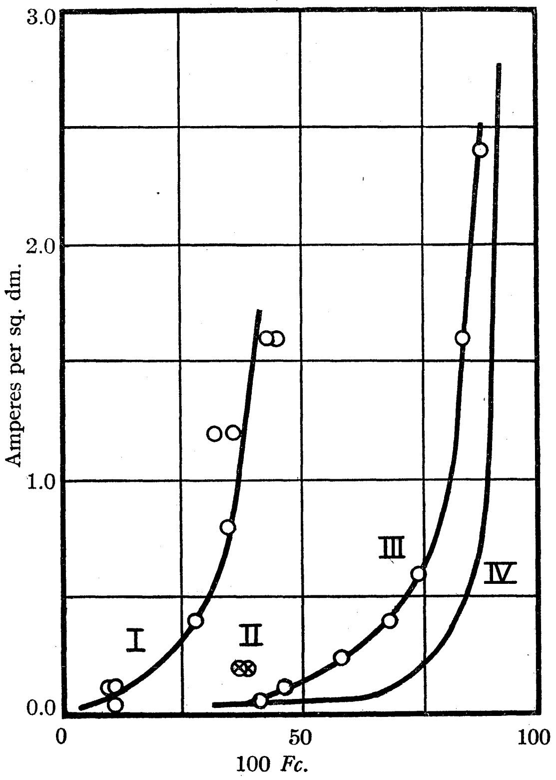


Fig. 1.—Effect of current density in electrolysis of methylmagnesium iodide: I, in butyl ether at 143°, bright electrodes; II, in butyl ether at 90°, bright electrodes; III, in ethyl ether, platinized anode; IV, in ethyl ether, bright electrodes.

Platinized Anode.—As was expected, the effect of platinizing the anode was a significant change in the methane–ethane ratio. The results are given in Table II. The perfect agreement between the first and eighth sample taken was good evidence that the platinized electrode was unchanged during the course of the electrolysis. One and one-half liters of gas was evolved before samples were taken in order to allow the electrode surface an opportunity to come to equilibrium.

The efficiency of electrolysis was entirely unaffected by platinizing the anode since an interpolation to the same concentration on our previously determined curve[1] also gives an efficiency of 76%. *Fc* showed the same dependence on current density as with bright electrodes, but is somewhat lower as may be seen in curves III and IV, Fig. 1. The platinizing seemed merely to cut down the apparent current density by exactly 5 in comparison with the bright electrode throughout the whole range studied. Evidently platinizing the anode served to increase its effective area by five so that the effective current density was decreased by that amount. Apparently the electrode merely provides an inert surface on which the reactions take place.

Summary

1. The theory that the solvent ether furnished the fourth hydrogen for the formation of the methane, with subsequent decomposition to give the secondary liquid and gaseous products found, was confirmed.

2. Butyl ether was more readily attacked by methyl radicals than was ethyl ether.

3. Increase in temperature favored the reaction with the solvent, increasing the proportion of methane.

4. The electrolysis efficiency was much less in butyl than in ethyl ether.

5. Platinizing the anode had no effect other than to increase the effective area by exactly five, with a resultant decrease in effective current density by that factor.

EVANSTON, ILL. RECEIVED JULY 30, 1936

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Effect of Ortho Substitution on the Absorption of the OH Group of Phenol in the Infrared[1]

BY OLIVER R. WULF, URNER LIDDEL AND STERLING B. HENDRICKS

Infra-red absorption that is characteristic of the presence of NH and OH groups in organic molecules exhibits in general a dependence upon the character of the rest of the molecule, particularly upon that of neighboring groups.[2] In the present researches the spectra of such molecules are being measured quantitatively, giving the results as curves of the molal absorption coefficient against position in the spectrum. This dependence of the spectra upon the constitution of the rest of the molecule indicates that this type of measurement will be powerful as a means of studying molecular structure, when a satisfactory theory of this type of spectrum is developed. Among the compounds showing the influence of neighboring groups on NH or OH absorption, the ortho substituted derivatives of phenol are, in some respects, the simplest.

Certain groups, when substituted ortho to the phenolic OH, lead to the formation of a hydrogen bond.[3] In these cases it has been shown that the absorption normally characteristic of the presence of the OH group in the region 6500–7500 cm.$^{-1}$ is absent, and this has been developed as an empirical criterion for the presence of such hydrogen bonds. On the other hand, other groups, when substituted ortho to the phenolic OH, do not cause the OH absorption to disappear, but they frequently do alter it in an interesting way. These cases are important in that they give positive results, that is, they afford some absorption which may be studied quantitatively to investigate this dependence on neighboring groups in the molecule. In a previous paper[2] the simplest representative of this latter class of compound was *o*-chlorophenol. In the present paper results are given for a number of ortho substituted phenols.

It is the purpose of this research to present as broad a survey as possible of this general type of absorption in organic molecules rather than to undertake as yet a detailed study of a few. It seems wiser to adopt this attitude, leaving an intensive study of single compounds until the theory of the absorption is developed to a point that warrants this. However, under these conditions it is necessary to emphasize, as has already been done, that minor characteristics of the absorption curves, such as slight displacements or dissymmetries, should not be given credence until an exhaustive study of the particular compound is made. Similarly, failure to show any absorption at some particular point must not be construed as meaning that very weak absorption may not be present there.

Experimental Procedure

The experimental details have already been described.[2] The absorption is measured in dilute carbon tetrachloride solution usually of the order of 0.01 molal. In the case of each compound presented below, at least two separate records were taken using two different solutions.

Certain of the compounds used were purchased from the Eastman Kodak Company and others were synthesized by methods already outlined in the literature. In every case some of their properties were checked with those recorded in the literature. In a few cases where there was some question as to the purity of the product, as was true in the case of pyrogallol and pyrogallol dimethyl ether, the absorption was studied before and after recrystallization and where no noticeable alteration in the spectrum was effected, it was assumed that the observed spectrum was essentially due to the compound itself. It is important to emphasize that the presence of very small amounts of impurities is not of great consequence in this work. Insofar as they do not contain the group being studied (*i. e.*, OH or NH) their presence can practically be neglected, while if they do contain such a group, their effect is simply proportional to the amounts present. If present in small amount, their effect will be a small alteration of the absorption curve, and minor characteristics, found in any of these curves, must be checked by further experimental work before being given importance, because of the rather wide limits of experimental error in the quantitative determination of the absorption coefficients themselves.[2]

Since pyrogallol and 1,8-dihydroxynaphthalene are only slightly soluble at room temperature, they were run at 60° as well, in order to secure an adequate concentration of the substance and hence of the absorption. Since no definite effect of temperature was observed, the runs at room temperature and at 60° were used together in determining the final or average curve.

Results

The curves, given in Fig. 1, present the results

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(1) Preliminary report of this work was presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Kansas City, Mo., in April, 1936.

(2) Wulf and Liddel, THIS JOURNAL, **57**, 1464 (1935).

(3) Hilbert, Wulf, Hendricks and Liddel, *Nature*, **135**, 147 (1935); THIS JOURNAL, **58**, 548 (1936); **58**, 1991 (1936). See also Errera and Mollet, *Compt. rend.*, **200**, 814 (1935); *J. phys. radium*, **6**, 281 (1935).

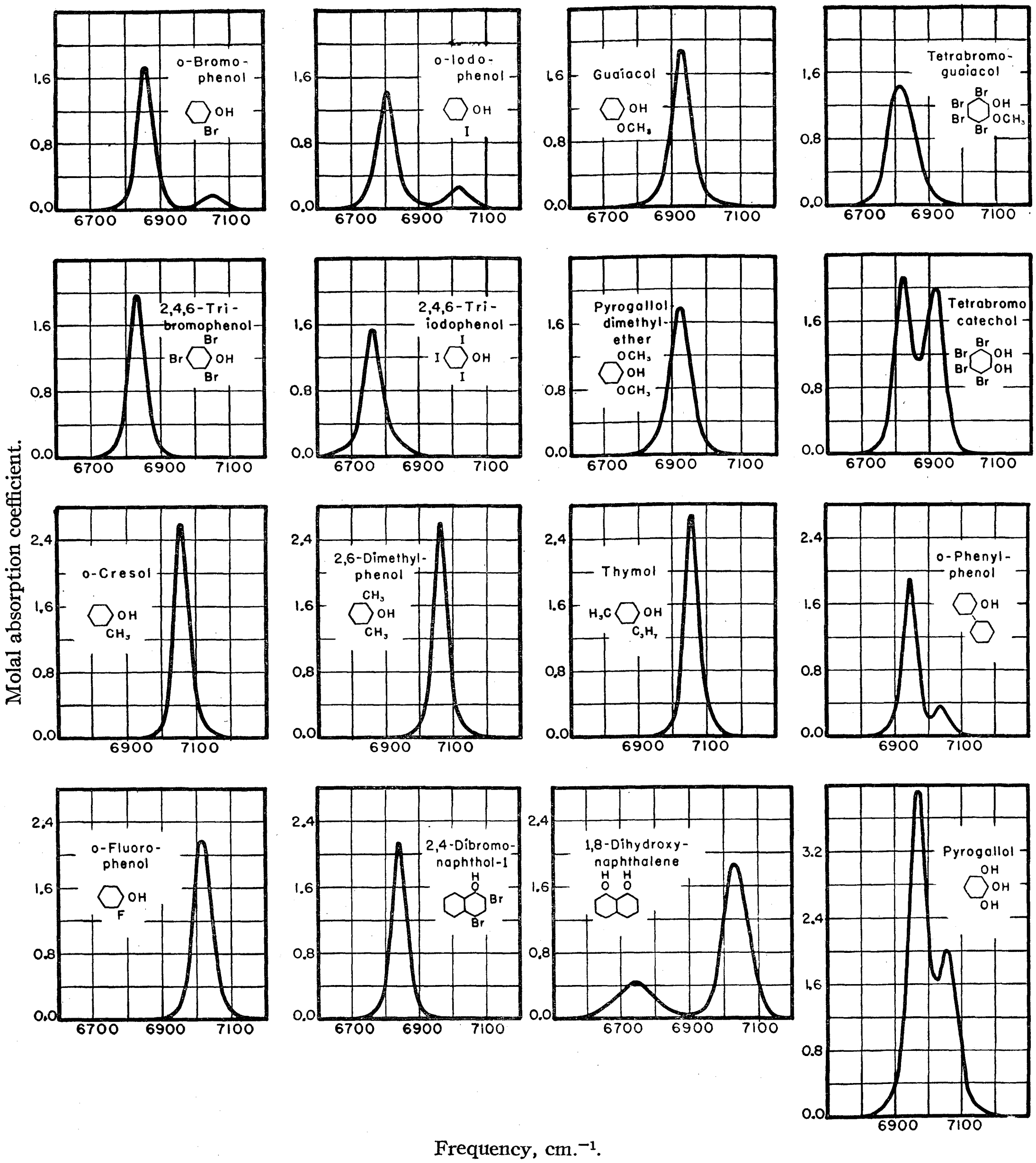

Fig. 1.—Molal absorption coefficients for some ortho substituted phenols.

in sufficient detail so that little further description need be given. In those cases where one of the ortho hydrogens of phenol remains, an absorption peak at approximately the phenol frequency is present. In most of the others this peak is missing, the evident exception being 2,6-dimethylphenol. In Table I the areas under the absorption curves are given, as was done in reference 2 where the areas for those compounds whose curves were published in that paper may be found.

A word must be said regarding the region 7100–7400 cm.$^{-1}$. Atmospheric water vapor absorption lies here, and makes observation difficult. Additional absorption of considerable strength would not be missed, and could be read though with less accuracy than that in other regions. It would, however, be possible to miss weak absorption, especially on days of high humidity, and therefore our curves must not be construed as indicating no absorption in this region. This applies to all results which we have published. Very weak absorption due to OH lies in this region. During an attempt to study in detail the effect of temperature upon the *o*-chlorophenol ab-

TABLE I

Substance	Molal absorption area, liter/sq. cm. mole
o-Bromophenol	125
o-Iodophenol	125
Guaiacol	145
Tetrabromoguaiacol	145
2,4,6-Tribromophenol	125
2,4,6-Triiodophenol	120
Pyrogallol dimethyl ether	140
o-Cresol	155
2,6-Dimethylphenol	150
Thymol	150
o-Phenylphenol	130
o-Fluorophenol	160
2,4-Dibromonaphthol-1	130
1,8-Dihydroxynaphthalene	235
Tetrabromocatechol	290
Pyrogallol	440

sorption, two further weaker peaks to higher frequencies were discovered while working on a very cold and dry winter day and at high concentrations. The weakest of these is probably due to OH, while the other might be ascribed to either OH or CH. There is indication that weak absorption in this region occurs in several if not all of the present compounds. It is not practical to measure this, however, at the concentrations used in this work, and no effort has been made to indicate its presence in the absorption curves. Hence reiteration of the words at the beginning of this paragraph must be made here to avoid misunderstanding.

Discussion

In reference 2 a simple theoretical discussion of the characteristics of this type of spectra was given, in which possible causes for the appearance of more than one single peak after substitution, as well as for pronouncedly broadened peaks, were mentioned. It was suggested that the appearance of several frequencies (peaks) of absorption was due to a coupling of the OH or NH group with a near-by group of similar frequency. Pauling has suggested recently[4] that the complexity of the spectra is due rather to two or more types of OH or NH groups having different characteristic frequencies. He points out that, because of resonance with other structures besides those of the Kekulé type, the C–O bond in phenol possesses some double bond character, which tends to cause the OH group to lie in the plane of the ring. The OH group then can orient itself stably in two positions which in phenol, however, are equivalent. Though different from phenol, these two positions are also equivalent for a symmetrical ortho disubstituted phenol, but not for the unsymmetrical case and are thus different for mono-ortho substituted phenols. In general, the OH group in the two forms of such a molecule, called by Pauling *cis* and *trans* forms, will lead to different characteristic absorptions. Furthermore, the amounts of the two different forms of molecule, present in equilibrium with one another, evidently will depend upon the difference in free energy between the two forms. There is, however, no evident quantitative relation between the free energy difference of any one pair of *cis* and *trans* forms and the frequency difference of their absorptions.

This interpretation is the only specific description of this type of absorption which we now have. It will therefore be helpful to attempt to interpret the present results as far as possible in accordance with it, in order to see to what extent it accounts for the observations.

Attempting now to interpret the absorption curves in terms of this picture, *o*-bromo- and *o*-iodophenol show in a similar way as does *o*-chlorophenol[2] two distinct peaks, one (*trans* form) approximately at the normal phenol frequency. The other peak (*cis* form) lies to lower frequencies and by a progressively increasing amount in the order *o*-chloro-, *o*-bromo-, *o*-iodophenol, indicating a progressively increasing proton attraction in this order. The increasing polarizability of the ortho substituent is the most evident way of accounting for this, and the result indicates that the dipole moments in the ortho groups $C^{+} \text{---} {}^{-}X$, where X is the halogen, are relatively unimportant since the dipole moments for these groups are in the opposite order, thus that of C–Cl being considerably greater than that for C–I. This may seem reasonable from the circumstance that the dipole is oriented approximately at right angles to the direction toward the H atom. A rough measure of the increase in polarizability is given by the change in the molecular refractivities of the three monohalogen substituted benzenes, which are *o*-chloro 31.1, *o*-bromo 34.0 and *o*-iodo 39.2, respectively, for sodium D, these values being computed from data taken from the "International Critical Tables," Vol. VII, p. 34.

In the case of *o*-fluorophenol a single peak occurs but this peak is somewhat broad and has its maximum at about 7015 cm.$^{-1}$, an appreciably

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[4] Pauling, THIS JOURNAL, **58**, 94 (1936).

lower frequency than that of the *trans* peak in the other three analogous ortho substituted phenols. The broadening is in accord with the hypothesis that the *o*-fluorophenol absorption is comprised of two frequencies as in the case of the other three compounds, one at about 7050 cm.$^{-1}$ and the other at 7015 cm.$^{-1}$ and that in this case they largely overlap one another.

In the symmetrical 2,4,6-trichloro-, tribromo- and triiodophenols but one peak appears, the *cis* peak, since the two positions of the OH group are now the same, and are *cis* in character. The peak in each case lies moreover at approximately the same position as the *cis* peak of the respective three mono-ortho substituted derivatives. Actually in all three cases the peak in the symmetrical tri-substituted compounds is slightly but definitely at a lower frequency than the *cis* peak of the respective ortho substituted compound. The difference, while rather small, appears to be real.

Where the ortho substituent is a group of atoms rather than a single atom, the situation is more complicated. In this case it is difficult to see what the combined effect of polarizability and of the several variously oriented dipoles within the group might be. However, several such compounds were measured and it is interesting to consider the character of the absorption which they afforded.

o-Cresol and thymol show only a single prominent peak at about the normal phenol frequency. In the case of *o*-cresol it is probable that proton repulsion would characterize the *cis* form because of the rather close proximity of the hydrogen of the hydroxyl group to the hydrogen atoms of the methyl group. The single peak could be interpreted either as due to equal amounts of *cis* and *trans* forms of practically the same frequency, analogous with phenol, or as due to the *trans* form alone, the *cis* form being of different frequency and of much greater free energy, hence not present in appreciable amounts. From the geometry of *o*-cresol the first alternative presumably is the more reasonable. While the situation in thymol is not so simple as in *o*-cresol, the absorption appears to be of the same type. But the choice between the two possible interpretations in the case of *o*-cresol is substantiated by the absorption of 2,6-dimethylphenol. Here both positions of the O–H group are *cis* positions, and still a single peak of roughly the phenol area and at approximately the phenol frequency appears.

Again, in *o*-hydroxybenzonitrile[5] the absorption consists of two peaks, a small one (*trans*) at approximately the normal phenol frequency and a larger one (*cis*) at a somewhat lower frequency, indicating a small proton attraction by the substituent group.

The spectrum of *o*-phenylphenol (2-hydroxydiphenyl) interpreted in terms of the same picture, also shows appreciable amounts of both *cis* and *trans* forms of the molecule present. This is of considerable interest since it suggests a conclusion as to the structure of the rest of the molecule. If the two rings were coplanar as they are crystalline diphenyl, the hydrogen atoms of the hydroxyl group would be in very close proximity to the near-by hydrogen of the substituted ring, even allowing severe distortion of the valence angles. The strong resultant repulsion would ensure the presence of only a *trans* form. Since both forms are found it is to be concluded from the picture that the two rings do not lie in the same plane, and indeed, from the geometry of the system, that they are considerably removed from such position even as they are in optically active diphenyl derivatives. With the two rings swung far out of a common plane the first carbon atom of the ortho substituted ring lies closest to the hydroxyl hydrogen, and if this near-by carbon atom exercises an appreciable proton attraction, this would lead to a *cis* form of lower energy than the *trans* form, and could give rise to the two peaks.

Especial interest attaches, moreover, to guaiacol. Proton attraction by the oxygen of the methoxy group might be expected, and this appears to be present. A comparison with the absorption of catechol helps to make the guaiacol absorption more understandable. As presented in reference 2, catechol shows two peaks of equal intensity, one at the normal phenol frequency, the other at a considerably lower frequency. Pauling has interpreted these as arising from a *cis* and a *trans* form within the same molecule, the hydrogen of one of the hydroxyl groups being in the *cis* position owing to the proton attraction of the neighboring oxygen, but the hydrogen attached to this second oxygen having only the *trans* position left to it, strong proton repulsion presumably preventing both hydroxyls turning toward one another. This second (*trans*) OH group is thus essentially the same as the OH

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(5) Hendricks, Wulf, Hilbert and Liddel, THIS JOURNAL, **58**, 1991 (1936).

group of phenol. In guaiacol one of the two hydroxyl hydrogens of catechol is removed, leaving, however, the corresponding hydroxyl oxygen in its old position. This leaves for the remaining hydroxyl group the *cis* position as the position of lowest energy. The guaiacol peak (*cis*) lies at a slightly lower frequency than the *cis* peak of catechol.

Important in a closely similar way is the absorption of 3-nitrocatechol, the curve for which has already been published.[3] Its absorption is very nearly the same as that of guaiacol. In 3-nitrocatechol the hydrogen of the hydroxyl group nearest the NO_2 group engages in a hydrogen bond, removing the OH absorption of this hydroxyl group. The remaining OH group shows the *cis* form absorption just as does guaiacol.

It appears, however, that in guaiacol and 3-nitrocatechol the difference in free energy between the *cis* and *trans* forms of the available OH group is greater than it is for instance in *o*-chlorophenol, *o*-hydroxybenzonitrile or even *o*-iodophenol, since no absorption due to a *trans* form can be seen. This is a necessary conclusion of the stereochemical interpretation *unless* the absorption coefficients for the two forms are greatly different from one another, in contrast to what is presumed to be true in the case of catechol. It has already been shown[2] that the absorption coefficient can be somewhat altered by the presence of another neighboring group.

In guaiacol the O–C of the methoxy group must be thought of as in the *trans* position, and this leaves an appreciable dipole moment (the O–C moment) so oriented as to give a resultant proton attraction. This might account for the deeper energy minimum in which the *cis* OH of guaiacol seems to lie as compared with the OH of *o*-iodophenol. Furthermore, it seems necessary to conclude that this greater free energy difference does not necessarily mean a greater shift in the absorption frequency for here the guaiacol peak is at a considerably higher frequency than is, for example, the peak of the cis form of *o*-iodophenol. It would appear that this could be the case. The form of the potential curve in which the vibrating hydroxyl swings will be different where simply the polarization of a near-by atom, such as the iodine atom, is concerned than it will where, as in guaiacol, the permanent dipole moment of another group, here the O–C moment, is so oriented as to exert attraction for the proton of the hydroxyl group. In this respect 3-nitrocatechol is similar except that here the active *cis* OH faces an OH locked in a hydrogen bond with the oxygen atom of the NO_2 group.

Pyrogallol shows a particularly interesting absorption. It is clear that, from the explanation suggested by Pauling for catechol, one would expect in pyrogallol a molecule possessing two *cis* OH groups and one *trans* group. In other words the third OH group when added to catechol finds the *cis* position available for it just as the *cis* position was available to the second group when added to phenol. The absorption of pyrogallol shows two peaks, one (*trans*) at approximately the normal phenol frequency and possessing an area approximately equal to phenol. The other peak (*cis*) is at lower frequencies and not far from the position of the *cis* peak of catechol. The area of this latter peak, moreover, is roughly twice that of phenol, and thus the absorption of this molecule is in rather striking accord with what might be expected, using Pauling's interpretation as a guide.

It is also interesting to compare the absorption of 1,8-dihydroxynaphthalene with that of catechol. It will be recalled that in catechol the configuration in which both OH groups were in *trans* positions appeared to occur in too small amounts to be noticeable, the two peaks possessing about the same area. That is, the catechol molecules were interpreted as being essentially all of one sort, this possessing one *cis* and one *trans* OH group. As mentioned above, this conclusion contained the assumption that the absorption coefficients of the two groups were the same. In 1,8-dihydroxynaphthalene the two OH groups are even closer together than in catechol, and the configuration in which the two groups turn toward one another is even more improbable than in catechol. The configuration possessing one *cis* and one *trans* group would certainly seem to be a possible one, and two peaks are indeed observed. However, while the total area is approximately that of two phenol-like OH groups, the area of the *cis* peak is considerably smaller than that of the *trans* peak. This would indicate that the configuration possessing two *trans* groups is also present in considerable amount, that is, that the difference in free energy between the *cis*–*trans* and *trans*–*trans* configuration is less than the corresponding free energy difference in catechol. It does not, however, seem probable that the hydrogen atom of the *cis*-hydroxyl group is sufficiently close to the oxygen atom of the adjacent group that repulsion offsets somewhat the proton attraction of this atom. Furthermore, the shift of the *cis* peak to lower frequencies is greater than that in catechol. It may be that here the absorption coefficients of the *cis* and *trans* forms are considerably different. If this is not the case, we are again confronted with the circumstance that a relatively large displacement of the *cis* peak from the normal phenol frequency does not necessarily mean a correspondingly large free energy difference between the *cis* and *trans* forms.

A further interesting opportunity to test the interpretation suggested by Pauling is to be had in some of the derivatives of the above mentioned compounds. In pyrogallol dimethyl ether the remaining hydroxyl group of pyrogallol would have only the *cis* position available to it, this *cis* position being similar to the *cis* position in guaiacol. The absorption does, indeed, consist of a single peak of approximately the area of a single OH group and at approximately the position of the guaiacol peak.

In tetrabromoguaiacol the position of the hydroxyl group which occurs in guaiacol itself (*cis*) presumably is not greatly changed, but in the position turned away from the oxygen atom of the O–CH_3 group, which position is essentially absent in guaiacol, the OH group finds a bromine atom adjacent in tetrabromoguaiacol. One would in first approximation expect proton attraction by the bromine atom similar to that in *o*-bromophenol and a *cis* peak at about the same position. The positions of the guaiacol peak and of the *cis* peak of *o*-bromophenol (or 2,4,6-tribromophenol) are not far removed from one another, and the broad peak observed for this compound may be interpreted as two overlapping peaks of approximately this frequency separation. It seems apparent, however, that, if this is the case, both peaks have been shifted somewhat to lower frequencies, recalling the observation that the *cis* peak in the monohalogen ortho substituted phenols seems to shift slightly to lower frequencies in the respective 2,4,6-trisubstituted phenols where both ortho positions are occupied by the halogen.

In 2,4-dibromonaphthol-1 the *cis* position of the OH group would be expected to be similar to the *cis* position of *o*-bromophenol, but in the *trans* position the adjacent hydrogen atom is considerably closer than in *o*-bromophenol, presumably leading to stronger proton repulsion. This would be expected to reduce the fraction of the molecules in the *trans* position, and indeed the *trans* peak is not observed, a single peak (*cis*) showing at approximately the position of the *cis* peak of *o*-bromophenol.

Finally in tetrabromocatechol the *cis* position of catechol should be present with roughly the same character, in first approximation, as in catechol itself, but the *trans* position no longer has a hydrogen atom adjacent, but a bromine atom, which exercises proton attraction, and which should lead to a *cis* peak at roughly the position of the *cis* peak of *o*-bromophenol. Two peaks are observed, but here again, as seemed probable also in tetrabromoguaiacol, the two peaks are shifted to somewhat lower frequencies than those occurring in the respective mono-ortho substituted compound, a characteristic apparently frequently to be found in phenols in which both ortho positions are occupied by a group exercising proton attraction. Moreover, it is to be noticed that here the configuration in which the two OH groups are turned away from one another would not be expected to possess as much excess free energy over the configuration one *cis*–one *trans* as was the case in catechol because of the attraction here exercised by the bromine atom. A similar remark applies of course to tetrabromoguaiacol as well. In other words, keeping in mind the suggested interpretation of the absorption of catechol, there seems to be no reason why the two peaks in these two compounds should be expected to possess the same area, and it may be that the small apparent difference in area of tetrabromocatechol is to be explained in this way. Finally, it is interesting to note that in both tetrabromocatechol and tetrabromoguaiacol, one quite definite prediction could be made beforehand on the basis of Pauling's interpretation, namely, that neither of these should possess characteristic OH absorption at the position of the normal phenol peak.

Thus the spectra of these compounds appear to possess characteristics which are rather strikingly in accord with Pauling's interpretation. At the same time they raise points which are not clear and which await further elucidation.

The authors are much indebted to Professor Linus Pauling for discussion of this type of spectra and for helpful advice as to its interpretation.

Summary

The absorption, characteristic of the presence of the OH group and in the region of its first vibrational overtone, has been measured quantitatively for certain ortho substituted phenols and the results have been presented as curves of the molal absorption coefficient against position in the spectrum.

The results have been discussed in the light of Pauling's recent interpretation of this type of spectra. For the most part the correspondence is remarkably close.

WASHINGTON, D. C. RECEIVED SEPTEMBER 10, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat of Fusion and Vapor Pressure of Stannic Iodide

BY GEORGE R. NEGISHI

The investigations of Hildebrand and coworkers[1] in this Laboratory during recent years upon the subject of intermolecular forces and solubility have included a study of tetrahalides as examples of molecules having widely differing volumes and intermolecular fields but with a common highly symmetrical structure. Stannic iodide is one of the substances concerning which a considerable body of solubility data has been accumulated; however, its evaluation has been unsatisfactory on account of lack of accurate knowledge of its heat of fusion and vaporization. The work herein described has been carried out in order to fill this gap.

Preparation and Purification of Stannic Iodide.—This compound was prepared and purified by the method described by Dorfman and Hildebrand,[1] followed by two fractional distillations under high vacuum (10^{-5} mm.). The purity of the final product was undoubtedly high, as indicated by sharp breaks in the cooling curve, and by the absence of premelting in the heat of fusion determinations.

The Melting Point.—The sample was distilled under high vacuum into a Pyrex tube, in the center of which extended a narrow Pyrex tube almost to the bottom. The temperature of the freezing mixture was measured by means of an alumel–chromel thermocouple inserted into the central narrow tube. The couple was calibrated against the melting points of water and tin, the boiling point of water and the transition point of sodium sulfate decahydrate. The thermoelectric current was measured by means of a Leeds and Northrup Student Type potentiometer. A change in temperature of 0.1° could be detected. The sample was heated in a copper cylinder 20 cm. high, 5 cm. in diameter and 9 mm. thick, provided with a heating coil and thermally insulated with Sil-o-cel. The temperature was regulated by means of a rheostat. During the measurements the temperature of the furnace was lowered rather rapidly to the freezing point of the stannic iodide, after that at about 0.05° per minute. The apparatus was shaken continuously on a rocker except when the readings were taken. The melting point was determined from the "break" in the cooling curve. The plot of the curve is shown in Fig. 1. The melting point thus determined was 144.5°. This value is to be compared with the values of 143.5,[1] 145.3[2] and 146.2°,[3] from other sources.

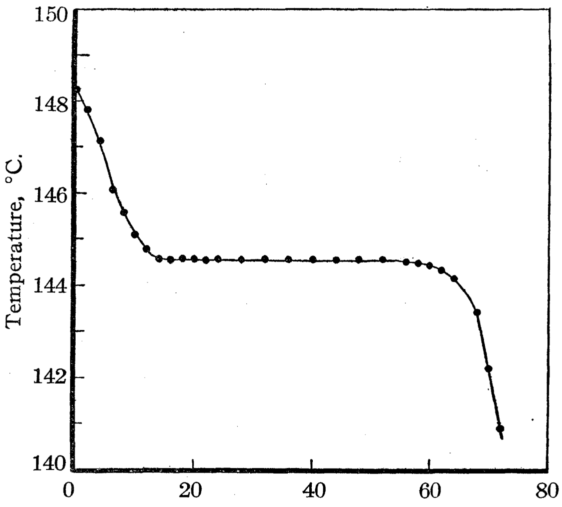

Fig. 1.

The vapor pressure was determined by means of a glass click gage as described by Smith and Taylor.[4] The click constant was determined at the pressures and temperatures of the actual runs. The constant increased with both increasing pressure and temperature up to a point where a permanent change set in. The "click-in" constant was found to be more reliable than that of "click-out," so only the former was calibrated. The space above the click gage (the manometer side) was evacuated to 10^{-2} mm. before each "click-in" was made. This was not necessary at lower temperatures, but above 200° it was essential.

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[1] M. E. Dorfman and J. H. Hildebrand, THIS JOURNAL, **49**, 729 (1927); Miriam E. Dice and J. H. Hildebrand, *ibid.*, **50**, 3023 (1928); J. H. Hildebrand and J. M. Carter, *ibid.*, **54**, 3592 (1932); J. H. Hildebrand, *ibid.*, **57**, 866 (1935).

[2] M. G. Raeder, *Z. anorg. allgem. Chem.*, **130**, 325 (1923).

[3] W. Biltz, *ibid.*, **203**, 277 (1932).

[4] D. F. Smith and N. W. Taylor, THIS JOURNAL, **46**, 1393 (1924).

The click gage used seemed to have experienced fatigue above 200°.

A tube containing the sample was broken off in an atmosphere of nitrogen, inside of a box dried with phosphorus pentoxide, and some of the solid was transferred to the apparatus. After evacuating it down to 10^{-5} mm. the side pieces were sealed off. The lower half of the apparatus was wrapped in a thin copper sheet. The apparatus up to 3.8 cm. from the stopcock was then placed in a furnace, which was similar to the one described above except that the height of the copper cylinder was 35.5 cm. The temperature of the sample was measured with a mercury thermometer inserted in the cylinder next to the bulb of the apparatus. All the thermometers used were calibrated against the Bureau of Standards calibrated mercury thermometers. The mercury columns in the manometer were read by means of a cathetometer which was graduated to 0.1 mm. The readings were reduced to 0°.

The temperature was kept within ± 0.05° for at least thirty minutes before runs were made. Usually it required from one and one-half to two hours to complete a series of three to five runs at a given temperature. Two complete sets of determinations were made over the range of temperature, one ascending, the other descending. The readings agreed within 0.1 mm. in most cases.

The results of the measurements are shown in Table I.

TABLE I

VAPOR PRESSURE OF STANNIC IODIDE FROM 160 TO 250°

Temp., °C.	Obsd. P, mm.	Calcd.
160.22	6.00	6.04
170.07	8.76	8.62
185.35	14.25	14.38
200.86	23.52	23.53
225.75	48.52	48.52
250.35	93.59	92.33

The last column of the table is calculated from the equation

$$\log P_{\text{mm.}} = 7.6571 - \frac{2971.36}{T} - \frac{3689.1}{T^2} \qquad (1)$$

empirically derived from the experimental data. The influence of the term in $1/T^2$ is very small. The extrapolated value of the boiling point is found to be 348° in comparison with 340°[5] and 346°[2] found elsewhere. The last two values are of unknown reliability since no experimental details are given and no special precautions to exclude oxygen and water vapor are mentioned, although stannic iodide decomposes readily in the presence of even slight amounts of oxygen or water vapor in the neighborhood of its boiling point. In our case, although the vapor pressure measurements made within the temperature range are reliable, the extrapolation beyond the range was so large that the uncertainty in the value of the boiling point might be appreciable. The heat of vaporization, calculated from equation 1, is 13,700 cal. per mole at 25° and 13,650 at the boiling point.

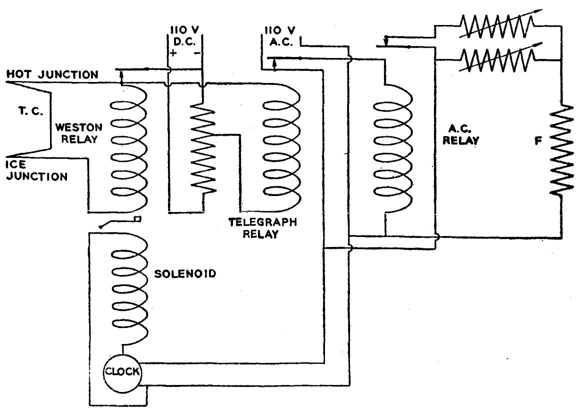

Fig. 2.—Temperature regulation circuit.

The heat of fusion was determined by the method of mixtures. The furnace was made of a heat-insulated solid copper block 12 cm. in diameter and 33 cm. long. In the center of the block to two-thirds of the way up from the bottom, was drilled a 1.5-cm. hole, which was 1 mm. larger than the diameter of the tube containing the sample. The tube was supported in the furnace by the wire inserted at the side of the block. Two holes of small diameter were drilled down from the top, one of them as closely as possible to the central bore. A No. 20 chromel–alumel calibrated thermocouple cased in a 5-mm. thin Pyrex tubing was inserted into this in order to measure the temperature of the furnace. A similar thermocouple for regulating the temperature of the furnace was inserted into the other. The block was heated electrically. The central bore was extended 3 cm. beyond the bottom with a monel tube of the same bore closed with a brass cap.

The calorimeter was made of a half-pint (210-cc.) silvered Dewar flask with a tightly fitting copper cover consisting of two copper sheets at 1 cm. apart. A "basket" of copper gauze was suspended from the cover near the bottom of the flask to catch the tube of stannic iodide as it dropped in from the furnace above. The heat capacity of the calorimeter was determined by the aid of a copper rod weighing 55 g. The rise in the temperature of the water was measured with a 6-junction (No. 32 copper–No. 26 advance) thermocouple whose junctions were cased in a thin 6-mm. Pyrex tube filled with pure naphthalene. The thermocouple was calibrated against the melting point of ice and the transition point of sodium sulfate decahydrate. The heat content of the Pyrex tubing used was determined at several temperatures.

The temperature of the furnace was regulated with a regulator built by Mr. Abrams of this Department. A diagram of it is shown in Fig. 2, which is self-explanatory except, perhaps, for the clock. This was so connected that it made a contact with the magnetic hammer every minute, which tapped the Weston relay in order to keep the fine wire of the relay from "sticking" to the contact. By means of this regulator, the temperature of the furnace was kept within ± 0.05° without any difficulty.

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(5) "Int. Crit. Tables," Vol. I, 1926, p. 163.

Measurements.—The tube containing the distilled sample of stannic iodide was heated in the furnace at a given temperature (within ± 0.05°) for at least one and one-half hours before it was dropped into the calorimeter, which contained a measured quantity of water at approximately the thermostat temperature, 25 ± 0.02°. The calorimeter was placed in the water thermostat; part of the copper cover was immersed in the water of the thermostat in order to keep its temperature uniform. The stirrer was then connected to the motor and the thermocouple was inserted into the calorimeter. The temperatures of both the water in the calorimeter and the furnace were read on the Leeds and Northrup type K_2 potentiometer, which was graduated to 0.5 microvolt, and it could be estimated easily to 0.1 microvolt. The potentiometer was connected to a sensitive galvanometer. With this set-up temperature changes of 0.001° in the calorimeter and of 0.01° in the furnace could be detected. Readings were made every two minutes until the rate of the change in the temperature of the water became uniform, then the sample tube was dropped into the calorimeter. About one minute elapsed between the time the stirrer was stopped and started again. The temperature change was recorded every two minutes until a uniform cooling rate was obtained. A complete run required from twenty-five to thirty-five minutes. The rate of heating due to stirring was on the average 0.001° per minute, and the rate of cooling was from 0.001 to 0.0012° per minute. The total temperature change in the calorimeter was from 0.6 to 2°.

Results and Discussion.—The value of the total heat capacity of the calorimeters used including 325 cc. of water, was approximately 340 cal., with the largest deviation amounting to 1.6 cal. for the first calorimeter and 0.15 cal. for the second. The specific heat of the Pyrex glass used could be expressed within ±0.1% from the measured values by $C_p = 0.1141 + 0.000253 23T$. The total heat of the copper rod used was derived from its specific heat equation

$$C_p = 0.09202 + 0.0000136T - \frac{452}{T}$$

determined empirically by Bronson, Chisholm, and Dockerty[6] from the results of their measurements.

The heat content of the solid with a mean deviation of ±20 cal. in the temperature interval between 25 and 144.5° is given by

$$C_p = 19.4 + 0.036T$$

where C_p is the molal heat capacity of the solid. The average deviation of the measured values from this equation is ±0.8% with the maximum deviation 1.5%. The curve for the total heat content of the liquid is a straight line, giving 40.1 ± 0.5 cal. per mole for the molal heat capacity in the range of temperature from 144.5 to 170°. We get 4600 ± 20 cal. for the molal heat of fusion. Hildebrand[7] estimated the value of ΔH_m from the entropy of fusion of other tetrahalides (chlorides and bromides) of the fourth group and from the solubility of stannic iodide in carbon disulfide, and obtained the value 3850 cal. per mole. This value is, of course, only an approximation and it is likely to be too small. If the melting and boiling points, the entropy of fusion and other physical properties of the halogens (except fluorine) are plotted, it is seen that changes from bromine to iodine are always greater than those from chlorine to bromine. A similar state of affairs results when the melting and boiling points of the tetrahalides of the fourth group are plotted. This indicates that the intermolecular forces are determined to a large extent by those halogen atoms surrounding the central atom and independent of it.[8] Moreover, these curves are roughly parallel to those of the halogens, but not coincident with them. This is to be expected from the fact that the molecular size and bond energies of these tetrahalides have some effect on their intermolecular forces and orientations in the liquid state.[9] Since the entropy of fusion of iodine is much greater than those of bromine and chlorine, we may assume that the entropy of fusion of stannic iodide should be greater than those of tetrachlorides and bromides.

If intermolecular forces of tetrahalides are determined largely by the halogen atoms surrounding the central atom, we should expect the solubility of stannic iodide in iodine and also that of iodine in stannic iodide[10] to obey closely the ideal law. This corresponds to the facts. The slope of the former solubility curve gives ΔH_m approximately equal to 4250. This value is lower than ours, but it is within their experimental accuracy.

Parks and Dodd[11] obtained $\Delta H_m = 4110$ cal. per mole from their rough experimental measurements employing also the method of mixtures. However, they have stated that there was a considerable amount of premelting near the melting point of the solid and so their results were not very reliable. We shall, therefore, take $\Delta H_m = 4600$ as the heat of fusion of stannic iodide at its melting point.

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(6) H. L. Bronson, H. M. Chisholm and S. M. Dockerty, *Can. J. Research*, **8**, 282 (1933).

(7) J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).

(8) W. M. Latimer, *ibid.*, **44**, 90 (1922).

(9) A. Peterlin, *Physik. Z.*, **37**, 43 (1936).

(10) (a) Van Klooster, *Z. anorg. Chem.*, **79**, 223 (1912); (b) W. Reinders and S. de Lange, *ibid.*, **79**, 230 (1912).

(11) Parks and Dodd, personal communication.

Acknowledgment.—I wish to thank Professor Hildebrand for his valuable suggestions and helpfulness during the course of this investigation, and Mr. John Lyman for his assistance in making the heat of fusion determinations.

Summary

The melting point of stannic iodide has been determined by the cooling method, and the value obtained was 144.5 ± 0.1°.

The vapor pressure of stannic iodide from its melting point to 250° has been determined by means of a glass click gage. The molal heat of vaporization calculated from the vapor pressure is 13,750 ± 50 cal. per mole at 25° and varies but little with temperature.

The heat of fusion of stannic iodide was found to be 4600 ± 20 cal. per mole at the melting point. The molal heat capacity of the solid can be expressed within 0.8% of the measured values in the temperature range 25° to the melting point by C_p 19.4 + 0.036T, while that of the liquid, from the melting point to 170° is 40.1 ± 0.5 cal. per mole.

BERKELEY, CALIFORNIA RECEIVED JULY 28, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

The Ultraviolet Absorption Spectra of Substituted Biphenyls[1]

BY LUCY W. PICKETT, GERTRUDE F. WALTER AND HELEN FRANCE

Investigations by Adams and others[2] have shown that those unsymmetrical derivatives of biphenyl which have substituents above a certain limiting size in the positions adjacent to the bond joining the two benzene nuclei may be resolved into stereoisomers. This phenomenon is explained as a result of the restriction of the rotation of the two benzene rings by the interference of the substituting groups. Some absorption spectra measurements made in a study of the physical properties of biphenyl derivatives showed unexpected differences in absorption which led to further investigation.

Methyl and chloro derivatives of biphenyl were chosen for the comparison because these groups do not show selective absorption in the region under investigation and are known to introduce comparatively slight modifications in the spectrum of benzene. Furthermore, these groups are sufficiently large to restrict the rotation of the benzene nuclei when they are in the 2,2′,6,6′-positions. The spectroscopic study was made with the simplest compounds available which had the above characteristics.

Experimental

Preparation of Compounds.—After purification the compounds were in each case crystallized from the optically pure solvent used in the measurements. After the absorption spectrum had been photographed, the material from which the sample was taken was further distilled or crystallized and photographs again taken. The second results agreed with the first in all cases except one as noted below in the discussion of the source and treatment of individual substances.

Biphenyl, m. p. 69–69.5°, obtained from Eastman Kodak Co., was purified by vacuum distillation and repeated crystallization from alcohol.

3,3′-Bitolyl,[3] b. p. 154° at 14 mm., was prepared by the condensation of *p*-iodotoluene with activated copper bronze and purified by two vacuum distillations. Although the product boiled constantly, a photograph taken at this time indicated slightly different absorption from that which was obtained from material distilled a third time. A fourth distillation yielded material identical with the latter.

4,4′-Bitolyl, m. p. 119.5–120°, was prepared by the condensation of *p*-bromotoluene and purified by vacuum distillation and crystallization from alcohol.

Bimesityl, m. p. 100–100.5°, was prepared from bromomesitylene by the method described by Moyer and Adams[4] and crystallized repeatedly from alcohol.

4,4′-Dichlorobiphenyl, m. p. 146.5–147°, was obtained from Eastman Kodak Co. and purified by recrystallization from alcohol.

2,4,6,2′,4′,6′-Hexachlorobiphenyl, m. p. 111.5–112°, was prepared from trichloroiodobenzene by condensation with copper bronze and recrystallized from alcohol. The trichloroiodobenzene was obtained from diazotization of trichloroaniline.

***o*-, *m*- and *p*-diphenylbenzenes,** m. p. 58, 87, 211.5°, were obtained from Eastman Kodak Co., and recrystallized repeatedly from benzene and alcohol.

Mesitylene, b. p. 66.4° at 24.5 mm., was obtained from Eastman Kodak Co., and vacuum distilled.

Absorption Spectra Measurements.—The absorption measurements were made with a Hilger quartz spectro-

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(1) This paper was presented at the New York meeting of the American Chemical Society, in April, 1935.

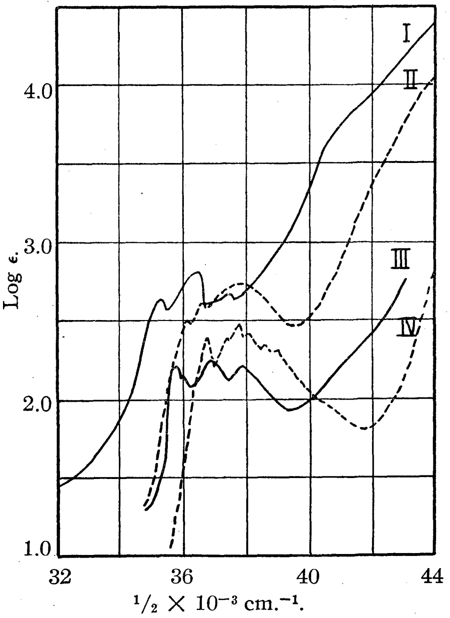
(2) An extensive review of this subject is given by Adams and Yuan. *Chem. Rev.*, **12**, 261 (1933).

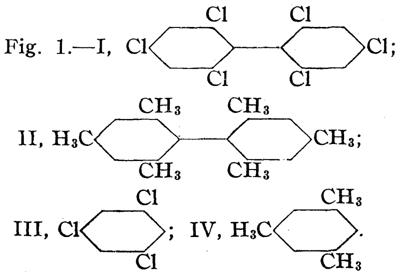
(3) This compound was prepared and photographed by Mary Dunlap.

(4) Moyer and Adams, THIS JOURNAL, **51**, 630 (1929).

graph (E-2) using a comparison method which has been described.[5] The source of light for most of the measurements was a condensed copper spark. In order to detect the presence of weak bands in the region of the band maxima the continuous light from a discharge through hydrogen was used for a series of closely spaced exposures made through slightly varying thicknesses of solution for each compound. Both ethyl alcohol and hexane were used as solvents and it was found that the curves obtained in the two solvents agreed closely except for very slight shifts toward the visible for the alcohol solutions. The absorption curves presented show the logarithm of the molecular extinction coefficient plotted against the wave number. Each curve represents over sixty experimental points which are not shown because they are so closely spaced.

Photographs of the solid biphenyl were made by mounting a very thin uniform crystal on a fluorite plate placed before the slit of the spectrograph normal to the light beam. The thickness was calculated from the interference color between crossed nicol prisms using the refractive indices determined by Hendricks and Jefferson.[6]





Discussion of Results

The absorption curves of 2,4,6,2′,4′,6′-hexachlorobiphenyl and bimesityl in alcohol solution are shown in Fig. 1. Each has a group of three absorption bands whose positions are as follows

Compound	Band maxima (1/λ cm.$^{-1}$)		
Bimesityl	36070	36480	37800
Hexachlorobiphenyl	35260	36350	37360

The position of the bands is practically the same in hexane and alcohol solutions, the difference being less than the error of measurement. It was especially noticeable in the chlorine compound that the bands had very sharp edges on the short wave length side.

For comparison are shown the absorption curves of the corresponding benzene derivatives, 1,3,5-trichlorobenzene and mesitylene as measured by Conrad-Billroth[7] and Wolf and Strasser.[8] The curve of the second compound is continued into the shorter wave region from data obtained in this Laboratory. It will be noticed that the band maxima of the most intense bands in the benzene derivative correspond to similar ones in the biphenyl compound which are displaced toward the visible. This shift is small and fairly constant (340, 350, 300 cm.$^{-1}$) for the chloro compounds but larger for those with methyl groups so that the second band of bimesityl almost coincides in frequency with the first band of mesitylene. The extinction coefficient of the band maxima of the biphenyl derivative is two or three times that of the corresponding benzene indicating that the absorption is nearly additive for the two benzene rings.

A similar comparison would be expected between monosubstituted derivatives of benzene and disubstituted derivatives of biphenyl but Fig. 2 shows that the curves for 3,3′- or 4,4′-bitolyl and 4,4′-dichlorobiphenyl in alcohol solution differ markedly from those of toluene[9] and monochlorobenzene.[10] In each case the narrow band structure is lost completely and the intensity increase is of the order of 100-fold. A difference of this kind is known to exist between benzene and biphenyl[11] and a recent article[12] by Seshan notes that the loss of banded structure is characteristic of the absorption of terphenyl and *s*-triphenylbenzene as well.

A study of the *o*-, *m*- and *p*-diphenylbenzenes in hexane solution with biphenyl included for com-

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[5] Carr, THIS JOURNAL, **51**, 3041 (1929).

[6] Hendricks and Jefferson, *J. Optical Soc. Am.*, **23**, 299 (1933); *cf.* Narasimham, *Indian J. Physics*, **6**, 233 (1931); Sundarajan, *Z. Krist.*, **93**, 238 (1936).

[7] Conrad-Billroth, *Z. physik. Chem.*, **B19**, 76 (1932); **B29**, 170 (1935); **B31**, 475 (1936).

[8] Wolf and Strasser, *ibid.*, **B21**, 389 (1933).

[9] Wolf and Herold, *ibid.*, **B13**, 201 (1931).

[10] Conrad-Billroth, *ibid.*, **B19**, 76 (1932).

[11] "International Critical Tables," Vol. V, p. 359.

[12] Seshan, *Proc. Indian Acad. Sci.*, **3A**, 148 (1936).

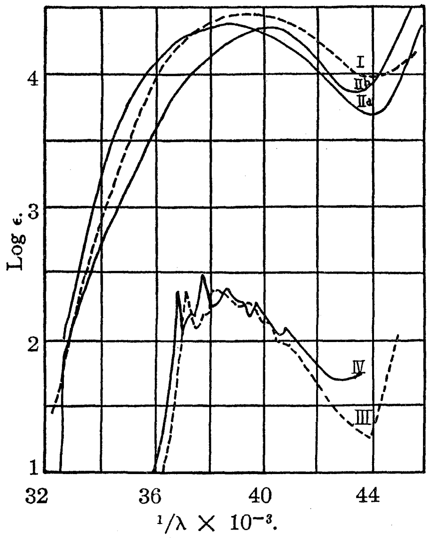
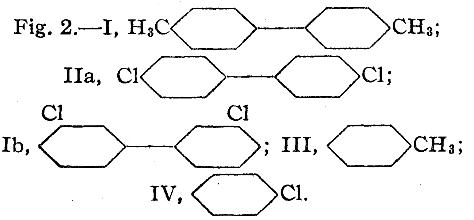


Fig. 2.—



parison is illustrated in Fig. 3. The absorption band of the meta compound is similar in position to that of biphenyl but of greater intensity while that of the para compound is displaced toward the visible and still slightly higher. In the ortho compound there is a second rise in absorption overlapping the band so that the minimum is not developed but the band which corresponds to those of the other isomers is of lower intensity.

In a study of several complete series of halogenated and methylated benzenes, Conrad-Billroth[7,13] has shown that the number and position of substituting groups causes some modification in the position and intensity of the absorption bands and has called attention to the para effect, namely, a heightened intensity exhibited by para compounds. The variation among biphenyl, dichlorobiphenyl and the bitolyls is of this order and is probably due to a similar cause. The magnitude of the intensity difference noted in the present paper is thought to require a different explanation.

An attempt at such explanation is hardly justified at present. The evidence shows that a molecule such as bimesityl absorbs light as two mesitylene molecules while bitolyl has a greatly increased probability of absorption compared to two toluene molecules. If the increased intensity of absorption directly results from the free rotation of the molecule, solid biphenyl should show less intense absorption than in solution. Measurements of single crystals showed that the absorption curve of solid biphenyl was shifted toward the visible by about 550 cm.$^{-1}$ from that of the solution and although the measurements did not extend to the top of the band there was no evidence of decrease in intensity of absorption. It is possible that the increased absorption may be dependent on the planar form of the molecule[14] since the most stable position for biphenyl in solution is probably planar, a form which the 2,2′,6,6′-derivatives cannot assume because of the interference of substituting groups. Similarly, *o*-diphenylbenzene is less likely to be planar than the *m*- or *p*-isomers. Regardless of explanation, these results suggest a possible means of distinguishing compounds of restricted rotation.

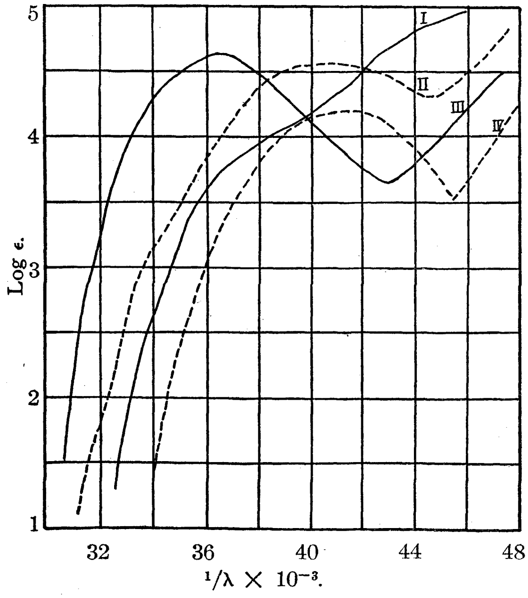


Fig. 3.—I, *o*-Diphenylbenzene; II, *m*-diphenylbenzene; III, *p*-diphenylbenzene; IV, biphenyl.

The effect of substitution of chloro and methyl groups on the wave length of the band maxima is just that which would be predicted from the results of a study of benzene derivatives.[13] The band is displaced toward the visible in all cases. This shift is greater for the chloro than the methyl derivatives, greater for the para than the meta compound, and approximately twice as great for the hexasubstituted as for the disubstituted compounds.

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(13) Also *Z. physik. Chem.*, **B20**, 222, 227 (1933).

(14) We are indebted to Dr. G. B. Kistiakowsky for suggesting this possibility.

The writers wish to express their appreciation to Dr. E. P. Carr and Dr. H. Stücklen for helpful suggestions.

Summary

Absorption curves showing molecular extinction coefficients in the region 32–46,000 cm.$^{-1}$ are given for five methyl and chloro derivatives of biphenyl and three diphenylbenzenes.

The compounds with restricted rotation differ markedly in the intensity and structure of the absorption band from those capable of free rotation.

SOUTH HADLEY, MASS. RECEIVED AUGUST 3, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

An X-Ray Study of Substituted Biphenyls

BY LUCY W. PICKETT

The explanation advanced for the stereoisomerism observed in certain unsymmetrical derivatives of biphenyl[1] is that the rotation of the benzene rings is restricted by the interference of sufficiently large groups in the 2,2′,6,6′-positions. The crystal structure of biphenyl derivatives with restricted rotation is thus of interest in confirming this explanation but so far no derivatives of this type have been solved completely. Magnetic measurements have been published recently[2] which may offer a clue to the orientation of the molecules and it thus seems advisable to make available the x-ray findings on substances of this type. The results of a continued investigation of some derivatives of biphenyl which were described in an earlier paper by Clark and Pickett[3] are here presented together with measurements on two similar compounds, racemic 3,3′-diaminobimesityl and quaterphenyl.

Experimental

Well-known experimental methods using single crystals and the Kα radiation of copper were employed. Rotation and Weissenberg photographs were used in the interpretation, and measurements of the relative intensity of reflections were made with the integrating photometer designed by Robinson.[4] Since the measurements made in this way are relative, the structure factors given in the paper include arbitrary constants. The preparation and melting points of the compounds are described in an earlier paper.[5] The optical observations were made with a Leitz petrographic microscope (GM).

The results of the unit cell and space group determinations are summarized in Table I while those results which present especial points of interest are considered individually in the following discussion. Most of the data in the table are like those presented in the earlier paper[3] but are included for convenient reference.

Bimesityl is reported in Groth[6] as monoclinic prismatic, exhibiting the forms (001), (100) and (110). A goniometric examination confirmed the angular measurements within the limits of experimental error and together with the x-ray data showed that the form designated as (110) was rather (012) (the *a*- and *c*-axes have been renamed to correspond with the usage for other biphenyls).

An optical examination of the tablets with extended (001) faces which are formed by crystallization from an alcohol–water mixture showed parallel extinction and positive elongation. The typical interference figure obtained shows one optic axis emerging at the edge of the field but by rotating the crystal on the *b*-axis an acute bisectrix figure was obtained which showed that the crystal is biaxial negative with small optic angle. The optic axes are in the (010) plane of this monoclinic crystal with the X-direction approximately 36° from the *c*-axis in the obtuse angle β.

Analysis of the x-ray photographs showed that the most probable space group is C_{2h}^5 or C_{2h}^4 depending on the questionable existence of a very weak (030) reflection. The conclusion is therefore that the *b* spacing is either exactly or practically halved. The intensities of the reflections

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[1] An extensive review of this subject was made by Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

[2] Krishnan and Banerjee, *Trans. Roy. Soc.* (London), **A234**, 265 (1935).

[3] Clark and Pickett, THIS JOURNAL, **53**, 167 (1931); Huggins, *ibid.*, **53**, 3823 (1931); Clark, *ibid.*, **53**, 3826 (1931).

[4] Robinson, *J. Sci. Instruments*, **10**, 233 (1933).

[5] Pickett, Walter and France, THIS JOURNAL, **58**, 2296 (1936).

[6] Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1919, Vol. V, p. 38.

TABLE I

SUMMARY OF CRYSTAL STRUCTURE DATA

Compound	Unit cell dimensions	*n*	Classification of missing reflections	Crystal class	Probable space group
Bimesityl	8.19 ± 0.03				
	8.54 ± .03	4	*h0l, l* odd	Monoclinic prismatic	
	22.10 ± .08		0*k*0, *k* odd (?)		C_{2h}^{5}
	95°46′				
1-3,3′-Diaminodimesityl	8.28 ± .02				
	8.63 ± .03	4	None	Monoclinic sphenoidal	C_{2}^{1}[a]
	22.50 ± .08				
	90°30′				
Racemic 3,3′-diaminodimesityl	8.45 ± .02		*h*00, *h* odd		
	8.45 ± .02	4	0*k*0, *k* odd		
	22.35 ± .08		00*l*, *l* odd		
Hexachlorobiphenyl	15.82 ± 0.04				
	8.42 ± .04	8	*hkl, k* + *l* odd	Monoclinic prismatic	C_{2h}^{6}[a]
	21.50 ± .06		*h0l, h* or *l* odd		
	91°49′				
2,2′-Diphenic acid	13.70 ± .07				
	11.95 ± .05	8	*h0l, h* odd	Monoclinic prismatic	C_{2h}^{5}[b]
	14.05 ± .07		0*k*0, *k* odd		
	91°40′				
Quaterphenyl	8.05 ± .02	2			
	5.55 ± .02		*h0l, h* odd	Monoclinic prismatic	C_{2h}^{5}
	17.81 ± .05		0*k*0, *k* odd		
	95.8° (app.)				

[a] The space group assignments differ from those in the early paper by Clark and Pickett,[3] *cf.* discussion. [b] This space group is the second alternative suggested by Clark.[3]

from a large number of planes have been measured and structure factors calculated therefrom. Attempts have been made to locate the positions of the individual atoms but the results thus far have been negative. Trial and error analyses show that the length of the molecule is not parallel to the *c*-axis although the unit cell dimensions indicate that the length is more or less parallel to this direction. One-dimensional Fourier projections of the density of the scattering matter along the normal to the (001) plane were made using all possible combinations of signs of terms but none of the contour maps obtained suggested the form of the molecule, probably because the projections so obtained were confused composites of more than one molecule.

***l*-3,3′-Diaminobimesityl** was prepared by Moyer and Adams.[7] Not only in unit cell dimensions but in the intensity of reflections from corresponding planes does this compound show a striking resemblance to bimesityl. It was first observed that like bimesityl the (*h0l*) and (0*k*0) planes where *l* and *k* are odd were missing but with long exposures, faint (101) and (010) reflections were unmistakably found. Since no other spacings were consistently halved, the space group C_2^1 was indicated with the molecules occupying two sets of equivalent positions, a possibility suggested by Dr. Huggins.[3] The evidence of the similar intensities shows that the molecules of the two compounds, bimesityl and *l*-3,3′-diaminobimesityl, must have very similar spatial arrangements. The two are alike in chemical structure except for the substitution of two hydrogen atoms by amino groups in the second. This suggests that whereas the second molecule of bimesityl in the unit cell may be derived from the first by reflection and a translation of one-half, corresponding molecules of the optically active compound would bear the same relation if the $\mathrm{NH_2}$ groups could be ignored, thus simulating the C_{2h}^5 symmetry. The presence of the asymmetrically placed amino groups makes reflection of the entire molecule impossible and lower real symmetry exists.

Racemic 3,3′-diaminobimesityl also prepared by Moyer and Adams[7] yields ambiguous results. Recrystallized from alcohol on a microscope slide, it forms square or rectangular tablets with parallel extinction and positive elongation from which acute bisectrix interference figures are obtained which indicate that the crystal is biaxially nega-

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[7] Moyer and Adams, THIS JOURNAL, **51**, 630 (1929).

tive. A Laue photograph with the x-ray beam parallel to the *a*-axis showed the two-fold symmetry. However Weissenberg photographs about perpendicular *a*- and *b*-axes appeared identical. It is possible that some type of twinning might give rise to these anomalous results.

2,4,6,2′,4′,6′-Hexachlorobiphenyl crystallizes from alcohol to form crystals with (001), (101), (111), (100) and (011) faces. Since no measurements of its crystal form have been reported,[8] goniometric measurements were made on six crystals which showed good reflections and the angular measurements recorded in Table II.

Table II

Angular Measurements of Hexachlorobiphenyl

Angle	No. of measurements	Range	Mean observed	Average deviation	Calculated value
(100):(001)	16	91°41′–91°56′	91°49′	4′	
(101):(111)	14	56°01′–56°11′	56°08′	3′	
(001):(101)	6	52°25′–52°33′	52°30′	2′	
(101):(100)	5	35°37′–35°46′	35°41′	4′	35°41′
(001):(011)	4	68°34′–68°47′	68°40′	4′	68°36′
(100):(011)	2	90°00′–90°34′	90°17′	17′	90°16′
(100):(111)	3	62°57′–63°11′	63°03′	5′	63°05′

These showed that the crystal is monoclinic prismatic with an angle β of 91°49′ and an axial ratio 1.8785:1:2.554. Extinction is unsymmetrical in the principal views. An acute bisectrix figure may be seen from the (101) face, which shows that the crystal is negative with a small optic angle. Examination of the x-ray photographs showed that of the planes with indices up to and including $h = 6$, $k = 3$, $l = 7$, those which may be classified as (hkl) where $k + l$ is odd and ($h0l$) where h or l is odd are missing. This led to the assignment of space group C_{2h}^6 instead of that reported in the earlier paper.

Quaterphenyl,[9] m. p. 310°, was kindly supplied by Dr. Robertson. It is very difficultly soluble and was finally crystallized in tiny flakes with (001) faces from monobromobenzene. Optical examination showed that the crystal is biaxially positive with the direction of vibration of the slow ray that which was later known to be the long axis of the molecule. The unit cell whose dimensions are shown in Table I is similar to those of biphenyl[3,10] or terphenyl[11] differing only in the length of the *c*-axis. Hertel and Romer[12] have reported the unit cell dimensions and space group of quaterphenyl.

The extremely small size of the crystal made it difficult to obtain reflections of measurable intensity from more than a small number of planes. Relative intensity values, measured photometrically are listed in Table III together with visual estimates of intensity of those reflections not suitable for measurement.

Table III

Observed and Calculated Intensities of Reflections from Quaterphenyl

Plane *hkl*	2 sin θ	Observed intensity Visual	Observed intensity Measured	Calcd. intensity $\theta = 34°$ $\phi = 12°$
001	0.086	Strong	42	98
002	.173	Medium	21	55
003	.259	Medium	20.1	51
004	.346	Strong	72	128
005	.432	Missing	0	0
006	.519	V. weak	1.5	3
007	.605	Weak	4.3	5
008	.692	Medium	21.6	22
009	.778	Medium	21.6	22
0010	.865	V. weak	1.7	1
200	.380	Weak		12
$20\bar{1}$	.385	Weak		7
$20\bar{2}$	.407	Weak		9
$20\bar{3}$	.444	Medium		20
$20\bar{4}$	.490	Missing		1
$20\bar{5}$	.550	Missing		3
$20\bar{6}$	.620	V. weak		5
$20\bar{7}$	.680	Medium	15.0	17
$20\bar{8}$	.760	M. strong	32.0	33
$20\bar{9}$	.837	Missing		0
$20\bar{10}$	.910	Missing		0
$20\bar{11}$	.990	Missing		0
$20\bar{12}$	1.070	V. weak		5
201	0.388	V. strong		682
202	.429	Missing		9
203	.475	Missing		1
204	.532	Missing		0
205	.598	Missing		0
206	.665	Missing		3
207	.740	Missing		1
208	.814	Missing		0
209	.890	Missing		2
2010	.964	Missing		0
2014	1.130	Weak		10
406	0.963	Weak		10

The position of the individual molecules in the unit cell was found through the assumption that their orientations are similar to biphenyl and terphenyl with a probable slighter tilt to the *c*-axis. After some trial and error experimentation, planar molecules with a carbon–carbon distance of 1.42

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[8] A private communication from Dr. Wherry which stated that the crystal was monoclinic with β = about 92° agrees with the present finding.

[9] This report was presented at a meeting of the American Chemical Society in September, 1933.

[10] Dhar, *Indian J. Physics*, VII (1), 43 (1932).

[11] Pickett, *Proc. Roy. Soc.* (London), **A142**, 333 (1933); Hertel and Römer, *Z. physik. Chem.*, **B21**, 292 (1933).

[12] Hertel and Römer, *ibid.*, **B23**, 226 (1933).

Å. in the ring and 1.48 Å. between rings were postulated, with centers of symmetry at the coördinates (000) and (1/2,1/2,0) and rotated 34° (θ) about the c-axis and 12° (ϕ) about the b-axis from an original position in the (100) plane with length parallel to the c-axis. The intensity of reflections from such a structure agreed well with the experimental values as shown in Table III. The lack of agreement in the lower orders of the (001) planes is not significant as the factors used in the calculation are uncertain in this region.

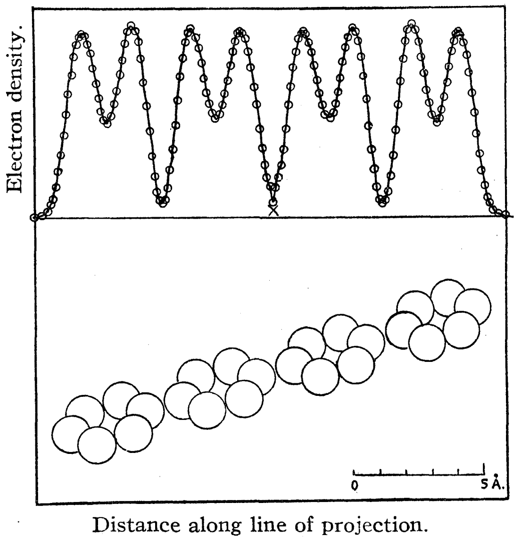

Fig. 1.—The projection of the electron density of quaterphenyl upon the line normal to the (001) plane is shown together with a diagrammatic representation of carbon atoms in an arrangement consistent with the projection. X is center of symmetry.

A one-dimensional projection of the electron density of the scattering matter in the crystal was made upon the normal to the (001) face. Relative F values were calculated from the measured intensities (I) of the first ten orders of the (001) planes according to the formula, $F = \left(I/1 + \frac{\cos^2 2\theta}{\sin 2\theta}\right)^{1/2}$ using the signs determined in the trial and error analysis described above. The electron density was found at points approximately 0.1 Å. apart (the unit cell length being divided into 180 parts), along the direction chosen for the projection, from the summation, $d = \Sigma F_{(001)} \cos 2\pi lz/c$. The values so obtained are plotted in Fig. 1 together with a molecular model which is consistent with the projection. The two molecules in the unit cell project as a single molecule since the atoms have like z-coördinates. Each peak apparently represents three unresolved atoms of carbon in each molecule.

From this experimental curve it is evident that the four benzene rings are extended coaxially while the equal width of peak suggests that the rings are coplanar. The length of projection of a single ring corresponds to that of a molecule with 1.42 Å. between the carbon atoms of the same ring and 1.48 Å. between those of adjacent rings if this molecule is placed at a tilt of 17.3° from the normal to the (001) face or 11.5° from the c-axis.

The above evidence does not exclude the possibility of a shorter molecule at a lesser tilt. For this reason, comparisons of observed and calculated structure factors were made for slightly differing structures (*e. g.*, for molecules with a distance between rings of 1.42 Å. and a tilt of 8.5°), using those planes which are accurately measurable and especially sensitive to change in length of the molecule, namely, (008), (009), $(20\bar{7})$ $(20\bar{8})$. The model described above with $\theta = 34°$, $\phi = 11.5°$, C–C = 1.48 Å. showed the best agreement with the experimental data. The structure factors of the above mentioned planes are insensitive to small changes in θ.

Krishnan and Banerjee[2] from measurements of magnetic susceptibilities independently reached the conclusion that the orientation of the quaterphenyl molecule was ±32° from the plane of symmetry and 17.1° from the normal to the (001) plane, results in close agreement with these.

The structure factors have been recalculated recently using the atomic f values for carbon in anthracene published by Robertson[13] and a carbon–carbon distance of 1.41 Å. which has been generally accepted for the aromatic carbon atom. Since there is less evidence for the distance 1.48 as existing between benzene rings these calculations were designed as a test of this distance. A comparison of structure factors for molecular models with $\theta = 32°$, $\phi = 11.3°$, a carbon–carbon distance in the ring of 1.41 Å. and the two alternatives 1.41 and 1.48 between rings is shown in Table IV with the experimental values. The results show conclusively that if the orientation of the molecule found from the magnetic susceptibility results and indicated independently by the x-ray work is correct, the distance between rings must be 1.48 rather than 1.41 Å. This is in accord with results of analyses of biphenyl[10] and terphenyl.[11]

[13] Robertson, *Proc. Roy. Soc.* (London), **A150**, 106 (1935).

TABLE IV

hkl	*F*, exptl.	*F*, calcd. C–C = 1.48	*F*, calcd. C–C = 1.41
008	49.5	49.3	37.4
009	53.0	53.1	65.0
$20\bar{7}$	40.5	38.1	27.3
$20\bar{8}$	63.6	66.0	75.3

Probable positions for the 48 carbon atoms in the unit cell are x,y,z; $\bar{x},\bar{y},\bar{z}$; $^1/_2 + x$, $^1/_2 - y,z$; $^1/_2 - x$, $^1/_2 + y,\bar{z}$; the values of x,y,z for the twelve carbon atoms in the half molecule are as follows

Atom	*x*	*y*	*z*
1	−0.018	0	0.040
2	+ .043	+0.186	.089
3	+ .009	+ .186	.165
4	− .087	0	.192
5	− .149	− .186	.144
6	− .115	− .186	.067
7	− .123	0	.272
8	− .061	+ .186	.321
9	− .096	+ .186	.398
10	− .192	0	.425
11	− .254	− .186	.376
12	− .220	− .186	.300

The writer wishes to acknowledge with appreciation the grant of the European Fellowship from the American Association of University Women which made possible the work; and to express to Sir William Bragg and the Managers of the Royal Institution her thanks for the privilege of making the measurements in the Davy Faraday Laboratory, and to Dr. K. Lonsdale for her helpful interest in the work.

Summary

Additional experimental data concerning the crystal structures of five biphenyl derivatives are presented.

The unit cell of quaterphenyl has the dimensions $a = 8.05$ Å., $b = 5.55$ Å., $c = 17.81$ Å., $\beta =$ approximately 95.8° and contains two centrosymmetrical molecules. Trial and error analyses together with a one-dimensional Fourier projection indicate that the molecules are oriented at an angle of 17.3° to the normal to the (001) plane in the acute angle β and that the carbon–carbon distance between benzene rings is 1.48 Å.

SOUTH HADLEY, MASS. RECEIVED AUGUST 3, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WELLESLEY COLLEGE]

Ultraviolet Absorption and Rotatory Dispersion of 3-Methylcyclohexanone[1]

BY H. S. FRENCH AND M. NAPS

The rotatory dispersion within an absorption band has thus far been recorded for only a limited number of compounds. We have been especially interested in such work on compounds containing the carbonyl group. It has been proved conclusively for several of these carbonyl compounds, especially camphor,[2] camphor-β-sulfonic acid,[3] and carvomenthone,[4] that the zero molecular rotation (and also the maximum of circular dichroism) occurs at a wave length greater by 60 to 110 Å. than the wave length of the maximum for the carbonyl absorption band. At least a slight shift in this direction may be noted in almost all the carbonyl compounds[5] thus far reported upon, although it is not so marked in the simpler ketones. This shift has been interpreted by some investigators[2,6] to mean an induced dissymmetry of the chromophore and a difference between the two carbon–oxygen valences. The use of rotatory dispersion curves in these cases shows therefore the non-homogeneity of an absorption band, or the fact that it is actually made up of two overlapping bands.

The present study was undertaken in order to collect further evidence concerning the carbonyl group by the use of a different cyclic ketone, 3-methylcyclohexanone,[7] simpler in structure than most of the carbonyl compounds previously used.

Previous determinations of the absorption spectrum of 3-methylcyclohexanone[8] were done

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[1] This work is included in a thesis submitted by Miss Naps to the Faculty of Wellesley College in partial fulfillment of the requirements for the degree of Master of Arts.

[2] Kuhn and Gore, *Z. physik. Chem.*, **B12**, 389 (1931).

[3] Lowry and French, *J. Chem. Soc.*, 2654 (1932).

[4] Lowry and Lishmund, *ibid.*, 709 (1935).

[5] Lowry and Gore, *Proc. Roy. Soc.* (London), **A135**, 13 (1932); Hudson, Wolfrom and Lowry, *J. Chem. Soc.*, 1179 (1933); Baldwin, Wolfrom and Lowry, *ibid.*, 696 (1935); Mathieu and Perrichtet, *Compt. rend.*, **200**, 1583 (1935); *J. phys. radium*, **7**, 138 (1936); Levene and Rothen, *J. Org. Chem.*, **1**, 116 (1936); *J. Chem. Phys.*, **4**, 48 (1936).

[6] Lowry and Walker, *Nature*, **113**, 565 (1924); Kuhn and Lehmann, *Z. Elektrochem.*, **37**, 549 (1931); Lowry, *ibid.*, **40**, 475 (1934); *Chemistry and Industry*, **477** (1935); Lowry and Allsopp, *Proc. Roy. Soc.* (London), **A146**, 313 (1934).

[7] This compound was kindly suggested to one of us by Professor T. M. Lowry of Cambridge University.

[8] Gelbke, *Jahrb. Radioakt. Elektronik*, **10**, 1 (1913); Henderson, Henderson and Heilbron, *Ber.*, **47**, 876 (1914); Purvis, *Proc. Cambridge Phil. Soc.*, **23**, 588 (1927).

either by the older Hartley–Baly method, or in solvents other than cyclohexane. Previous determinations of its rotatory power[9] have been carried out only for a limited number of wave lengths in the visible region of the spectrum. There have been no previous determinations of its rotatory dispersion in the ultraviolet.

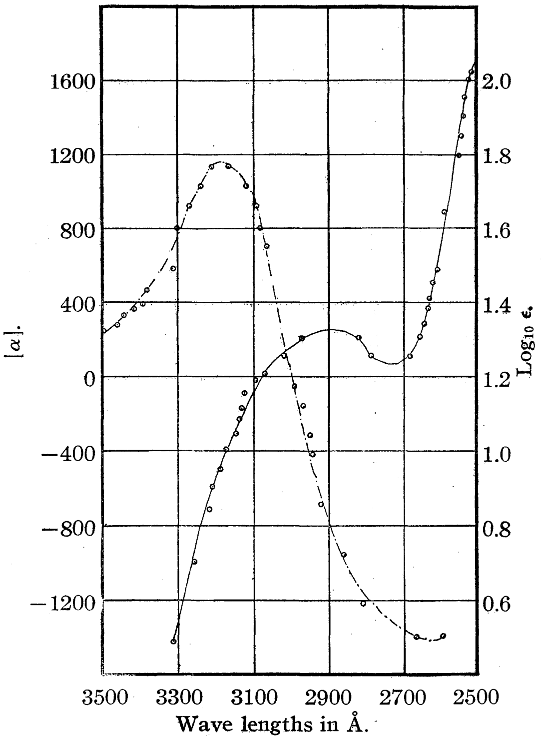

Fig. 1.—3-Methylcyclohexanone in cyclohexane: absorption spectrum, ————; rotatory dispersion, —·—·—·

The method for obtaining the absorption spectrum data has already been described in a communication from this Laboratory.[10] The rotatory dispersion data were obtained by the same method used in a previous publication.[3] The ultraviolet polarimeter was a new instrument, but was made by Hilger according to Lowry's specifications, and no new method was involved.

The 3-methylcyclohexanone is readily obtained in its optically active form by the hydrolysis of naturally-occurring optically active pulegone, and it is easily purified through its bisulfite addition compound.[11] The cyclohexane solvent used in both determinations was purified by the usual method.[12]

The results are shown in Tables I and II and in the curves.

TABLE I

ABSORPTION SPECTRUM OF 3-METHYLCYCLOHEXANONE IN CYCLOHEXANE

Concn. (a) 0.1003 *M;* (b) 0.0501 *M;* (c) 0.0114 *M*

	λ	$\log_{10} \epsilon$		λ	$\log_{10} \epsilon$
(a)	3355	0.30	(b)	2965	1.30
(a)	3310	.48	(b)	2815	
(a)	3260	.70	(b)	2660	
(a)	3220	.84	(b)	2641	1.34
(a)	3210	.90	(b)	2635	1.38
(a)	3185	.95	(b)	2620	1.45
(a)	3170	1.00	(b)	2612	1.48
(a)	3145	1.04	(c)	2595	1.64
(a)	3135	1.08	(c)	2550	1.79
(a)	3130	1.11	(c)	2545	1.85
(a)	3125	1.15	(c)	2539	1.90
(a)	3095	1.18	(c)	2535	1.95
(b)	3065	1.20	(c)	2515	2.02
(b)	3015	1.25	(c)	2499	2.06
(b)	2785		(c)	2488	2.09
(b)	2678		(c)	2470	2.12

TABLE II

ROTATORY POWER OF 3-METHYLCYCLOHEXANONE IN CYCLOHEXANE

Concn.: (a) 0.0928 g. per cc.; (b) 0.0093 g. per cc.; (c) 0.00093 g. per cc.; (d) 0.00037 g. per cc.; (e) 0.00019 g. per cc.

	λ	[α]		λ	[α]
(a)	4447	45.7	(b)	3314	564.5
(a)	4118	67.2	(c)	3068	689.6
(a)	4032	78.0	(c)	3076	797.1
(a)	4022	88.8	(c)	3306	
(a)	3878	99.6	(c)	3084	905.2
(a)	3786	121.1	(c)	3271	
(a)	3737	131.9	(c)	3116	1013.0
(a)	3704	142.7	(c)	3239	
(a)	3646	164.2	(c)	3166	1120.5
(a)	3609	175.0	(c)	3212	
(a)	3595	185.8	(c)	2987	−64.7
(a)	3546	207.3	(d)	2965	−161.7
(a)	3521	218.1	(e)	2948	−323.3
(a)	3497	239.7	(d)	2941	−431.0
(a)	3458	261.2	(d)	2918	−700.5
(b)	3445	327.6	(d)	2852	−969.8
(b)	3413	349.1	(d)	2805	−1239.6
(b)	3393	370.7	(e)	2667	−1401.0
(b)	3380	456.8	(e)	2598	

As expected, the positive and negative maxima of rotation occur approximately at the wave lengths corresponding to the half-width of the absorption band. The zero rotation is at 2970 Å., while the maximum of absorption is at 2890 Å. ($\log_{10} \epsilon = 1.34$). The zero rotation is thus displaced 80 Å. toward the red end of the spectrum.

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[9] Wallach, *Ann.*, **332**, 337 (1904); Tschugaeff, *Z. physik. Chem.*, **76**, 469 (1911); Rupe and Kambli, *Ann.*, **459**, 195 (1927); Tschugaeff and Chesno, *Trans. Sci. Chem. Pharm. Inst.* (*Moscow*), No. 19, 181 (1928).

[10] Acly and French, THIS JOURNAL, **49**, 847 (1927).

[11] Rupe and Glenz, *Ann.*, **436**, 202 (1924); Rupe and Kambli, *ibid.*, **459**, 206 (1927).

[12] Lowry and Hudson, *Trans. Roy. Soc.* (London), **A232**, 126 (1933).

There is therefore by this study added one more bit of evidence for the induced dissymmetry of the carbonyl group, and for the non-homogeneous nature of its absorption band.

Work is being continued along the same lines in this Laboratory on other cyclic ketones, and on similar compounds involving doubly-bound oxygen.

Summary

Tables and curves are given for the ultraviolet absorption and rotatory dispersion of 3-methylcyclohexanone in cyclohexane solution. These afford further evidence for the non-homogeneous nature of the carbonyl absorption band, and for the induced dissymmetry of the carbonyl group.

WELLESLEY, MASS. RECEIVED SEPTEMBER 15, 1936

[FROM THE LABORATORY OF BIOLOGICAL CHEMISTRY, WASHINGTON UNIVERSITY SCHOOL OF MEDICINE]

The Oxidation–Reduction Potentials of Derivatives of Thioindigo. I. Thioindigo Tetrasulfonate

BY PAUL W. PREISLER AND LOUIS H. HEMPELMANN

Until the mathematical formulation of the potential changes of the two-step oxidation–reduction process, involving one electron per step, by Michaelis[1] and by Elema,[2] resulting from their work upon the natural pigment pyocyanine, the potentials of all organic oxidation–reduction systems previously measured, which required two electrons per molecule for reduction, were considered to be one-step processes involving a pair of electrons.

Sullivan, Cohen and Clark,[3] who originally investigated systems of indigo sulfonate–leuco indigo sulfonate, considered these to be of the one-step two-electron class. Preisler and Shaffer[4] found that in the *p*H range of 10 to 12, red intermediate colors were formed, between the blue colors of the oxidants of indigo sulfonates and the yellow colors of the fully reduced reductants, when the oxidants were reduced by gradual addition of sodium hydrosulfite. A determination of the oxidation–reduction potentials in alkaline buffers revealed that these systems exhibited the characteristics of a two-step process.

An investigation of the potentials of simple and substituted sulfonates of the closely related thioindigo[5] is being conducted, to ascertain whether these exhibit the two-step oxidation–reduction process, to obtain further information on the nature of intermediary reduction products, and to study the effects of substitution on the potentials.

Since the initiation of this work, Remick[6] has reported on the potentials of thioindigo disulfonate and its reduction product and has concluded that his results with this compound show "... that the dye underwent a dimolecular reduction, involving but one electron per molecule of dye. The experimental data conform with the following mathematical formulation and establish this as the first system observed to undergo a thermodynamically reversible, dimolecular, oxidation–reduction reaction. No evidence of a second step was found." His mathematical formulation is developed on the assumption that this type of chemical reaction occurs.

This unusual interpretation of the thioindigo–leuco thioindigo system prompts the presentation at this time of results of work on the potentials of thioindigo tetrasulfonate, a representative derivative, which have been found to follow the same general mathematical formulations to which other previously studied organic systems seem to conform.

The potentials of the thioindigo tetrasulfonate–leuco thioindigo tetrasulfonate mixtures in acidic buffers of *p*H below 3 give typical curves approaching in shape those of a one-step two-valent process and in buffers of *p*H above 10.5 give curves showing transition into the shapes characteristic of the two-step process. In the *p*H range below 3, the E'_0–*p*H curve of the system oxidant–semiquinone lies in a region of more negative potential, and the E'_0–*p*H curve of the system semiquinone–reductant in a region of more positive potential, than that of the resultant oxidant–reductant curve; in the *p*H range above 10.5 the relative

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(1) L. Michaelis, *J. Biol. Chem.*, **96**, 703 (1932).

(2) B. Elema, *Rec. trav. chim. Pays-Bas*, **50**, 807, 1004 (1931); *J. Biol. Chem.*, **100**, 149 (1933).

(3) M. X. Sullivan, B. Cohen and W. M. Clark, *U. S. Public Health Reports*, **38**, 1669 (1923).

(4) P. W. Preisler and P. A. Shaffer, abstracts of papers presented at the American Chemical Society meeting, Chicago, Ill., 1933 (manuscript in preparation).

(5) P. Friedländer, *Ber.*, **39**, 1060 (1906); *Ann.*, **351**, 410 (1907).

(6) A. E. Remick, THIS JOURNAL, **58**, 733 (1936).

positions are reversed. The much deeper red colors of the partly reduced solutions in buffers above *p*H 10.5 offer additional evidence of semiquinone formation.

Experimental

Thioindigo tetrasulfonate may be prepared as a well-crystallized tetrapotassium salt by the following method. Suspend 10 g. of powdered thioindigo[7] (Rowe: Colour Index No. 1207) in 100 cc. of metallic-salt-free 30% excess sulfur trioxide, fuming sulfuric acid, in a long-necked flask lightly stoppered with a glass bulb. Heat for four hours or longer in a suitable bath at 145–150° under a hood since sulfur trioxide fumes are evolved copiously. Cool, pour the mixture into 1 liter of water and filter. Add small portions of 50% filtered potassium carbonate solution until but little carbon dioxide is evolved on addition and the mixture is still slightly acid to congo red. Filter off the light red precipitate and wash with a filtered 5% KAc–0.3% HAc solution to remove sulfate. Dissolve the precipitate in 1 liter of water, heat to boiling, add 100 cc. of a filtered 50% KAc–3% HAc solution and allow to cool slowly. Filter off the crystalline red salt and wash at least ten times with filtered 5% KAc–0.3% HAc solution and then at least ten times with 95% alcohol followed by some absolute alcohol; yield about 80%.

Analyses of material prepared by this method were made for sulfur and potassium: sulfur by fusion with sodium dioxide, potassium perchlorate and benzoic acid, in a Burgess–Parr bomb, precipitating as barium sulfate, igniting and weighing; for potassium by ashing to potassium sulfate and weighing. Samples were dried for five hours at 200° or at 135° and 5 mm. The moisture of different preparations varied from 6 to 9%.

Potassium: found, 20.03, 19.97, 20.01, average 20.00%; calcd., 20.34%. Sulfur: found, 24.66, 24.68, average 24.67%; calcd., 25.02%. Sulfur–potassium atomic ratio, 1.505, corresponding to 6.02 S to 4.00 K, calcd. 6 to 4. The slightly low values for potassium and sulfur are perhaps due to incomplete drying. Some of the moisture in the original sample is probably in the combined state, since the sample becomes much darker red on heating. The position of the KSO_3-groups was not determined but by analogy to indigo they are considered to be in the 5,5′,7,7′-positions.

The potentials of two platinum electrodes, immersed in the buffered solution of the thioindigo tetrasulfonate and its reduction products, were measured by a potentiometer system against a saturated calomel cell connected to the solution by a 5% agar–saturated potassium chloride bridge. Electrodes usually agreed to within 0.0002 volt. The calomel cell was standardized against a hydrogen electrode in 0.05 *M* acid potassium phthalate. The *p*H values of the buffers were determined by a hydrogen electrode.

The mixture of oxidant and its reduction products was made by titrating the deoxygenated, buffered, oxidant solution with a reducing agent similarly prepared. The volume at the beginning of the titration was 55 cc. and about 10 to 15 cc. was added. The E_0' values and slopes were determined graphically; the table summarizes the results.

POTENTIALS OF MIXTURES OF EQUIVALENT AMOUNTS OF OXIDANTS AND REDUCTANTS IN BUFFERS AT VARIOUS *p*H

*p*H	E_0' ox–red volt	$(E^1/_4 - E^3/_4)/2$	E_0' ox–semi	E_0' semi–red	Type buffer
0.04	0.408	(Between			HCl
.78	.362	0.014–0.015)			HCl
1.09	.345				HCl
1.48	.323				Citrate
2.05	.290				Citrate
2.97	.236				Citrate
3.56	.200				Citrate
4.00	.177				Citrate
4.46	.162				Citrate
4.73	.147				Citrate
5.42	.116				Acetate
6.53	.084				Phosphate
7.48	.047				Veronal
8.52	.018	0.015	−0.037	+0.073	Veronal
9.75	−.019	.018	− .037	− .001	Carbonate
10.29	−.034	.024	− .040	− .028	Carbonate
10.93	−.054	.030	− .034	− .074	Phosphate
11.18	−.059	.036	− .029	− .089	Phosphate

The buffers were 0.05 to 0.10 *M* in buffering ion and the reactants about 0.0005 *M;* no correction was made for the *p*H changes accompanying the reduction. An equivalent amount of sodium hydroxide was added to the titanium trichloride titrating solutions to compensate for the excess hydrochloric acid (7.493 *N*) in the commercial titanium trichloride (1.29 *M*) preparations. Titanium trichloride was used as reducing agent in buffers from *p*H 0.04 through 4.73; sodium hydrosulfite in the more alkaline buffers.

Commercial tank nitrogen, deoxygenated by passing over heated copper, was used to deoxygenate and stir the solutions. Temperature variations were less than 0.1° and the bath was maintained at 30.0°.

The number of equivalents involved in the complete reduction of indigo tetrasulfonate was determined by comparing the quantity of standard titanium trichloride solution required to reduce a known quantity with that required by a standard ferric chloride solution: 0.404 g. of thioindigo tetrasulfonate containing 5.6% moisture, was made up to 100.00 cc. Of this solution, 5.00 cc. was added to 50.00 cc. of hydrochloric acid, the final *p*H of this mixture being 0.78. At this *p*H, the potential mixture curve most closely resembled a two-electron shape curve, as given by $E_h = E_0' - (RT/nF) \log_e [(\text{Red})/(\text{Ox})]$, the E_0' values calculated from experimental measurements, taken at 1-cc. intervals, were within 0.001 volt of the theoretical E_0' for all mixtures containing from 6.3 to 94.9% of reductant. This solution required for complete reduction to a pale yellow solution, 15.8 cc. of a titanium trichloride solution in similar buffer. Five cc. of a 0.0101 *N* ferric chloride solution added to 50.00 cc. of about 1 *N* hydrochloric acid with titrated titanium trichloride of the same strength as used in the indigo tetrasulfonate determination required 15.6 cc., both end-points being determined graphically. Calculation shows that within the limits of

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[7] Obtained through the courtesy of the Society of Chemical Industry in Basle.

experimental error, two equivalents of reducing agent per mole of indigo tetrasulfonate were used. Similar relationships hold at all other pH values studied. The data of Knecht and Hibbert[8] on the use of titanium trichloride for determination of thioindigo led to the same conclusion.

The initial concentration of the oxidant was changed by adding 35 cc. of the above solution of hydrochloric acid of proper strength to make final pH of 0.78 and diluted to 55.00 cc. and then titrated with a titanium trichloride solution of seven times the concentration of the previously used solution. The E_0' of this titration was within 0.001 volt of the E_0' of the above titration. The maximum calculated pH change would correspond to about 0.002 volt. Concentration apparently has but little effect on potential in this pH region. All other titrations were made at about 0.0005 M initial oxidant concentration. The effect of concentration changes in the region of apparent semiquinone formation was not studied because of certain decompositions of the materials in the alkaline buffers, which would make the results questionable. The occurrence of semiquinones, rather than meriquinones, is not absolutely established but the results fit the general theoretical considerations and are analogous to those with indigo sulfonates where semiquinone formation seems the most likely explanation.

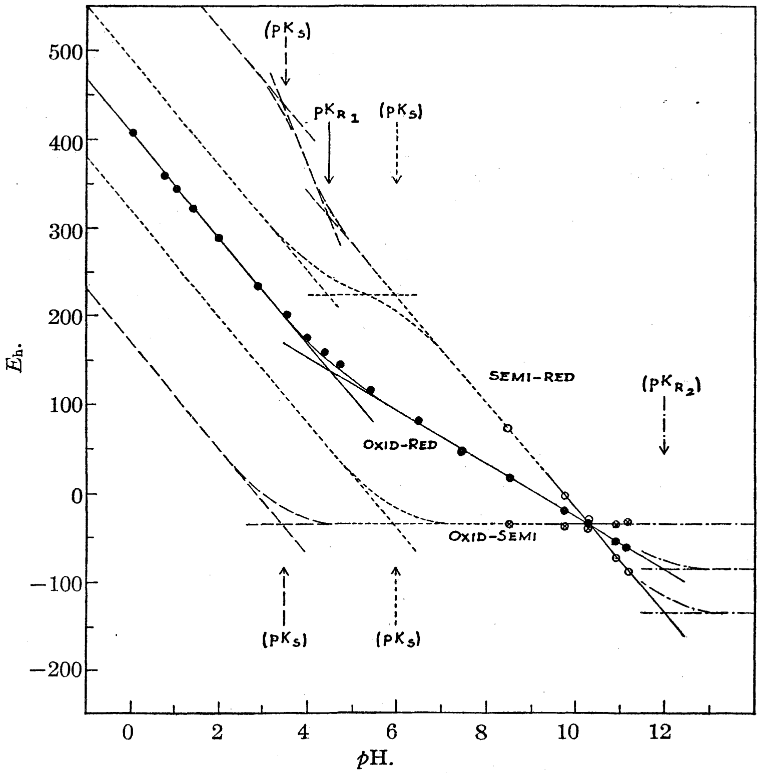

Fig. 1.

Discussion

The relationships existing between the two component oxidation–reduction systems and their resultant can be more easily recognized by a study of the graph showing the corresponding curves of E_0' against pH.

The change in slope of the resultant oxidant–reductant E_0'–pH curve at pH 4.5 indicates an ionization in the reductant; a color change to deeper yellow accompanies the ion formation. The experimental points from pH 8.5 to 11.2 set the slopes of the two primary E_0'-pH curves in this region. The pK of the semiquinone may be either lower or higher than this first pK at 4.5 of the reductant: if lower, the slopes of the semiquinone–reductant E_0'–pH curve (shown by the long-dash line), as it extends into more acid regions from pH 8.5, will change from 0.06 to 0.12 at the pK of the reductant and then to 0.06 again at the pK of the semiquinone; and, if higher, it will change (shown by the short-dash line), from 0.06 to 0.00 at the pK of the semiquinone and from 0.00 to 0.06 at the pK of the reductant. The slope of the oxidant–semiquinone E_0'–pH curve is 0.00 at pH 8.5 or higher pH and will change to a slope of 0.06 at the pK of the semiquinone. The relative positions of the pK values will determine which order of slopes will prevail, the curves drawn are for illustration of the effect only and do not represent accurate location.

An exact estimation of the pK of the semiquinone cannot be made with the data at hand: the instability of the potentials and the momentary deepening of the red color on addition of reducing agent in buffers about pH 5 suggests that a different ionic species of the semiquinone with somewhat slower reaction rate is perhaps present in this region, although its relative position to the first pK of the reductant is indeterminate. This would suggest that the pK of semiquinone is higher than the pK of reductant and that the system is of the type indicated by the short-dash lines.

The decomposition of materials in buffers of pH greater than 11.5 prevents the estimation of the second pK of the reductant. At higher pH than this pK, all E_0'–pH slopes would be 0.00 (shown by short-dash long-dash line).

The above interpretation seems consistent with the results obtained and follows the general theory

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[8] E. Knecht and E. Hibbert, *Ber.*, **40**, 3821 (1907).

which apparently holds for other readily reversible electromotively active organic oxidation–reduction systems. Preliminary experiments with certain other substituted thioindigo sulfonates indicate that these also exhibit semiquinone formation.

The formulation by Remick for the thioindigo disulfonate–leuco thioindigo disulfonate system was developed by considering that the reduction of two molecules of oxidant involving two electrons, one for each molecule, resulted in the formation of one molecule of reductant. This interpretation cannot be applied to the data presented for the tetrasulfonate, which show that one molecule of oxidant requires two reducing equivalents for conversion into one molecule of reductant. The introduction of the additional two sulfonic acid groups probably would not change the fundamental character of the reduction process of the thioindigo nucleus. The oxidation–reduction process for the several homologous indigo sulfonates has been found to be of the same type.

A comparison of the constants of indigo tetrasulfonate ($E_0 = 0.365$ volt and $pK_{R1} = 6.9$) and thioindigo tetrasulfonate ($E_0 = 0.409$ volt and $pK_{R1} = 4.5$) reveals that the substitution of S for N into the two heterocyclic organic nuclei would increase the E_0 value and the acidic dissociation of the reductant.

The instability of the oxidant or its reduction products and the semiquinone formation make thioindigo tetrasulfonate unsuitable for use as an oxidation–reduction potential indicator, except in acid pH regions below about pH 2.5.

Summary

The tetrapotassium salt of thioindigo tetrasulfonate has been prepared after direct sulfonation of thioindigo with fuming sulfuric acid. The oxidation–reduction potentials of the system thioindigo tetrasulfonate–leuco thioindigo tetrasulfonate have been determined for the pH range 0.0 to 11.5. The orange-red oxidant is converted into the yellow reductant by a reaction involving two reduction equivalents per molecule. The constants of the system established are $E_0 = 0.409$ volt and the first pK of the reductant is 4.5. Formation of a deeper red semiquinone was noted in the pH region from 8.5 to 11.5. Except in acid solution of pH less than 2.5, the material is not particularly suitable as an oxidation–reduction indicator.

ST. LOUIS, MO. RECEIVED AUGUST 31, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SCHOOL OF PHARMACY OF THE UNIVERSITY OF MARYLAND]

The Preparation of Some Organic Mercurials from Diazonium Borofluorides

BY MELVIN F. W. DUNKER,[1] EDGAR B. STARKEY AND GLENN L. JENKINS

Of the many methods of making aromatic mercury compounds, only two have made use of the diazonium salts. McClure and Lowy[2] noticed that on reducing electrolytically a diazonium solution using mercury electrodes, a small amount of mercurial was formed. They were also successful in preparing the corresponding mercury derivatives by stirring the diazonium solution with finely divided mercury produced mechanically. Nesmejanow[3] has succeeded in preparing the mercury derivatives of nuclei containing no group or groups such as alkyl, halogen, hydroxyl, etc., by treating the diazonium chloride–mercuric chloride double salt with precipitated copper powder; but when the nuclei contained groups such as carboxyl, nitro, sulfonic acid, etc.,[4] temperatures ranging from −10 to −70° were necessary.

Using more stable diazonium compounds such as the diazonium borofluorides of Balz and Schiemann,[5] and by producing very finely divided mercury by reduction with stannous chloride directly in the reaction mixture, it was found that some aromatic mercurials could be prepared in better yields. The replacement of the diazonium group with mercury was carried out at room temperature. In the course of the preparation of the necessary diazonium borofluorides, better yields were obtained by diazotizing in borofluoric acid.

The probable equations are illustrated by the following

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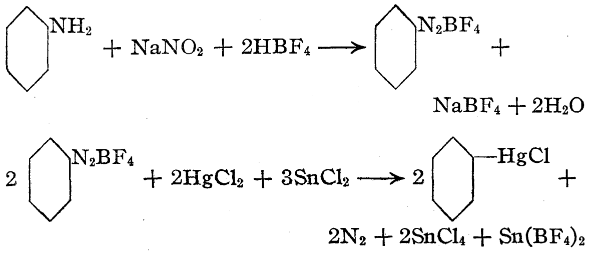
[1] Abstracted in part from a thesis submitted by Melvin F. W. Dunker to the Graduate School of the University of Maryland for the degree of Master of Science.

[2] McClure and Lowy, THIS JOURNAL, **53**, 319 (1931).

[3] Nesmejanow, *Ber.*, **62**, 1010 (1929).

[4] Nesmejanow and co-workers, *ibid.*, **67**, 130 (1934).

[5] Balz and Schiemann, *ibid.*, **60**, 1186 (1927).



Experimental

Diazonium Borofluorides.—The preparation of phenyl diazonium borofluoride illustrates the improved method referred to above.

To a mixture of 21.6 g. of aniline in 115 cc. of 50% fluoboric acid cooled in an ice-bath and stirred vigorously was added slowly a solution of 18 g. of sodium nitrite in 36 cc. of water. The diazonium compound was collected on a Büchner funnel, washed once with fluoboric acid, twice with alcohol and then thoroughly with ether. The yield was 90 to 97% of the theoretical amount as compared to 63% reported by Balz and Schiemann.[5] The yields of the other diazonium borofluorides are given in the table.

Phenylmercuric Chloride.—To a rapidly stirred suspension of 12.7 g. of $SnCl_2 \cdot 2H_2O$ and 7.0 g. of mercuric chloride in 50 cc. of acetone and 25 cc. of water was slowly added a solution of 5.0 g. of $C_6H_5N_2BF_4$ and 10.5 g. of mercuric chloride in 200 cc. of acetone. When the effervescence had ceased, the mixture was refluxed for about ten minutes and filtered hot, washing the residue with small portions of hot acetone. On standing, 5.25 g. of phenylmercuric chloride crystallized out, representing 60% of the theoretical based on aniline as compared to 51% obtained by Nesmejanow[3] and 70% obtained by the same author[4] at −70°. When the above reaction was carried out at 0 to 5°, a yield of 16% was obtained.

***p*-Chloromercuri-benzenesulfonic Acid, *o*-Chloromercuri-benzoic Acid, *p*-Chloromercuri-benzoic Acid.**—These compounds were prepared in the same manner, except that the diazonium borofluorides and mercuric chloride were added as a suspension rather than a solution, the volume of the solvent being reduced from about 300 to 100 cc. or less. The mercurial was extracted from the mixture with ammonium hydroxide and then converted to the free acid.

5-Chloromercuri-salicylic Acid.—In this case no appreciable yield was obtained using stannous chloride. To a suspension of 0.04 mole of precipitated copper powder and 0.016 mole of mercuric chloride in 150 cc. of water was added a dry mixture of 0.016 mole of the diazonium compound and 0.016 mole of mercuric chloride. The solid was filtered out and extracted with 10% sodium hydroxide. The sodium hydroxide solution was decolorized with charcoal and precipitated with hydrochloric acid. The mercurial was crystallized from acetone and then from alcohol.

In an attempt to prepare 2-chloromercuri-*p*-phenolsulfonic acid by the above method, the product obtained as indicated by analysis seemed to be 2,6-dichloromercuri-*p*-phenolsulfonic acid. Rupp and Herrmann[6] reported the mono-mercury compound to be unstable, changing to the di-mercury compound on crystallization from water.

***p*-Chloromercuri-diphenyl.**—Five grams of *p*-diphenyldiazonium borofluoride and 5 g. of mercuric chloride were mixed with 50 cc. of glacial acetic acid and added slowly to 5 g. of mercuric chloride and 8 g. of $SnCl_2 \cdot 2H_2O$ in 50 cc. of acetone. The mixture was stirred for two hours and filtered. On standing in a refrigerator, the filtrate deposited shiny white plates. The mercurial was crystallized from acetone. The crystals melted at 329° with decomposition. When copper powder was used, no mercurial was obtained. If the reaction mixture was cooled strongly, the decomposition was very slow. It is believed that this is the first report of the preparation of this compound.

Further applications of this method of synthesis of mercurials are being studied.

TABLE I

Aryl radical	Yield of diazonium compd., %	Chloromercuri compds. % yield based on amine	% Hg Calcd.	% Hg[a] Found
Phenyl	90–97	60	64.1	64.5
p-Sulfophenyl	99	46	50.6	49.9
			(as Na salt)	
o-Carboxyphenyl	46	34	56.2	55.1
p-Carboxyphenyl	76	Not detd.	56.2	55.8
p-Phenylphenyl	94	Small	51.6	51.8
3-Carboxy-4-hydroxyphenyl	75–85	26	53.7	53.4
2-Hydroxy-5-sulfophenyl	(In soln.)	Not detd.	62.3	60.0

[a] The mercury analyses were made by the method of Tabern and Shelberg, *Ind. Eng. Chem., Anal. Ed.*, **4**, 401 (1932).

Summary

1. Several aryl mercurials have been prepared by replacing the diazonium borofluoride group using freshly reduced mercury.

2. A new compound, *p*-chloromercuri-diphenyl has been prepared.

3. An improved method for the preparation of diazonium borofluorides is reported.

BALTIMORE, MARYLAND RECEIVED JUNE 15, 1936

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(6) Rupp and Herrmann, *Arch. Pharm.*, **254**, 500 (1916).

[Contribution from the Chemical Laboratory of the State University of Iowa]

The Reaction of Potassium Amide in Liquid Ammonia with Diarylbromoethenes

By George H. Coleman, William H. Holst and Roy D. Maxwell

The behavior of certain diarylchloroethenes and ethanes with potassium amide in liquid ammonia has been reported in a previous paper.[1] These compounds are not affected by boiling alcoholic potassium hydroxide but are very rapidly changed with the loss of hydrochloric acid by potassium amide in liquid ammonia to the corresponding tolanes. To illustrate, 1,1-di-*p*-tolyl-2-chloroethene forms *p,p'*-dimethyltolane. A series of such para substituted compounds was studied and as anticipated only symmetrical tolanes were obtained.

The present paper is a report of work with diarylbromoethenes having substituents in the ortho and in the meta positions of the aryl radicals. The bromoethenes were used since they could be prepared more easily than the corresponding chlorine compounds. In order to determine whether bromoethenes would undergo the rearrangement with potassium amide as readily as chloroethenes, the reaction was first tried with 1,1-diphenyl-2-bromoethene and 1,1-di-*p*-tolyl-2-bromoethene. Good yields of tolanes were formed.

The following ortho and meta substituted bromoethenes were used: 1,1-di-*o*-tolyl-2-bromoethene; 1,1-di-*o*-methoxyphenyl-2-bromoethene; 1,1-di-*m*-tolyl-2-bromoethene; and 1,1-di-*m*-methoxyphenyl-2-bromoethene. In each case the corresponding symmetrical tolane was obtained.

With respect to the mechanism of the reaction the question of whether a proton or the halide ion is first removed from the molecule was considered. The loss of a proton due to the presence of a base (in this case the amide ion, NH_2^-) has been proposed as the initial step in several related reactions.[2] However, the mechanism given by Whitmore and Fleming[3] for the formation of trimethylethylene and *t*-amyl acetate in the reaction of neopentyl iodide with silver acetate in acetic acid seems more applicable to the present case. According to this mechanism the diarylbromoethene first loses the halide ion leaving a carbon atom with a sextet of electrons. This carbon attracts a pair of electrons from the next carbon atom, the aryl group held by the shifting electron pair moving with it. The system thus formed is still electronically deficient. This deficiency is satisfied by the shift of an electron pair to form a triple bond and liberate a proton, thus forming a tolane.

If the loss of a proton is assumed as the first step the formation of a tolane can also be explained by a somewhat similar mechanism. However Buttenberg[4] obtained a mixture of diphenylvinyl ethyl ether and tolane when 1,1-diphenyl-2-chloroethene was heated with sodium ethylate at about 200°. The formation of diphenylvinyl ethyl ether is not readily explained if the removal of a proton is assumed as the first step. In the present work with potassium amide no amine was found in the reaction product but this would not necessarily exclude the mechanism proposed.

In the work with diarylchloroethenes[1] it had been observed that the yields of tolanes were 90% or above for all the compounds used except those containing the *p*-ethylphenyl, *p*-*n*-propylphenyl and *p*-*n*-butylphenyl groups. From these compounds liquid mixtures were formed containing not more than 60% of the pure tolanes. In seeking the cause for this difference the purity of the starting material was considered. Since these diarylchloroethenes were liquids the purity could not be as easily determined as with solids. Therefore several diaryldibromoethanes and diaryldichloroethanes, all of which were solids were prepared, carefully purified and treated with potassium amide in liquid ammonia. The compounds used were: 1,1-diphenyl-2,2-dibromoethane, 1,1-diphenyl-2,2-dichloroethane, 1,1-di-*p*-tolyl-2,2-dibromoethane, 1,1-di-*p*-tolyl-2,2-dichloroethane, 1,1-di-*p*-ethylphenyl-2,2-dibromoethane and 1,1-di-*p*-ethylphenyl-2,2-dichloroethane. From the phenyl and *p*-tolyl compounds the yields of tolanes were about 90–95% of the theoretical. With the *p*-ethylphenyl compounds the products were again oily mixtures from which yields of only 50–70% of pure tolanes could be separated.

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(1) Coleman and Maxwell, This Journal, **56**, 132 (1934).

(2) (a) Mills, *J. Soc. Chem. Ind.*, **51**, 750 (1932); (b) Hauser and Moore, This Journal, **55**, 4526 (1933); (c) Drake and McElvain, *ibid.*, **56**, 699, 1810 (1934); (d) Olivier, *Rec. trav. chim.*, **53**, 1093 (1934); (e) Hauser, Le Maistre and Rainsford, This Journal, **57**, 1056 (1935).

(3) Whitmore and Fleming, *J. Chem. Soc.*, 1269 (1934). See also This Journal, **54**, 3274 (1932).

(4) Buttenberg, *Ann.*, **279**, 327 (1894).

TABLE I

DIARYLBROMOETHENES, *sym*-DIARYLDIBROMOETHANES AND TOLANES

Substances	B. p. and m. p. °C.	Mm.	Br Analyses, % Calcd.	Found
1,1-Di-*o*-tolyl-2-bromoethene	150–155	1.5	27.87	28.01
1,1-Di-*m*-tolyl-2-bromoethene	186–191	10	27.87	28.22
1,1-Di-*o*-methoxyphenyl-2-bromoethene	M. p. 101.6–102.6		25.08	25.25
1,1-Di-*m*-methoxyphenyl-2-bromoethene	225–230	6	25.08	25.86
1,2-Di-*o*-tolyl-1,2-dibromoethane	M. p. 171–172		43.48	43.41
1,2-Di-*m*-tolyl-1,2-dibromoethane	M. p. 166.5–167		43.48	43.64
m,m'-Dimethyltolane	M. p. 73.5–74			
m,m'-Dimethoxytolane	M. p. 63–63.5			
o,o'-Dimethoxytolane	M. p. 124.5–125			
o,o'-Dimethyltolane	138–142	0.75	n^{20}_D 1.6228	

The structures of the tolanes were proved by two methods. One was the synthesis of the corresponding stilbene from monochloroacetal and Grignard reagents and the conversion of the stilbene to the symmetrical dibromoethane from which the tolane was formed by treatment with alcoholic potassium hydroxide. The other method was the reduction of the tolanes to bibenzyls with boiling absolute alcohol and sodium.[5] This method was also used to prove more conclusively the structures of some of the tolanes reported in the previous paper.[1]

Experimental Part[6]

Diarylbromoethenes.—The bromoethenes were prepared by treating the corresponding unsymmetrical diarylethenes with bromine by a modification of the method used by Hepp.[7] The dibromo compounds formed by the addition of bromine were unstable and lost hydrogen bromine either during the reaction or the subsequent heating.

The unsymmetrical diarylethenes were prepared by treating the methyldiarylcarbinols with phosphorus pentachloride or thionyl chloride to form the methyldiarylchloromethanes followed by subsequent splitting out of hydrochloric acid by treatment with alcoholic potassium hydroxide or pyridine. The methyldiarylcarbinols were prepared by the method of Allen and Converse.[8]

The general procedure used in preparing the diarylbromoethenes is illustrated by the following preparation of 1,1-di-*o*-tolyl-2-bromoethene. Fourteen and one-half grams of di-*o*-tolylmethylcarbinol was dissolved in 100 cc. of carbon tetrachloride. After cooling the mixture to 0°, 7.6 g. of thionyl chloride was slowly added with occasional shaking. After addition, the reaction was allowed to proceed at room temperature for four hours. Fifteen grams of pyridine was added and the mixture was allowed to stand overnight. A solid, pyridine hydrochloride, formed and was filtered off, after which the solution was washed with water to remove excess pyridine and then dried with calcium chloride. After separating from the calcium chloride 11 g. of bromine was added and the mixture allowed to stand one hour with occasional shaking. A little cyclohexene was added to remove the excess bromine and the solvent evaporated under reduced pressure. Thirteen grams of crude liquid remained. Upon distillation under reduced pressure, two fractions were obtained: Fraction (1) 1.9 g. boiling below 120° (1.5 mm.). Fraction (2) 10.9 g. boiling at 140–155° (1.5 mm.) (90% at 150–155°).

Anal. of Fraction (2). Calcd. for $C_{16}H_{15}Br$: Br, 27.87. Found: Br, 28.01.

The physical properties and analyses of the bromoethenes not previously recorded are given in Table I.

Tolanes.—The general procedure used in carrying out the reaction of potassium amide with bromoethenes was essentially the same as that reported by Coleman and Maxwell[1] with chloroethenes. The following preparation of *m,m'*-dimethyltolane will illustrate. Two grams of metallic potassium was dissolved in 350 cc. of liquid ammonia contained in a Dewar flask. The potassium was converted to the amide and 5 g. of 1,1-di-*m*-tolyl-2-bromoethene dissolved in ether was slowly added. After evaporation of the ammonia, the product was extracted with ether and the ethereal solution washed and dried. The solvent was evaporated under reduced pressure and 3.4 g. (91%) of crude solid, melting at 68–70°, remained. Upon recrystallization from 95% alcohol, 3.2 g. (89%) of pure *m,m'*-dimethyltolane melting at 73.5–74° was obtained. The tolanes prepared are given in Table I.

Stilbenes.—The preparation of the symmetrically substituted stilbenes was carried out by the method described by Späth.[9] *o,o'*-Dimethylstilbene and *m,m'*-dimethylstilbene were both obtained in this manner.

Bromination of Stilbenes.—The procedure followed is illustrated by the following preparation of 1,2-di-*o*-tolyl-1,2-dibromoethane. One gram of *o,o'*-dimethylstilbene was dissolved in 10 cc. of dry carbon tetrachloride. To this solution 0.8 g. of bromine in 10 cc. of carbon tetrachloride was added. A white crystalline solid melting at 171–172° was obtained; yield 1.6 g. The two *sym*-diaryldibromoethanes prepared are given in Table I.

Tolanes from *sym*-Diaryldibromoethanes.—One gram of 1,2-di-*m*-tolyl-1,2-dibromoethane was refluxed with alcoholic potassium hydroxide for three hours. The solution was decanted from the potassium bromide and 50 cc. of ether added. This solution was washed with water, sepa-

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(5) Aronstein and Holleman, *Ber.*, **21**, 2833 (1888).

(6) All melting points and boiling points are corrected.

(7) Hepp, *Ber.*, **7**, 1410 (1874).

(8) Allen and Converse, *Organic Syntheses*, Coll. Vol. I, 1932, p. 221.

(9) Späth, *Monatsh.*, **35**, 469 (1914).

rated and dried. The solvent was evaporated under reduced pressure. One-half gram of the crude tolane melting at 66–68° was obtained. Upon recrystallization from 95% alcohol, 0.48 g. of pure *m,m'*-dimethyltolane melting at 73.5–74° was obtained. A mixed melting point with *m,m'*-dimethyltolane prepared from 1,1-di-*m*-tolyl-2-bromoethene showed no depression.

The same procedure was used with 1,2-di-*o*-tolyl-1,2-dibromoethane. *o,o'*-Dimethyltolane was obtained, n^{20}_D 1.6214. The index of refraction of the tolane prepared from 1,1-di-*o*-tolyl-2-bromoethene was n^{20}_D 1.6228.

Bibenzyls.—All tolanes were reduced by the following method which is a modification of the one described by Aronstein and Holleman.[5] One gram of tolane was dissolved in 15 cc. of absolute alcohol. The solution was heated to boiling and immediately poured, with caution, into a flask containing 1.5 g. of metallic sodium, cut in small pieces and freed from oxide and ligroin. The flask was then attached to a reflux condenser and the mixture refluxed until all the sodium was dissolved.

The mixture was cooled and 60 cc. of distilled water was added to decompose the sodium ethylate after which the entire solution was extracted with 100 cc. of ether. The ethereal solution was dried, filtered and the solvent evaporated under reduced pressure. One and one-tenth grams of crude bibenzyl melting at 49–51° remained. One gram of pure bibenzyl melting at 51.5–52.5° was obtained upon recrystallization from 95% alcohol. A mixed melting point with pure bibenzyl showed no depression. The bibenzyls prepared by this procedure are given in Table II.

TABLE II

BIBENZYLS

Substance	M. p., °C.	Reported in literature, °C.
Bibenzyl	51.5–52.5	52.5
p,p'-Dimethylbibenzyl	81–81.5	82
m,m'-Dimethylbibenzyl	Oil	Oil
o,o'-Dimethylbibenzyl	65.5–66	66.5
p,p'-Dimethoxybibenzyl	126.4–126.8	126–127
m,m'-Dimethoxybibenzyl	39.5–39.8	39–40
o,o'-Dimethoxybibenzyl	84–84.4	86–87
3,3',5,5'-Tetramethylbibenzyl	86–86.6	.....
p,p'-Diethylbibenzyl	69.8–70.2	.....

unsym-**Diaryldichloroethanes.**—The following unsymmetrical diaryldichloroethanes were prepared from dichloroacetal and aromatic hydrocarbons by the methods described by Buttenberg[4] and by Wiechell:[10] 1,1-diphenyl-2,2-dichloroethane, 1,1-di-*p*-tolyl-2,2-dichloroethane and 1,1-di-*p*-ethylphenyl-2,2-dichloroethane.

unsym-**Diaryldibromoethanes.**—Three unsymmetrical diaryldibromoethanes corresponding to the chloroethanes were prepared from dibromoacetal and aromatic hydrocarbons. The following procedure for the preparation of 1,1-di-*p*-tolyl-2,2-dibromoethane is typical.

Twenty-five grams of dibromoacetal[11] was dissolved in 20 g. of toluene in a 500-cc. Erlenmeyer flask. This mixture was cooled to 5–8° and 75 cc. of concd. sulfuric acid added with stirring at such a rate that the temperature did not rise above 50°. The mixture was stirred for one hour after addition of the acid. It was then poured into 600 cc. of ice and water, whereupon a solid separated; 16.8 g. (50%) melting at 93–96° was obtained. After recrystallization from 95% alcohol the melting point was 95.5–96.5°.

Tolanes from Diaryldibromoethanes and Diaryldichloroethanes.—The reactions of these compounds with potassium amide were carried out in essentially the manner described for the ethenes except that the relative amount of potassium amide was doubled. The results for the six compounds used are listed in Table III. The products were identified by mixed melting points with authentic samples.

TABLE III

DIARYLDICHLOROETHANES AND DIARYLDIBROMOETHANES WITH POTASSIUM AMIDE IN LIQUID AMMONIA

Substance	M. p., °C.	Yield of tolanes, %
1,1-Diphenyl-2,2-dibromoethane	79.5–80.5	95
1,1-Diphenyl-2,2-dichloroethane	74–75	91
1,1-Di-*p*-tolyl-2,2-dibromoethane	95.5–96	92
1,1-Di-*p*-tolyl-2,2-dichloroethane	80–80.5	86
1,1-Di-*p*-ethylphenyl-2,2-dibromoethane	79–79.5	73
1,1-Di-*p*-ethylphenyl-2,2-dichloroethane	56–56.5	52

Summary

1. The action of potassium amide in liquid ammonia on 1,1-diaryl-2-bromoethenes causes the loss of a molecule of hydrogen bromide and the rearrangement of the molecule to form substituted tolanes.

2. A mechanism for the reaction is suggested. A given substituent in the phenyl group of the ethene is found in the same position relative to the point of attachment of the phenyl radical in the corresponding tolane.

IOWA CITY, IOWA

RECEIVED AUGUST 31, 1936

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[10] Wiechell, *Ann.*, **279**, 337 (1894).

[11] Dworzak, *Monatsh.*, **46**, 255 (1925).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Reduction of Acetobromoarabinose by Zinc and Acetic Acid[1]

BY GEORGE E. FELTON

The reaction of a suspension of zinc dust in acetic acid on an acetobromo sugar was carried out first by Emil Fischer.[2] The object of his experiment was to replace the bromine atom of the acetobromoglucose by hydrogen to obtain thereby an acetylated anhydrosorbitol derivative, tetraacetyl styracitol. As is now well known the product sought was not obtained by this method. However, a good yield of an unsaturated acetylated glucose derivative, named triacetyl glucal, was secured. The glucal and similar derivatives of other hexoses, pentoses and disaccharides have since proved of great value in the synthesis of new compounds, so that the discovery of this reaction is now considered a very fortunate occurrence in carbohydrate chemistry.

As a step in the preparation of *l*-arabinal, to be used for degradation to *l*-erythrose by means of ozone splitting[3] acetobromoarabinose was reduced numerous times by means of zinc and acetic acid. The yields obtained by Austin and Humoller[4] with zinc containing 5% of a copper–zinc couple were practically exactly duplicated by using a few drops of chloroplatinic acid for each preparation as had been suggested by Bergmann, Schotte and Rennert[5] in the preparation of rhamnal.

Gehrke and Aichner[6] reported that the products of the zinc and acetic acid reduction of acetobromoarabinose were a low boiling compound of watery consistency, diacetylarabinal and a higher boiling very viscous compound, triacetylarabinose. The triacetylarabinose was identified by acetylating to give a known tetraacetate. Besides the two reported compounds a third product has now been obtained. This product remained in the distilling flask after the diacetylarabinal and triacetylarabinose had been driven off as much as possible. The new compound was secured in crystalline form by taking up the residue in hot alcohol and allowing the solution to cool. If a large amount of sirup remained in the flask, the alcohol solution had to be seeded to effect a separation of the crystalline compound.

The properties of this new compound were as unexpected as those of the first glucal preparation. The derivative contained no halogen, unsaturated linkages, or free reducing groups detectable by boiling Fehling's solution. From benzene it was obtained in the form of needles melting at 167–169°, whereas from absolute alcohol it appeared as diamond-shaped plates melting at 184.5–185.5°. Each form was readily converted into the other and neither contained any solvent of crystallization. The compound was obtained from 95% alcohol occasionally in the lower melting form but most often in the higher.

After acid hydrolysis the compound reduced Fehling's solution, thereby suggesting a glycosidic linkage. The freezing point lowering in benzene showed a molecular weight of about 390. Four acetyl groups were found by alkaline hydrolysis. Carbon and hydrogen analyses agreed most closely with the values calculated for a tetraacetyl desoxypentose disaccharide.

The acetyl groups were removed by barium hydroxide hydrolysis and the acetyl free sugar obtained in crystalline form. It possessed an unsharp decomposition point of about 177–180°. The acetyl free product did not reduce Fehling's solution until after acid hydrolysis. The carbon and hydrogen analysis agreed with the values calculated for a desoxypentose disaccharide.

Attempts to prepare a benzylphenylhydrazone, after hydrolyzing by refluxing with dilute hydrochloric acid, failed to yield a crystalline derivative. This negative result may have been due to decomposition of the simple sugar formed by the hydrolysis.

Experimental

Reduction of Acetobromo-*l*-arabinose.—The reduction of acetobromoarabinose was carried out according to the procedure of Levene and Mori[7] for the preparation of diacetylxylal. The diacetylarabinal and triacetylarabinose formed from 90 g. of acetobromoarabinose were distilled

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[1] This investigation was supported in part by a grant from the Iowa State College Industrial Science Research fund for the study of carbohydrate degradation and utilization.

[2] Fischer and Zach, *Sitzb. kgl. preuss. Akad. Wiss.*, **16**, 311 (1913).

[3] Felton and Freudenberg, THIS JOURNAL, **57**, 1637 (1935).

[4] Austin and Humoller, *ibid.*, **56**, 1152 (1934).

[5] Bergmann, Schotte and Rennert, *Ann.*, **434**, 86 (1923).

[6] Gehrke and Aichner, *Ber.*, **60**, 918 (1927).

[7] Levene and Mori, *J. Biol. Chem.*, **83**, 809 (1929).

off in a vacuum as completely as possible without heating the bath to over 150°. The residue remaining in the distilling flask was dissolved in 10 cc. of warm 95% alcohol. This solution was allowed to stand at room temperature until crystallization of the new compound reached completion. Cooling to 0° would precipitate sirupy reducing compounds which had not been removed by the distillation. The crystallization at room temperature was very satisfactory although low yields of the non-reducing compound necessitated the use of seed crystals. The solid product was then filtered and purified by recrystallization from a small amount of absolute alcohol. One recrystallization served to free the product from reducing materials and further recrystallizations caused no more change in its physical constants. The crystals were diamond-shaped plates and melted at 184.5–185.5°; $[\alpha]^{23}\mathrm{D}$ +69.2° (0.1705 g. in 9.98 cc. of chloroform in a 1.1-dm. tube rotated 1.30° to the right). Recrystallized from benzene the compound formed needles which melted at 167–169°; $[\alpha]^{23}\mathrm{D}$ +69.5° (0.1774 g. in 9.98 cc. of chloroform in a 1.1-dm. tube rotated 1.36° to the right). Neither crystalline form lost any weight on drying over phosphorus pentoxide at 78° in a vacuum.

The new compound was secured in yields of from 0.1 to 1 g. for each 90 g. of acetobromoarabinose reduced. The yields of diacetylarabinal and triacetylarabinose were 34 g. and 8 g., respectively.

The compound was easily soluble in chloroform, warm alcohol, ethyl acetate and acetic acid, slowly soluble in benzene, insoluble in cold alcohol and ether and very insoluble in water.

The non-reducing material gave a molecular weight of 390 (0.5706 g. in 80.5 g. benzene gave a freezing point lowering of 0.094°). A tetraacetyl desoxypentose disaccharide would have a molecular weight of 418.

Anal. Calcd. for $C_{18}H_{26}O_{11}$ (418): C, 51.65; H, 6.26; CH_3CO, 41.1. Found: C, 51.44; H, 6.25; CH_3CO, 40.7.

Desoxypentose Disaccharide.—Three-tenths gram of tetraacetyl desoxypentose disaccharide was deacetylated by dissolving in 25 cc. of water containing 1 g. of barium hydroxide. The solution was freed of excess barium hydroxide by carbon dioxide. The barium carbonate was removed by filtration and the water evaporated off under reduced pressure. The residue, which still contained inorganic salts, was extracted several times with warm absolute alcohol and the alcohol was removed by a vacuum distillation. The residue remaining in the distilling flask was extracted with a small amount of water to free the preparation from any compound which had not been deacetylated. The water solution was evaporated slowly in a vacuum desiccator over phosphorus pentoxide. After the water had been removed the compound solidified. The yield was 0.16 g. or 90%. After recrystallization from isopropyl alcohol and ether the desoxypentose disaccharide melted at 177–180°. The melting point was not sharp and there was a great deal of decomposition.

Anal. Calcd. for $C_{10}H_{18}O_7$ (250): C, 48.00; H, 7.25. Found: C, 47.80; H. 6.81.

Acknowledgment—The author wishes to express his appreciation to Dr. R. M. Hixon and Dr. W. Freudenberg for their advice and suggestions and to Dr. I. B. Johns for the micro-analyses.

Summary

The reduction of acetobromoarabinose was found to yield a non-reducing compound which had not been previously reported. The analysis of the new compound showed it to be a tetraacetyl desoxypentose disaccharide. The free disaccharide was also prepared in crystalline form.

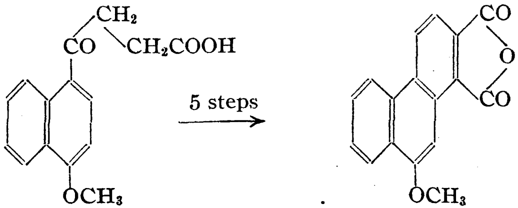
AMES, IOWA RECEIVED SEPTEMBER 29, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Synthesis of Phenanthrene and Hydrophenanthrene Derivatives. IV. Hydroxylated Compounds

BY L. F. FIESER AND E. B. HERSHBERG

This work was undertaken with the idea that the introduction of hydroxyl or methoxyl groups into the phenanthrene dicarboxylic anhydrides[1] and the hexa- or octahydrophenanthrene dicarboxylic anhydrides[2] previously described might afford substances of oestrogenic activity, the presence of hydroxyl and carbonyl groups in different parts of the molecule establishing at least a superficial resemblance to oestrone. One such compound was prepared from the condensation product of succinic anhydride and α-methoxynaphthalene, I, by reduction, esterification, condensation with ethyl oxalate, cyclization and dehydrogenation, giving 9-methoxyphenanthrene-1,2-dicarboxylic anhydride, II.



I II

An anhydride of a second type was obtained

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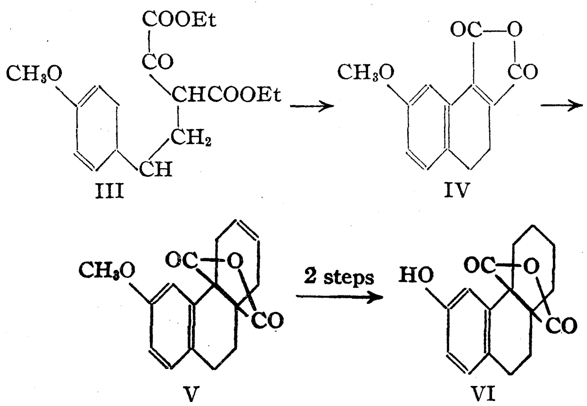
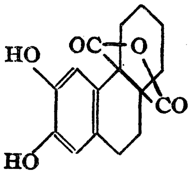
(1) Fieser and Hershberg, THIS JOURNAL, **57**, 1851 (1935).

(2) Fieser and Hershberg, *ibid.*, **57**, 2192 (1935).

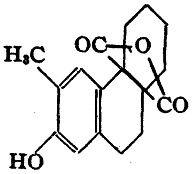
from γ-(4-methoxyphenyl)-butyric acid, readily prepared from anisole and succinic anhydride, through the oxalyl derivative III, the unsaturated anhydride IV, and the butadiene addition product V. After saturation of the active double bond this was demethylated satisfactorily, giving VI.



The 6,7-dihydroxyoctahydrophenanthrene-11,12-dicarboxylic anhydride VII was prepared similarly starting with veratrole, while VIII was obtained from Martin's γ-(3-methyl-4-methoxyphenyl)-butyric acid.[3] The only noteworthy observation to be recorded in connection with the syntheses is that in the Bougault cyclization of oxalyl derivatives such as III, or that from I, with sulfuric acid the unsaturated anhydride is often accompanied by a considerable amount of the corresponding aromatic anhydride. Since this has not been observed in other cases it appears that methoxyl groups render the dihydro derivatives particularly susceptible to the dehydrogenating action of sulfuric acid. By using acid just strong enough to effect the cyclization, the aromatization in some cases can be prevented or at least minimized. It should be noted that by heating the unsaturated compounds or the crude mixtures with sulfur, naphthalene derivatives of use in general synthetic work can be obtained easily in good yield. The 6-methoxy-, 7-methoxy- and 6-methoxy-7-methyl derivatives of 1,2-naphthalic anhydride (naphthalene-1,2-dicarboxylic anhydride) are described in this paper.



VII



VIII

In the first paper of this series[1] we cited a preliminary report from Dr. G. Pincus regarding the physiological activity of phenanthrene-1,2-dicarboxylic anhydride and its 3,4-dihydro derivative. The statements unfortunately were incomplete and misleading, as it was implied that the standard technique of bio-assay had been employed. Actually the anhydrides have given only negative results when injected subcutaneously into either spayed mice or immature rats even in large dosages. The reported cornifications were observed following the intraperitoneal injection into spayed mice of two 0.1-cc. doses of a solution of the material in sesame oil made twelve hours apart, and the appearance of a single cornified smear in any individual in six days was considered positive. In later experiments Pincus and Werthessen[4] abandoned the first technique as unreliable and developed a second special test method, also based on intraperitoneal injections, which seems to have promise as a preliminary guide. They report that in this more rigid test phenanthrene-1,2-dicarboxylic anhydride and its dihydro compound are inactive in relatively large dosages but that the compounds II, VI, VII and VIII described in the present paper give positive results and seem to be comparable with 1-keto-1,2,3,4-tetrahydrophenanthrene in oestrogenic activity, as judged by the special test. According to their ratings the dihydroxy compound VIII is the most active substance of the group and is more potent than ketotetrahydrophenanthrene.

Experimental Part[5]

Condensation of Phenol Ethers with Succinic Anhydride.—The Friedel and Crafts reactions of anisole and veratrole with succinic anhydride have been conducted in carbon bisulfide[6] or benzene[7] solution (no yields given) and, apparently with better results, using nitrobenzene[8,9] or tetrachloroethane.[10] After many trials in this Laboratory with these and other ethers, we found the following procedure very satisfactory and convenient: 0.4 mole of anisole (or veratrole) is dissolved with 0.42 mole of succinic anhydride in 400 cc. of tetrachloroethane and 100 cc. of nitrobenzene. The stirred solution is cooled to 0–5° (thermometer in liquid) and 0.84 mole of aluminum chloride ($AlCl_3$) is added gradually, keeping the temperature at 0–5°. At the end of the addition (one to two hours) a clear solution usually is obtained and it is allowed to stand

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[3] Martin, THIS JOURNAL, **58**, 1438 (1936).

[4] Pincus and Werthessen, *Science*, **84**, 45 (1936).

[5] All melting points are corrected. Analyses by Mrs. G. M. Wellwood.

[6] Bargellini and Giua, *Gazz. chim. ital.*, **42**, I, 197 (1912).

[7] Krollpfeiffer and Schäfer, *Ber.*, **56**, 630 (1923).

[8] Haworth and Mavin, *J. Chem. Soc.*, 1485 (1932).

[9] Rosenmund and Schapiro, *Arch. Pharm.*, **272**, 313 (1934).

[10] Mitter and De, *J. Indian Chem. Soc.*, **12**, 747 (1935).

at 0–5° (packed in ice in the cold room) for three days, during which time a complex sometimes separates. After adding ice and hydrochloric acid and removing the solvent with steam, the product is either allowed to crystallize directly or it is dissolved in soda solution, the solution is clarified with Norite and acidified. The keto acid is obtained in a colorless or nearly colorless condition quite satisfactory for further use. In this way β-(4-methoxybenzoyl)-propionic acid was obtained as colorless needles, m. p. 146–147°, in 85% yield. The results were duplicated by W. P. Campbell and by H. L. Holmes, the latter using as much as 173 g. of anisole in one experiment. By the same procedure β-(3,4-dimethoxybenzoyl)-propionic acid, m. p. 157–159°, was obtained in 67% yield, and H. L. Holmes obtained the same yield using 341 g. of veratrole. In other experiments with veratrole it was found that when using the tetrachloroethane–nitrobenzene mixture the yield dropped to 40% or less when the amount of aluminum chloride was changed from two equivalents to either one or three equivalents, and that the yield was also decreased by conducting the reaction at room temperature (43%, m. p. 152–154°). Following the procedure of Haworth and Mavin,[8] using nitrobenzene alone and operating at room temperature, we obtained material somewhat inferior (brown, m. p. 150–155°) to that above in slightly better yield (73%). Using carbon bisulfide[6] the yield was low (46%) and product of poor quality.

β-(4-Methoxy-1-naphthoyl)-propionic[11] acid was prepared by the above procedure but using tetrachloroethane alone as the solvent, the yield of material melting at 170–172° being 98%; the recrystallized acid melted at 171–172°.

Clemmensen Reduction.—A report has already been made[3] of the yields obtained by Martin's modified method of reduction in the preparation of γ-(4-methoxyphenyl)-butyric acid (ethyl ester, b. p. 177–178°, 15.5 mm.), γ-(3,4-dimethoxyphenyl)-butyric acid (ethyl ester, b. p. 186–189°, 8.5 mm.) and **γ-(4-methoxy-1-naphthyl)-butyric acid** (ethyl ester, b. p. 239–242°, 16 mm.). Crystallized from alcohol and from benzene–ligroin, γ-(4-methoxy-1-naphthyl)-butyric acid formed small colorless plates, m. p. 129–130°.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.74; H, 6.59. Found: C, 73.92; H, 6.18.

γ-(3-Methoxy-4-methylphenyl)-butyric acid (ethyl ester, b. p. 171–173°, 11 mm.) was prepared from β-(*p*-toluyl)-propionic acid (230 g.) according to Martin,[3] the yields throughout being essentially as reported.

Conversion of the γ-Arylbutyric Esters into Cyclic Unsaturated Anhydrides.—The condensations of the esters with ethyl oxalate were carried out with the use of potassium ethylate, although in subsequent experiments in this Laboratory it was found that sodium ethylate is satisfactory with at least some of the methoxy compounds (H. L. Holmes). In the standard procedure 0.104 mole of potassium, cleaned by boiling with purified dioxane, was powdered under toluene in a nitrogen atmosphere and treated in ether suspension under reflux with 0.104 mole of absolute ethyl alcohol. At the end of the reaction 0.15 mole of ethyl oxalate was added and the resulting clear solution was treated with 0.1 mole of the γ-arylbutyric ester in absolute ether. In all 300–350 cc. of ether was used. The solution usually was refluxed for eight to ten hours to complete the reaction, and the potassium derivative of the product often separated during this time in a solid condition or as an oil. In this case the salt was separated by filtration or decantation, washed with dry ether, and decomposed with ice-cold 60% sulfuric acid in the presence of ether, the oxalyl derivative being recovered by extracting with ether and flashing off the solvent at the water pump. Any material remaining in the mother liquor was similarly recovered and worked separately. Some experimentation was necessary in each case to determine the strength of sulfuric acid most suitable for effecting the cyclization of the oxalyl derivative, and the specific data are noted below. Unlike the unsubstituted unsaturated anhydrides, the methoxylated compounds have a tendency to undergo partial dehydrogenation under the influence of the sulfuric acid and the aromatic anhydrides are often present in the crude reaction products.

7 - Methoxy - 3,4 - dihydronaphthalene - 1,2 - dicarboxylic Anhydride.—The potassium salt of the oxalyl derivative separated nearly completely as a solid, and 24.5 g. of the salt was added in small portions to 75 cc. of 60% sulfuric acid, stirred mechanically and cooled in an ice–salt bath. The resulting oily suspension was heated for fifteen minutes on the steam-bath, cooled, treated with 150 cc. of 80% sulfuric acid and heated fifteen minutes longer, when the oil had changed to a yellow solid. On pouring the mixture into water, collecting and washing the product, 13.6 g. (77% yield from the butyric ester) of good anhydride was obtained. The material from the ether mother liquor yielded 0.8 g. of less pure anhydride. After repeated crystallization from benzene–ligroin (readily soluble in benzene) the compound was obtained as bright yellow, heavy prismatic needles, m. p. 164.5–165°.

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.79; H, 4.39. Found: C, 67.93; H, 3.97.

In one experiment cyclization of the oxalyl derivative with concentrated sulfuric acid at 20° was tried. The material was largely sulfonated and the water-insoluble product was found to contain a considerable amount of the aromatic anhydride (see Table I), which was obtained pure after five crystallizations from benzene.

6,7 - Dimethoxy - 3,4 - dihydronaphthalene - 1,2-dicarboxylic Anhydride.—The potassium salt separated as an oil and this was washed and converted into the free oxalyl derivative which, for cyclization, was heated for twenty minutes on the steam-bath with 70% sulfuric acid. The product separated as a bright red, crystalline solid and was washed with 60% acid and with water; yield crude (m. p. 180–186°) 56%. The anhydride is moderately soluble in benzene and gives a pure yellow solution; the recrystallized material forms bright red needles from this solvent, m. p. 192.5–193.

Anal. Calcd. for $C_{14}H_{12}O_5$: C, 64.59; H, 4.65. Found: C, 64.79; H, 4.67.

When the ester condensation was interrupted after three and one-half hours, the anhydride obtained from the cyclization of the potassium salt which separated corresponded

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[11] Ruzicka and Waldmann, *Helv. Chim. Acta*, **15**, 907 (1932).

to a 43% yield. Treatment of the material from the ether mother liquor with 70% sulfuric acid gave 6,7-dimethoxy-1-tetralone,[8] m. p. 99.5–100° (purified) in 34% yield. This undoubtedly came from unreacted anisylbutyric ester.

6-Methoxy-7-methyl-3,4-dihydronaphthalene-1,2-dicarboxylic Acid.—In the ester condensation the red-orange ethereal solution deposited no salt and the crude oxalyl compound was obtained by adding cold dilute sulfuric acid and extracting with ether. For cyclization the oil was heated with 78% sulfuric acid at 70–80° for thirty minutes, giving very nearly pure anhydride in 82% yield. After two crystallizations from benzene (moderately soluble) the substance melted constantly at 189.8–190.3° and formed thin, yellow diamond-shaped plates. The cyclization was also accomplished by heating nearly to boiling for a few minutes with a solution of zinc chloride in glacial phosphoric acid.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.82; H, 4.96. Found: C, 69.07; H, 5.17.

6-Methoxy-3,4-dihydronaphthalene-1,2-dicarboxylic Anhydride.—The oxalyl derivative prepared from ethyl γ-(*m*-methoxyphenyl)-butyrate[3] on cyclization with 75% sulfuric acid at 80° for fifteen minutes gave a mixture of the unsaturated and aromatic anhydrides. A fairly sharp separation was accomplished with ether, in which the dihydro compound alone dissolves easily. The aromatic anhydride, described in Table I, was identified by comparison with a sample obtained by sulfur dehydrogenation of the dihydro derivative. The latter, purified by repeated crystallization from benzene–ligroin, formed yellow needles, m. p. 164–165°.

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.79; H, 4.39. Found: C, 67.83; H, 4.49.

9-Methoxy-3,4-dihydrophenanthrene-1,2-dicarboxylic Anhydride.—The potassium derivative of the oxalyl ester largely separated as a solid after two hours of refluxing, and after standing for six hours longer the salt was collected, washed and decomposed with cold acid. The crude product, a pale yellow oil, was stirred with 84% sulfuric acid on the steam-bath for fifteen minutes, when conversion to an orange solid was complete. Washed with 84% acid and with water, this melted in the range 185–205° and proved to be a mixture of the unsaturated and the aromatic anhydrides. The latter is the less soluble of the two and was obtained pure after repeated crystallization from benzene (Table I); the former was isolated by fractional crystallization from glacial acetic acid (readily soluble). It forms reddish orange needles, m. p. 194–197°, which separate in a brilliant condition but become opaque on drying.

Anal. Calcd. for $C_{17}H_{12}O_4$: C, 72.83; H, 4.32. Found: C, 73.07; H, 4.42.

Aromatic Anhydrides.—The substances isolated as by-products in the cyclization experiments are listed in Table I. They can be obtained also by heating the unsaturated anhydrides with the calculated amount of sulfur in a bath at 240–250° for fifteen to twenty minutes, followed by distillation at diminished pressure and crystallization. Benzene was found to be a good solvent in each case.

Diels–Alder Reaction.—The addition products listed in Table II were prepared as follows (or with double the quantities). About 25 g. of fresh butadiene was distilled into a mixture of 10 g. of the appropriate unsaturated anhydride and 15 cc. of dioxane contained in a Pyrex tube and cooled in a bath of solid carbon dioxide with the eutectic mixture of chloroform and carbon tetrachloride (equal parts), and the tube was sealed and heated at 160–180° for thirteen to fifteen hours. After opening the tube in the same cooling mixture the excess butadiene was evaporated by gentle warming and the product was obtained as a clean solid free from polymer by distillation in high vacuum in 75–85% yield. This material invariably contained a small amount of a colored impurity having the properties of the aromatic anhydride corresponding to the starting material and evidently arising by a dehydrogenation or disproportionation in the course of the reaction. This is considerably less soluble in benzene–ligroin than the addition product and can be eliminated by crystallization, but a more convenient method is based upon the greater resistance of the addition product to hydrolysis. The crude material is crystallized once from a concentrated benzene–ligroin solution and shaken with warm dilute aqueous-alcoholic alkali until the yellow or orange material has been hydrolyzed and dissolved and the largely unattacked addition product is left in a completely colorless condition. Crystallization from benzene–ligroin then gives pure material.

The 6-methyl-7-methoxy derivative was converted into the dipotassium salt of the corresponding acid by re-

TABLE I

-1,2-DICARBOXYLIC ANHYDRIDES

Compound	Cryst. form	M. p., °C.	Analyses % C Calcd.	Analyses % C Found	Analyses % H Calcd.	Analyses % H Found
7-Methoxynaphthalene-	Yellow needles	194–195	68.39	68.57	3.54	3.55
6-Methoxy-7-methyl-	Yellow prisms	215–215.5	69.39	69.63	4.17	4.31
6-Methoxynaphthalene-	Yellow micro needles	210–210.5	68.39	68.67	3.54	3.77
9-Methoxyphenanthrene-	Orange-yellow needles	251–252	73.35	73.07	3.63	3.60

TABLE II

-1,4,9,10,11,12-HEXAHYDROPHENANTHRENE-11,12-DICARBOXYLIC ANHYDRIDES

Substituent	Cryst. form (all colorless)	M. p., °C.	Analyses % C Calcd.	Analyses % C Found	Analyses % H Calcd.	Analyses % H Found
6-Methoxy-	Diamond-shaped prisms	126.5–127	71.81	72.21	5.67	5.88
6,7-Dimethoxy-	Prisms	138.6–138.8	68.79	68.44	5.77	5.61
6-Methyl-7-methoxy-	Prisms	152–152.5	72.43	72.38	6.11	6.11

TABLE III

-1,2,3,4,9,10,11,12-OCTAHYDROPHENANTHRENE-11,12-DICARBOXYLIC ANHYDRIDES

Substituent	Cryst. form (all colorless)	M. p., °C.	Analyses			
			% C		% H	
			Calcd.	Found	Calcd.	Found
6-Methoxy-	Needles or prisms	159–159.5	71.28	71.48	6.33	6.65
6,7-Dimethoxy-	Prismatic clusters	146.5–147	68.31	68.30	6.38	6.53
6-Methyl-7-methoxy-	Needles	149.5–150	71.95	71.78	6.73	6.81

fluxing with 4 *N* potassium hydroxide until dissolved and adding stronger alkali, and the dry salt (iridescent leaflets) was heated slowly in a bath from 350 to 420°, applying suction. The small amount of yellow oil which distilled was heated with selenium at 300° and the extracted product, **2-methoxy-3-methylphenanthrene,** after sublimation and crystallization from methyl alcohol, melted at 132–132.5°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.49; H, 6.31. Found: C, 86.55; H, 6.54.

The picrate formed orange needles, m. p. 142.5–143°, from benzene–ligroin.

Anal. Calcd. for $C_{22}H_{17}O_8N_3$: N, 9.31. Found: N, 9.25.

2,3 - Dimethyl - 6 - methoxy - 1,4,11,12,13,14 - hexahydrochrysene-13,14-dicarboxylic anhydride, obtained by heating the corresponding unsaturated anhydride with 2,3-dimethylbutadiene at 100° for two days, formed colorless prisms, m. p. 181–182°, from benzene–ligroin.

Anal. Calcd. for $C_{23}H_{22}O_4$: C, 76.48; H, 6.13. Found: C, 76.48; H, 6.13.

Octahydrophenanthrene Anhydrides.—The three addition products listed in Table II were converted into the saturated compounds of Table III by hydrogenation in glacial acetic acid solution in the presence of Adams catalyst at atmospheric pressure. The absorption of gas was complete in five to ten minutes (3-g. samples) and the products were obtained in nearly quantitative yield. Benzene–ligroin was used for recrystallization.

Dimethyl 6,7-dimethoxy-1,2,3,4,9,10,11,12-octahydrophenanthrene-11,12-dicarboxylate, obtained by converting the anhydride into the free acid and esterifying with diazomethane, formed colorless microcrystals, m. p. 134.5–135.5°.

Anal. Calcd. for $C_{20}H_{26}O_6$: C, 66.26; H, 7.24. Found: C, 66.32; H, 7.56.

Demethylation.—The ethers of Table III were demethylated by refluxing 1 g. of the material with 10 cc. each of glacial acetic acid and 48% hydrobromic acid for three to five hours. On dilution with water the product separated as an oil which became crystalline after standing for several hours; average yield 80%.

6 - Hydroxy - 1,2,3,4,9,10,11,12 - octahydrophenanthrene-11,12-dicarboxylic anhydride crystallized from benzene as colorless prismatic needles, m. p. 160–160.5°.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.56; H, 5.92. Found: C, 70.69; H, 5.66.

6,7 - Dihydroxy - 1,2,3,4,9,10,11,12 - octahydrophenanthrene-11,12-dicarboxylic anhydride formed small round crystal clusters, m. p. 147.5–148.5°, from benzene. It is very soluble in alcohol, moderately soluble in hot benzene, slightly soluble in hot water.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.64; H, 5.59. Found: C, 66.69; H, 5.58.

The diacetyl derivative, prepared with the use of acetic anhydride and sodium acetate, formed colorless iridescent plates from alcohol, m. p. 151.5–152°.

Anal. Calcd. for $C_{20}H_{20}O_7$: C, 64.48; H, 5.43. Found: C, 64.63; H, 5.55.

The dibenzoyl derivative was prepared by boiling the substance in pyridine solution with benzoyl chloride for five minutes, adding water, and treating the precipitated oil with alkali, when it at once solidified. Crystallized from alcohol, it formed clusters of short needles, m. p. 175–175.5°.

Anal. Calcd. for $C_{30}H_{24}O_7$: C, 72.55; H, 4.88. Found: C, 72.65; H, 4.93.

6 - Methyl - 7 - methoxy - 1,2,3,4,9,10,11,12 - octahydrophenanthrene-11,12-dicarboxylic anhydride formed colorless microcrystals from benzene–ligroin, m. p. 134.5–135.5°.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.30; H, 6.33. Found: C, 71.30; H, 6.33.

Summary

Hydroxyl or methoxyl derivatives of phenanthrene-1,2-dicarboxylic anhydride and of octahydrophenanthrene-11,12-dicarboxylic anhydride which are of interest in the study of oestrogenic activity are described in this paper.

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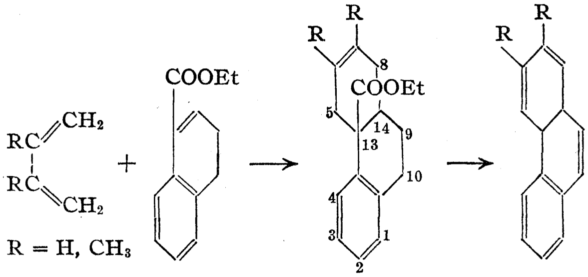
The Synthesis of Phenanthrene and Hydrophenanthrene Derivatives. V. The Addition of Dienes to Cyclic α,β-Unsaturated Esters

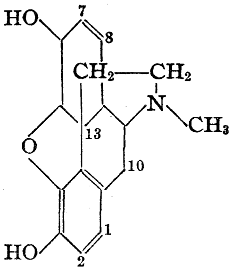
BY L. F. FIESER AND H. L. HOLMES

Having found that derivatives of maleic anhydride in which the active ethylenic linkage is incorporated in an alicyclic ring are capable of entering into the Diels–Alder reaction with dienes,[1] the possibility of effecting a similar addition in the case of cyclic α,β-unsaturated esters has been investigated in the hope that this might provide a route to hydrophenanthrene derivatives of a type hitherto inaccessible by synthesis. The reaction was tried first with ethyl Δ^1-dihydro-1-naphthoate (I) prepared by reducing α-naphthoic acid with sodium amalgam and rearranging the labile Δ^2-dihydro derivative with alkali according to v. Baeyer and Schoder,[2] followed by Fischer esterification.[3] With both butadiene and 2,3-dimethylbutadiene addition to the double bond of the ester was found to occur slowly, giving hexahydrophenanthrene carboxylic esters of the type II. The reactions did not proceed as well as in the case of Δ^1-dihydronaphthalene-1,2-dicarboxylic anhydride[1] and the conversion invariably was far from complete, but the pure esters (II) were obtained in 21–27% yield by heating the components at 100° for eight days or at 150° for forty-one hours. The addition products, one of which was obtained as a liquid and the other as a low-melting solid, are easily separated from the starting material by taking advantage of the great resistance to hydrolysis of the tertiary ester group. By refluxing a mixture of I and II with 10% potassium hydroxide the unsaturated ester can be completely hydrolyzed without appreciably affecting the addition product. The corresponding acids were obtained as crystalline solids by saponification of the esters with sodium ethylate at 180°. The substances have not yet been investigated in sufficient quantity to determine whether more than one *dl*-mixture is present. That the addition products have the expected structures was established by their conversion on dehydrogenation with selenium, either as the esters or as the free acids, into phenanthrene and 2,3-dimethylphenanthrene.[1,4]

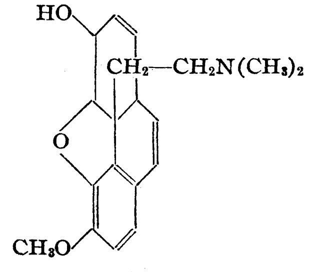


I II III

These observations are of particular interest in connection with the morphine problem. In the Gulland–Robinson formula (IV) for this alkaloid the ethanamine chain is assumed to be attached to the phenanthrene skeleton at a position (C_{13}) corresponding to that occupied by the carbonyl group of the synthetic compounds described above. The location of this end of the C–C–N chain, however, is the one point regarding the structure which still remains to be unambiguously established. The present synthesis makes available for the first time substances of known structure having a carbon substituent at the position which is indicated as being the most likely point of attachment of the ethanamine chain, and it offers promise of providing a route to compounds which may be obtainable from morphine, for example by the further degradation of α-methylmorphimethine, V.



IV



V

In order to approach sufficiently closely to the morphine type of structure it seemed essential to develop a flexible method of procuring substituted dihydro-α-naphthoic esters suitable for the preparation of hydrophenanthrene carboxylic

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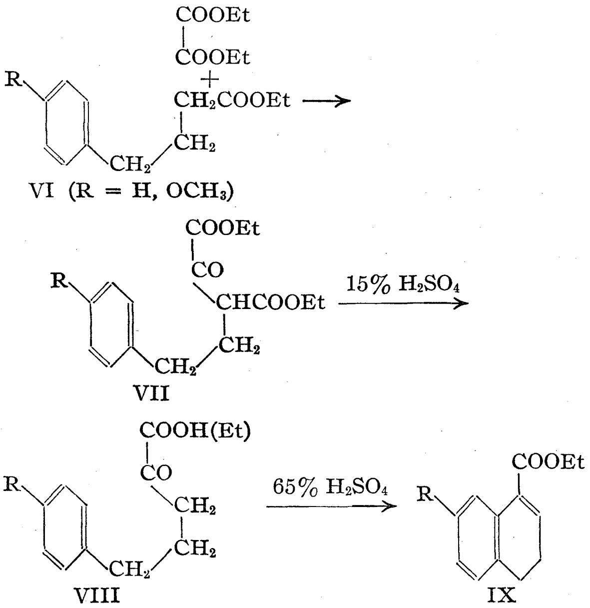
[1] Part II. Fieser and Hershberg, THIS JOURNAL, **57**, 2192 (1935).

[2] v. Baeyer and Schoder, *Ann.*, **266**, 176 (1891).

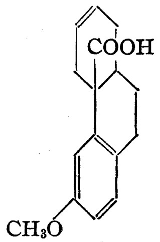
[3] Rabe, *Ber.*, **31**, 1896 (1898).

[4] Haworth, Mavin and Sheldrick, *J. Chem. Soc.*, **454** (1934).

acids carrying a hydroxyl or methoxyl group in the 3-position (morphine numbering, see formula II), and possibly also in the 4-position. The method used by v. Baeyer and Schoder[2] in the case of the parent compound would require difficultly accessible or unknown aromatic acids as starting materials, if indeed it is applicable to such substances, and we turned to synthesis. α-Oxalyl-γ-phenylbutyric esters of the type VII are readily obtainable by the ester condensation from the γ-phenylbutyric esters easily prepared from benzene or anisole and succinic anhydride, and after some trial it was found that hydrolysis and decarboxylation can be accomplished by boiling the esters for fifteen to eighteen hours with 15% sulfuric acid. α-Keto-δ-phenylvaleric acid (VIII) and its *p*-methoxy derivative were obtained in this way in over-all yield from VI of about 70%. Cyclization to the dihydro-α-naphthoic ester (IX) was brought about by warming the keto esters (VIII) with 65% sulfuric acid for one to two hours on the steam-bath, and the yields again were good. The Δ^1-dihydro-1-naphthoic acid obtained by this synthesis was fully identified by comparison with the product prepared by the previous method.[2] The 7-methoxy-Δ^1-dihydro-1-naphthoic acid yielded on dehydrogenation with sulfur an acid having the properties recorded for 7-methoxy-1-naphthoic acid.[5] Contrary to the experience of Darzens[6] in an analogous case, no decarboxylation occurred in the course of the dehydrogenation of the above acid or of 7-methoxy-1,2,3,4-tetrahydro-1-naphthoic acid. The synthesis provides a convenient route to aromatic acids of the type indicated as well as to their dihydro derivatives, and further applications are being investigated.



Butadiene was successfully added, if in low yield, to ethyl 7-methoxy-Δ^1-dihydro-1-naphthoate, affording after hydrolysis 3-methoxy-5,8,9,-10,13,14-hexahydrophenanthrene-13-carboxylic acid (X). With the introduction of a methoxyl group in the position occupied by a similar group in the case of codeine, a part of the proposed program has been realized. A start has been made in the direction of introducing a second methoxyl group at C$_4$ by the synthesis of 5-bromo-7,8-dimethoxy-3,4-dihydro-1-naphthoic acid, but a report of this work will be deferred to a later publication. In addition to the proposed inquiry regarding the structure of morphine it is planned to investigate the use of acids such as X as starting materials for the synthesis of basic substances of possible morphine-like actions.



X

Experimental Part[7]

Synthesis of Δ^1-Dihydro-α-naphthoic Acids

α-Keto-δ-phenylvaleric Acid.—One hundred grams of ethyl γ-phenylbutyrate was condensed with ethyl oxalate in the presence of sodium ethylate according to the procedure previously outlined[1] and the crude α-oxalyl-γ-phenylbutyric ester, after removal of the solvent ether and the excess diethyl oxalate by vacuum distillation, was refluxed vigorously with 700 cc. of 15% sulfuric acid for fifteen hours, when the at first steady evolution of carbon dioxide had practically ceased. The keto acid appeared as a viscous brown oil. This was taken up in ether, washed with water, and the acid was extracted with 200 cc. of 10% sodium hydroxide solution. The alkaline extract was clarified with Norite and acidified, and the light yellow oil was taken up in ether and dried. Evaporation of the solvent left an oil which failed to solidify, and this was consequently esterified with ethyl alcohol and hydrogen chloride. The ethyl ester distilled at 165–170° (12 mm.); yield 72 g. (62.5%). On redistillation the chief fraction boiled at 164° (13 mm.), and 5 g. of the purified ester was saponified by refluxing for one hour with 25 cc. of 20% alkali. The solution was clarified and acidified, and after thorough cooling the keto acid solidified; yield 4.3 g. (98%). The substance crystallized from hexane in the form of colorless blades, m. p. 68–69.5°. It is very soluble in alcohol or benzene in the cold and moder-

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(5) Davies, Heilbron and Irving, *J. Chem. Soc.*, 2715 (1932).

(6) Darzens, *Compt. rend.*, **199**, 1132 (1934).

(7) All melting points are corrected.

ately soluble in boiling hexane. A sodium salt crystallizing in plates separates from an aqueous solution containing a moderate excess of sodium carbonate.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.75; H, 6.25. Found: C, 68.56; H, 6.25.

Δ^1-Dihydro-α-naphthoic Acid.—For cyclization 72 g. of ethyl α-keto-δ-phenylvalerate was stirred mechanically with 450 cc. of 65% sulfuric acid and heated for two hours on the steam-bath. The material did not dissolve and changed little in appearance in the course of the reaction. The mixture was cooled and poured onto 1 kg. of ice, and the light green oil was extracted with ether and the solution washed with water. The ethereal extract was mixed with 500 cc. of 5% sodium hydroxide and after boiling off the ether the mixture was refluxed for two hours to hydrolyze some ester present and the solution was clarified with Norite, cooled and acidified. The product separated as a solid (56.5 g.) which was obtained in a nearly pure condition by crystallization from hexane; yield 48.5 g. (85%). After several recrystallizations the acid melted constantly at 120–121°.

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 69.86; H, 6.72. Found: C, 69.71; H, 7.07.

A sample of the unsaturated acid prepared according to v. Baeyer and Schoder[2] and crystallized from ethyl acetate and from hexane melted at the same temperature as the synthetic substance and did not depress its melting point. The observations are in agreement with the statement of v. Auwers and Möller[8] that the acid melts at 121° rather than 125°.[2]

The ethyl ester was prepared according to Rabe[3] in 91% yield, b. p. 170–172° (19 mm.), n^{25}D 1.5561. Dehydrogenation of the unsaturated acid (1 g.) with sulfur (0.19 g.) at 230–240° gave after vacuum distillation 0.93 g. of light yellow α-naphthoic acid which on crystallization was obtained colorless, m. p. 161.4–161.6°.

α-Keto-δ-(4-methoxyphenyl)-valeric Acid.—Ethyl γ-(4-methoxyphenyl)-butyrate (90 g.) was condensed with ethyl oxalate (90 g.) using the ethylate from 9.88 g. of sodium (twenty hours of refluxing) and following the procedure[1] for the parent compound. After removing the ether from the reaction product the crude oxalyl derivative was refluxed vigorously with 800 cc. of 15% sulfuric acid for eighteen to twenty-four hours. The oily layer was taken into ether and dried, and on removing the solvent the keto acid was obtained as a solid; yield, after one crystallization, 72.2 g. (80%). The acid is sparingly soluble in hexane and crystallizes as thin colorless plates. The melting point is like that of camphor;[9] the substance begins to liquefy at about 65° and the last crystal skeleton disappears at 74°. Addition of sodium chloride to the sodium carbonate solution causes the separation of characteristic hair-fine needles of the sodium salt.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.87; H, 6.35; neut. eq., 222. Found: C, 64.70; H, 6.46; neut. eq., 219.

The ethyl ester was prepared by esterification with absolute alcohol and hydrogen chloride, washed and dried in ether with magnesium sulfate, and distilled; b. p. 190–192° (10 mm.), n^{20}D 1.5080, yield 92%. In another experiment 150 g. of ethyl γ-(4-methoxyphenyl)-butyrate, run in two portions, gave 169 g. (72%) of the keto ester.

7-Methoxy-Δ^1-dihydro-1-naphthoic Acid.—A mixture of 25 g. of ethyl α-keto-δ-(4-methoxyphenyl)-valerate and 200 cc. of 65% sulfuric acid was stirred vigorously on the steam-bath (75–80°) for one hour and then poured onto ice. The oily product, which appeared to be partially hydrolyzed ester, was taken into ether and, after removal of solvent, refluxed for two hours with 100 cc. of 9% sodium hydroxide, and the alkaline solution was clarified with Norite and acidified. The acid separated as an oil which soon solidified (19.8 g.). On crystallization from water, in which the substance is moderately soluble, 14 g. (68.5%) of pure material was obtained as colorless plates, m. p. 116–117°. It also crystallizes well from hexane (sparingly soluble) in plates; it is very soluble in benzene in the cold.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.54; H, 5.94. Found: C, 70.09; H, 5.96.

The ethyl ester was obtained by Fischer esterification in 85% yield, b. p. 186–187° (9 mm.).

7-Methoxy-1-naphthoic Acid.—7-Methoxy-Δ^1-dihydro-1-naphthoic acid (0.6 g.) was heated with 0.1 g. of sulfur at 230–240° for one-half hour and the product distilled at 9 mm. and crystallized from hexane, yielding 0.5 g. of yellow needles. After further recrystallization the substance was obtained as long, slender, colorless needles, m. p. 169–170° (lit. 167–168°, uncorr.).[5] Demethylation with hydrobromic and acetic acids and crystallization from water gave 7-hydroxy-1-naphthoic acid, m. p. 255–256° (lit. 253–254°, uncorr.[10]).

7-Methoxy-1,2,3,4-tetrahydro-1-naphthoic acid, prepared by hydrogenation with Adams catalyst, crystallized from dilute alcohol as colorless prisms, m. p. 137.5–138.5°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.86; H, 6.72. Found: C, 69.75; H, 6.96.

Like the dihydro derivative, the tetrahydro compound gave 7-methoxy-1-naphthoic acid on dehydrogenation with sulfur. In neither case was any β-naphthol methyl ether detected in the mother liquors.

Diels–Alder Reaction

5, 8, 9, 10, 13, 14 - Hexahydrophenanthrene - 13 - carboxylic Acid.—A mixture of 11 g. of ethyl Δ^1-dihydro-1-naphthoate and 10 g. of butadiene was heated in a sealed tube at 150° for forty-one hours. After evaporating the butadiene still present the liquid material was distilled from the polymer, the boiling range being 155–214° at 8 mm. (7 g.). This was refluxed for four hours with 30 cc. of 10% potassium hydroxide and the unsaponified oil remaining was washed and dried in ether and distilled. **The ethyl ester** was obtained after redistillation as a viscous oil, b. p. 164–166° (5 mm.), yield 3 g. (21%).

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.99; H, 7.99. Found: C, 79.40; H, 7.89.

For saponification 0.48 g. of the ester was heated with a solution prepared from 2 g. of sodium and 30 cc. of absolute alcohol at 170° for eighteen hours. On diluting the alkaline solution and acidifying, the acid separated as a solid (0.4 g.). Crystallized from dilute methyl alcohol it

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[8] v. Auwers and Möller, *J. prakt. Chem.*, **217**, 144 (1925).

[9] This was not recognized at the time of the preliminary report, *Science*, **83**, 558 (1936).

[10] Royle and Schedler, *J. Chem. Soc.*, **123**, 1641 (1923).

formed rectangular microprisms, m. p. 137–138°. Further crystallization from hexane, in which the acid is readily soluble, gave compact clusters of microprisms, m. p. 141.5–142.5° with some previous softening. An extensive fractionation was not undertaken.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.97; H, 7.02. Found: C, 79.37; H, 7.40.

On dehydrogenation with selenium at 300° for twenty-one hours the once crystallized acid (0.55 g.) yielded a hydrocarbon (0.21 g.) which after crystallization melted at 96–97° and was identified as phenanthrene by mixed melting point.

6, 7 - Dimethyl - 5, 8, 9, 10, 13, 14 - hexahydrophenanthrene-13-carboxylic Acid.—The ethyl ester was prepared as above from 15 g. of the unsaturated ester and 18 cc. of 2,3-dimethylbutadiene, heating being continued for eight days at 100°. After treatment with 10% potassium hydroxide the ethyl ester was distilled as a liquid which solidified; b. p. 166° (4 mm.), m. p. 49.5–50°, yield 5.7 g. (27%).

Anal. Calcd. for $C_{19}H_{24}O_2$: C, 80.23; H, 8.51. Found: C, 79.61; H, 8.84.

The free acid, prepared as above (85% yield), crystallized from very dilute alcohol as small, colorless prisms, m. p. 162–163°. Recrystallization from hexane (readily soluble) gave small, hard, crystalline clusters, m. p. 168–169° with some previous softening.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.70; H, 7.81. Found: C, 80.17; H, 7.87.

On dehydrogenation with selenium for thirty-six hours, 1.7 g. of the crude acid yielded 0.7 g. of purified crystals melting at 78–78.5° and identified by mixed melting point determination as 2,3-dimethylphenanthrene.[1]

3 - Methoxy - 5, 8, 9, 10, 13, 14 - hexahydrophenanthrene-13-carboxylic Acid (X).—A mixture of 20 g. of ethyl 7-methoxy-Δ^1-dihydro-1-naphthoate and 15 g. of butadiene was heated for twenty-one hours at 220–245°. The crude ester mixture (18.6 g.) was refluxed with 70 cc. of 20% alkali for four hours and the residual oil was dried and distilled, b. p. 202–204° (14 mm.); yield 3.3 g. (13%). On saponification of the ethyl ester with sodium ethylate as above the free acid was obtained from dilute alcohol as colorless microprisms, m. p. 139.5–141° with previous softening.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.41; H, 7.03. Found: C, 74.03; H, 7.01.

Summary

Hydrophenanthrene derivatives having a carboxyl group at the 13-(or 12-) position can be obtained by the addition of dienes to Δ^1-dihydro-1-naphthoic esters. A convenient synthesis of the unsaturated esters consists in the acid hydrolysis of α-oxalyl-γ-arylbutyric esters to α-keto-δ-arylbutyric acids and cyclization of the keto esters with sulfuric acid. These methods afford a new approach to substances having some features of the morphine structure.

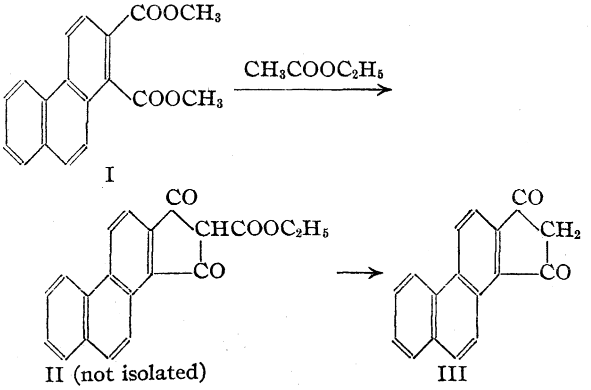
CAMBRIDGE, MASS. RECEIVED AUGUST 5, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Synthesis of Phenanthrene and Hydrophenanthrene Derivatives. VI. 1',3'-Diketocyclopentenophenanthrenes

BY L. F. FIESER, M. FIESER AND E. B. HERSHBERG

Having found a convenient method of preparing phenanthrene-1,2-dicarboxylic anhydride by synthesis,[1] it was of interest to undertake the conversion of the substance into a compound having the 1,2-cyclopenteno ring system. The anhydride was converted into the dimethyl ester I either by the Fischer esterification of the corresponding acid, obtained through the dipotassium salt, or by the direct action of methyl alcoholic hydrogen chloride. On condensation with ethyl acetate in the presence of sodium I yielded a diketo ester II which was hydrolyzed to 1',3'-diketo-1,2-cyclopentenophenanthrene, III (or the enolic form). The pure diketone was obtained in 76% yield. Employing anhydrides prepared from intermediates already described,[1,2] the isomeric diketone IV and the dimethylene (ace-) derivative V were synthetized in good yield.



I

II (not isolated)

III

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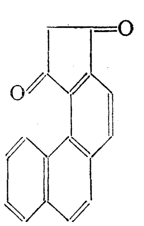
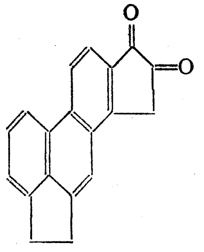
[1] Fieser and Hershberg, THIS JOURNAL, **57**, 1851 (1935).

[2] Fieser, Fieser and Hershberg, *ibid.*, **58**, 1463 (1936).

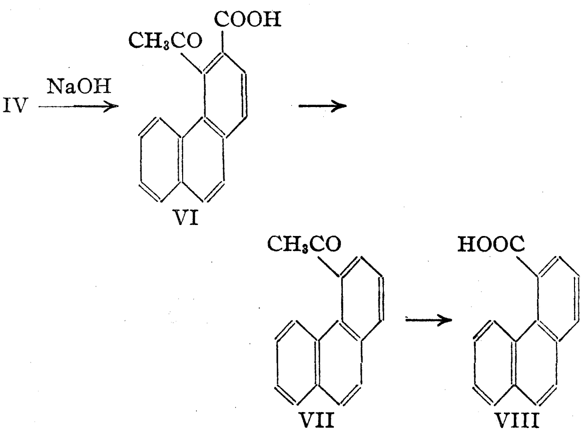


IV



V

The isomeric phenanthrindanediones III and IV dissolve in dilute alkali even in the cold to give red solutions. On refluxing for several hours the color fades and acetylphenanthroic acids are formed in good yield. The substance obtained from the 3,4-isomer IV proved to be a single individual of the structure VI, for on decarboxylation with copper carbonate and quinoline it yielded the hitherto unknown 4-acetylphenanthrene (VII).



The structure of the latter compound follows from the non-identity with the 3-isomer and from the fact that on hypochlorite oxidation it yields a substance having the properties of the known 4-phenanthroic acid.[3] The material resulting from the cleavage of the diketo-1,2-cyclopentenophenanthrene had the composition and properties of a mixture of the two possible acetylphenanthroic acids and evidently there is no great preference for cleavage at one or the other ketonic group. The contrasting behavior of the isomer IV is interpreted as being due to the protection of the carbonyl group in the hindered 4-position, and this constitutes another example of the blocking effect of the neighboring aromatic ring.[4]

In the special test for oestrogenic activity developed by Pincus and Werthessen[5] 1',3'-diketo-1,2-cyclopentenophenanthrene appears to be comparable in potency with 1-keto-1,2,3,4-tetrahydrophenanthrene, while the isomer IV is entirely inactive.

Experimental Part[6]

Phenanthrene-3,4-dicarboxylic anhydride was obtained in 90% yield by heating the dihydro compound[1] with the calculated amount of sulfur in a bath at 320–330° and distilling the product when the evolution of gas was complete. The anhydride is sparingly soluble in glacial acetic acid, fairly readily soluble in xylene, and it crystallizes from the latter solvent as fine, lemon yellow needles, m. p. 253.5–254°.

Anal. Calcd. for $C_{16}H_8O_3$: C, 77.39; H, 3.25. Found: C, 77.37; H, 3.19.

8,9-Acephenanthrene-1,2-dicarboxylic anhydride, prepared similarly in equally good yield, formed fine orange-yellow needles, m. p. 297–298°, uncorr., from dioxane (moderately soluble).

Anal. Calcd. for $C_{18}H_{10}O_3$: C, 78.82; H, 3.68. Found: C, 78.62; H, 3.97.

Dimethyl phenanthrene-1,2-dicarboxylate was at first prepared through the dipotassium salt, which was obtained by refluxing the anhydride (1 g.) with a solution of potassium hydroxide (7 g.) in water (20 cc.) and methyl alcohol (10 cc.) for one-half hour and adding saturated potassium chloride solution. The crystalline salt (1.3 g.) which separated on cooling was added to methyl alcohol saturated with hydrogen chloride, and after two days at room temperature the mixture was refluxed for five hours. On dilution with water the ester separated as a pale yellow solid. On crystallization from methyl alcohol two forms were obtained, the less soluble substances appearing as pale yellow needles, m. p. 131.8–132.2°, and the material from the mother liquor forming colorless, pearly plates, m. p. 132.5–133°. No depression was observed on mixing the samples, and on hydrolysis both yielded, after dehydration of the acid on heating, the original anhydride. A better method of preparation consists in refluxing the anhydride (2 g.) with methyl alcohol saturated with hydrogen chloride for about twenty hours. The anhydride slowly dissolved and the solution after being concentrated and cooled deposited the yellow needle-form of the ester (2.1 g.).

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.44; H, 4.79. Found: (yellow needles) C, 73.10; H, 4.43; (colorless plates) C, 73.87; H, 5.07.

The 3,4-dihydro derivative, obtained in good yield through the dipotassium salt of the unsaturated acid, crystallized from methyl alcohol as colorless needles or plates, both melting at 109.8–110°.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.95; H, 5.45. Found: C, 72.75; H, 5.58.

Dimethyl phenanthrene-3,4-dicarboxylate was best prepared directly from the anhydride by boiling with methyl

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[3] Kruber, *Ber.*, **67**, 1000 (1934).

[4] Fieser, THIS JOURNAL, **51**, 1898, 1938 (1929).

[5] Pincus and Werthessen, *Science*, **84**, 45 (1936).

[6] The melting points are corrected except as noted, using the precision apparatus of Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 312 (1936), and employing 0.1° Anschütz thermometers (total immersion) calibrated with a thermometer with the Bureau of Standards certificate. Analyses by Mrs. G. M. Wellwood.

alcohol and hydrogen chloride; yield quantitative. It formed large, transparent prisms, m. p. 114.5–114.8°, from ether–petroleum ether. The substance is very soluble in alcohol or glacial acetic acid.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.45; H, 4.80. Found: C, 73.34; H, 4.80.

The ester was also obtained by esterification of the free acid with diazomethane, and the samples were identical. **Phenanthrene-3,4-dicarboxylic acid** was prepared by hydrolyzing the anhydride with boiling alkali and carefully neutralizing the filtered solution with acetic acid. Very faintly yellow, glistening plates of a monohydrate were deposited on cooling.

Anal. Calcd. for $C_{16}H_{10}O_4 \cdot H_2O$: C, 67.59; H, 4.26. Found: C, 67.50; H, 4.40.

Dimethyl 8,9-acephenanthrene-1,2-dicarboxylate, prepared from the anhydride, alcohol and hydrogen chloride (thirty-six hours), separated as fine, faintly yellow needles from glacial acetic acid, m. p. 170.6–171°.

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 74.98; H, 5.04. Found: C, 74.68; H, 5.10.

1′,3′-Diketo-1,2-cyclopentenophenanthrene (III).—Dimethyl phenanthrene-1,2-dicarboxylate (4.85 g.) was dissolved in 50 cc. of ethyl acetate and 2 g. of fine sodium shavings was added. After refluxing for two hours on the steam-bath 25 cc. more ethyl acetate and 1 g. of sodium were added. This was repeated two hours later and the reaction was stopped after refluxing for six hours. The mixture was pasty with the precipitated sodium derivative of the diketo ester and this was collected after cooling and washed with dry ether. The salt was then decomposed by boiling with 200 cc. of 95% alcohol and 5 cc. of concentrated hydrochloric acid for about ten minutes, during which time carbon dioxide was evolved and the heavy sodium salt partly dissolved and was eventually all transformed to a bulky, light yellow solid. After cooling, the precipitated diketone was collected and washed well with water and then with alcohol. After crystallization by dissolving the substance in 75 cc. of dioxane and adding 50 cc. of 95% alcohol to the hot solution, there was obtained 3.1 g. (76% yield) of the pure diketone. Smaller runs gave yields up to 85%.

The diketone crystallizes well from the above mixture or from benzene and forms short, light yellow needles melting at 240.5–241.5°, dec., when heated in a Pyrex capillary. In a soft glass capillary the sample does not melt but gradually decomposes in the range 240–245°. It dissolves slowly in dilute alkali in the cold, easily on warming, to a cherry red solution. If acidified at once the solution deposits the unchanged material.

Anal. Calcd. for $C_{17}H_{10}O_2$: C, 82.93; H, 4.11. Found: C, 82.75; H, 4.08.

1′,3′-Diketo-3,4-cyclopentenophenanthrene (IV).—The condensation of the appropriate ester (3 g.) was conducted as above except that in these (earlier) experiments only one addition of fresh sodium and ethyl acetate was made. The orange diketo ester salt (5 g.) was rubbed to a paste with 15 cc. of alcohol and 5 cc. of a solution of 10 cc. of concentrated hydrochloric acid in 50 cc. of water was added with stirring. The salt dissolved in the cold to a clear yellow solution and on gentle boiling carbon dioxide was evolved and the diketone separated as light yellow needles in a very pure condition; yield 1.26 g. (50%). The substance is moderately soluble in benzene and readily soluble in glacial acetic acid; it crystallizes from these solvents as light yellow needles, m. p. 201.4–202°. The solubility is greater than that of the isomer and the other properties are as above.

Anal. Calcd. for $C_{17}H_{10}O_2$: C, 82.93; H, 4.11. Found: C, 82.92; H, 4.26.

A monosemicarbazone was deposited from a solution of the components in glacial acetic acid on short boiling. The substance separated as small, pale yellow plates, dec. 300–305°, in a condition suitable for analysis. It is very sparingly soluble in the usual solvents.

Anal. Calcd. for $C_{18}H_{13}O_2N_3$: N, 13.87; Found: N, 13.58.

1′,3′-Diketo-1,2-cyclopenteno-8,9-acephenanthrene (V) was obtained by the procedure described immediately above in 65% yield. The substance is very sparingly soluble in the usual solvents and moderately soluble in tetrachloroethane, from which it crystallizes as fine, bright yellow needles melting at 338–340°, dec., uncorr.

Anal. Calcd. for $C_{19}H_{12}O_2$: C, 83.80; H, 4.45. Found: C, 82.68, 82.76; H, 4.37, 4.41.

4-Acetyl-3-phenanthroic Acid.—The red solution of 1 g. of the diketone IV in 50 cc. of 1 *N* sodium hydroxide turned pale brown after refluxing for six hours. The material which precipitated on acidification was dried and crystallized from benzene–ligroin giving pale yellow crystals melting at 201–202°; yield 0.9 g. (84%). After two recrystallizations from benzene the keto acid was obtained as clusters of colorless, prismatic needles, m. p. 201.5–202.5°.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.24; H, 4.58. Found: C, 77.29; H, 4.81.

4-Acetylphenanthrene.—As attempted decarboxylation of the keto acid without solvent was unpromising, a solution of 0.48 g. of the substance in 3 cc. of quinoline was treated with about 50 mg. of basic copper carbonate and heated at 240–260° for forty-five minutes, most of the carbon dioxide being eliminated in about fifteen minutes. The quinoline solution was diluted with ether, filtered, and extracted with dilute mineral acid to remove the quinoline and with dilute alkali to remove any unchanged acid. After distillation of the ether the residue was distilled at 2 mm., giving a light yellow oil which readily solidified on cooling. After crystallization from ligroin or petroleum ether, in which the substance is moderately soluble, there was obtained 0.27 g. (68% yield) of ketone, m. p. 88.5–90.5°. After two recrystallizations it formed large clusters of heavy colorless plates, m. p. 89.8–90.3°.

Anal. Calcd. for $C_{16}H_{12}O$: C, 87.23; H, 5.50. Found: C, 87.19; H, 5.01.

A solution of the acetyl compound and phenylhydrazine after being boiled for a few minutes and diluted with water yielded only the unchanged ketone.

The picrate forms easily using methyl alcohol as the solvent. It crystallizes as long, slender, yellow needles melting at 129.5–130.5°.

Anal. Calcd. for $C_{16}H_{12}O \cdot C_6H_3O_7N_3$: N, 9.35. Found: N, 9.33.

For conversion to **4-phenanthroic acid**, 0.1 g. of 4-acetylphenanthrene was boiled for one and one-half hours with a sodium hypochlorite solution prepared from 1 g. of the commercial calcium salt (H. T. H.). After cooling, filtering and destroying the excess reagent, the product was precipitated by acidification and crystallized from dilute alcohol. It formed glistening, colorless plates, and after thorough drying at 130° to remove solvent, the acid melted at 171.5–173°. Kruber[3] reports the value 170–171°, uncorr.

Cleavage of 1′,3′-Diketo-1,2-cyclopentenophenanthrene.—After refluxing a solution of the diketone (1.2 g.) in 1 *N* sodium hydroxide for ten hours the light brown solution was filtered from a small amount of purple material and acidified. The acidic product which precipitated was crystallized from benzene, giving 0.96 g. of material. After a second crystallization the substance, m. p. 190–193°, had approximately the composition of a mixture of acetylphenanthroic acids.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.24; H, 4.58. Found: C, 77.63, 77.40; H, 5.22, 5.36.

In further recrystallizations the melting point of the less soluble portion rose to about 216°, but an assuredly homogeneous product was not obtained.

Summary

The condensation of the 1,2- and 3,4-dicarboxylic esters of phenanthrene with ethyl acetate proceeds smoothly, affording diketocyclopentenophenanthrenes of interest in the study of oestrogenic activity. The alkaline cleavage of the 1,2-derivative proceeds in both possible directions, whereas with the 3,4-diketone steric hindrance at the 4-position is so pronounced that the reaction affords pure 4-acetyl-3-phenanthroic acid. This on decarboxylation yields the new 4-acetylphenanthrene.

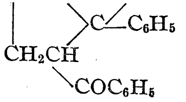
CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.
RECEIVED AUGUST 12, 1936

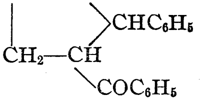
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Rearrangement of 1-Phenyl-5-benzoylcyclopentene Oxide

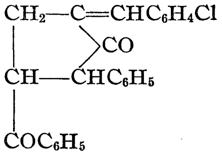
BY S. H. BABCOCK, JR., AND REYNOLD C. FUSON

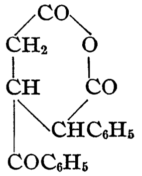
The chief product in the reduction of 1,4-dibromo-1,4-dibenzoylbutane with zinc dust and sodium iodide has been shown to be 1-phenyl-5-benzoylcyclopentene oxide (I).[1] The oxide was accompanied by an isomer which appeared to be derived from it by rearrangement. This isomer was obtained also (1) by the action of alcoholic hydrogen chloride on the oxide; (2) by treatment of a solution of the oxide in glacial acetic acid with ozone; and (3) together with I by the action of perbenzoic acid on 1-phenyl-5-benzoylcyclopentene. It has now been shown that the oxide readily undergoes rearrangement when dissolved in hot glacial acetic acid, and that the rearrangement product is identical with that reported by Fuson and Farlow. The compound has proved to be 2-phenyl-3-benzoylcyclopentanone (II).

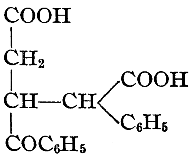

I


II

The structure of this compound has been established by a degradation process leading to the formation of α-phenyl-β-benzoylglutaric acid (V). The ketone condensed readily with *p*-chlorobenzaldehyde to give a chlorobenzal derivative (III).


III


IV


V

When treated with ozone this compound gave *p*-chlorobenzaldehyde, *p*-chlorobenzoic acid and an anhydride (IV) corresponding to that of α-phenyl-β-benzoylglutaric acid (V). By hydrolysis of the anhydride the acid was obtained in the two forms required by theory. One of these melted at 176–177°, and, when heated in the presence of alkali, isomerized to the other, which melted at 135–136°.

Mention should be made of the fact that under certain conditions the rearrangement of the oxide

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[1] Fuson and Farlow, THIS JOURNAL, **56**, 1593 (1934).

to the cyclopentanone could be interrupted at an intermediate state. The intermediate compound has not been investigated fully, but it appears likely that it is the theoretically possible geometrical isomer of II.

Experimental

1-Phenyl-5-benzoylcyclopentene Oxide.—The general procedure of Conant and Lutz,[2] and Fuson and Farlow[3] was followed. It was found, however, that the reactants could be used in more nearly equivalent quantities—a modification which increased the yield of oxide by rendering its purification less troublesome. From 200 g. of 1,4-dibromo-1,4-dibenzoylbutane, 40 g. of zinc dust and 186 g. of hydrated sodium iodide was obtained 44 g. of the pure oxide.

Rearrangement of 1-Phenyl-5-benzoylcyclopentene Oxide

(a) **By the Action of Hydrogen Chloride in Alcohol.**—One gram of the oxide was shaken for ten minutes with 25 cc. of absolute alcohol saturated with dry hydrogen chloride. The mixture was then quickly filtered and poured onto 100 g. of cracked ice. The product, after crystallization from methanol, melted at 159–159.5° (corr.) and, when mixed with the sample prepared by Fuson and Farlow, showed no lowering of the melting point.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1; mol. wt., 264. Found: C, 81.7; H, 6.2; mol. wt. (Rast), 260, 270.

(b) **By Heating with Glacial Acetic Acid.**—A solution of 1 g. of the oxide in 25 cc. of glacial acetic acid was heated in such a manner that at the end of two minutes the temperature had reached 100°. It was then poured onto 50 g. of ice. After repeated recrystallization from methanol the product melted at 123.5–124.5°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.8; H, 6.4.

This method of treatment usually gave a product melting at 116–119° which was very difficult to purify. This substance was dissolved in boiling glacial acetic acid, and the solution was then diluted with hot water until a slight cloudiness was noted. This was discharged by heating, and the solution was allowed to cool. The product softened at 110–113°, and melted at 152–154°. This compound, when subjected to a second treatment similar to that just described, melted at 153–155°. A mixture of this with the oxide melted at 154–157°.

That the substance melting at 116–119° was an intermediate in the conversion of the oxide to the cyclopentanone was further supported by the fact that a hot, slightly alkaline solution of alcohol converted it into the pure cyclopentanone.

Reactions of 2-Phenyl-3-benzoylcyclopentanone

(a) **With Alcoholic Hydrogen Bromide.**—Treatment with this reagent for four days at 0° produced no change.

(b) **With Bromine.**—Bromination in chloroform solution gave a product which crystallized from alcohol in the form of yellow-orange needles melting at 136.5–137.5°.

Anal. Calcd. for $C_{18}H_{14}O_2Br_2$: C, 51.0; H, 3.3. Found: C, 51.4; H, 3.0.

Attempts to dehalogenate the dibromide by treatment with pyridine, zinc dust or sodium iodide all failed to give products which could be characterized.

(c) **With *p*-Chlorobenzaldehyde.**—One-half gram of the ketone and 0.5 g. of the aldehyde gave 1 g. of a solid which, after two recrystallizations from benzene and high-boiling petroleum ether, melted at 207–207.5°.

Anal. Calcd. for $C_{25}H_{19}OCl$: C, 77.6; H, 5.0. Found: C, 77.5; H, 4.9.

Ozonization of 8 g. of the *p*-chlorobenzal derivative gave a mixture of *p*-chlorobenzaldehyde, *p*-chlorobenzoic acid and 5.5 g. of **α-phenyl-β-benzoylglutaric anhydride.** The anhydride crystallized from benzene in needles melting at 183–184°.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.4; H, 4.8. Found: C, 73.3; H, 5.1.

The anhydride was dissolved in a 10% sodium hydroxide solution and the solution was filtered and acidified. The free **α-phenyl-β-benzoylglutaric acid,** after recrystallization from a mixture of ethyl acetate and petroleum ether, melted at 176–177°.

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.3; H, 5.1; neut. equiv., 156. Found: C, 69.0; H, 5.3; neut. equiv., 156.

Concentration of the mother liquors yielded an isomeric acid melting at 135–136° (from benzene).

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.3; H, 5.1; neut. equiv., 156. Found: C, 69.3; H, 5.4; neut. equiv., 155, 159.

The acid melting at 176–177° was heated for six hours with a 6% solution of alcoholic potassium hydroxide. Acidification of the resulting mixture gave the isomeric acid (melting at 135–136°).

Summary

It has been shown that 1-phenyl-5-benzoylcyclopentene oxide (I) rearranges to 2-phenyl-3-benzoylcyclopentanone (II) when treated with alcoholic hydrogen chloride.

The structure of the rearrangement product has been established by a degradation process leading to the formation of α-phenyl-β-benzoylglutaric acid which has been obtained in the two forms predicted by theory.

URBANA, ILL. RECEIVED JUNE 22, 1936

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[2] Conant and Lutz, THIS JOURNAL, **49**, 1090 (1927).

[3] Fuson and Farlow, *ibid.*, **56**, 1593 (1934).

[CONTRIBUTION FROM THE DYESTUFF LABORATORY OF THE MENDELEEV INSTITUTE OF CHEMICAL TECHNOLOGY]

Bisulfite Compounds of Azo Dyes. V. Bisulfite Reaction of Azo Dyes Containing Two Auxochromes

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While investigating the reaction of azo dyes with sodium bisulfite, it was determined in 1911 that the presence of a naphthalene component containing an amino or hydroxy group is necessary for the formation of bisulfite compounds.[1] On treatment with bisulfite, aminoazo dyes hydrolyze, giving off ammonia, and are converted to hydroxyazo dyes which form bisulfite compounds. In refuting the hypothesis of Spiegel, accepted at that time, according to which sodium bisulfite adds on to the azo group, giving the salt of hydrazo-N-sulfonic acid of the type $RN(SO_3Na)$-NHR', in 1915 the inadequacy of this theory was proved by a number of facts.[2] Of these, we consider the following most significant.

(1) The analogous physical and chemical properties of bisulfite compounds of dyes obtained by treating azo dyes with bisulfite and compounds obtained by coupling diazotized bisulfite compounds of aminonaphthols with benzene azo components (*e. g.*, phenol).

(2) The diazo dye obtained from α-naphthol and two molecules of diazotized aniline, $HOC_{10}H_5$-$(N{=}NPh)_2$, gives bisulfite compounds with only one molecule of sodium bisulfite, not with two as it should according to Spiegel, given two azo groups.

(3) All bisulfite compounds of azo dyes are colored—yellow, orange, red—while hydrazo compounds are colorless.

These and other considerations, developed in detail in former investigations, led us to the conclusion that the reactivity of azo dyes of the naphthalene series toward bisulfite is caused not by the azo group but by the auxochrome (NH_2 or OH) group in the naphthalene component of the dye and that the azo group of the dye plays a secondary role in this reaction, similar to that of the sulfo group in sulfonic acids of naphthols or naphthylamines, aiding or hindering the reaction according to the relative positions of the groups N=N and the reactive group OH or NH_2.

In a further work with S. W. Bogdanow, we succeeded in broadening this analogy to cover the bisulfite reaction of nitrosonaphthols.[3]

The analogous behavior of naphtholsulfonic acids and naphthol azo dyes in the bisulfite reaction was confirmed by physico-chemical investigation of the bisulfite compound of 2-naphthol-1-sulfonic acid.[4]

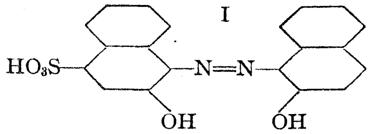
In the products of the reaction between bisulfite and naphtholsulfonic acids, nitrosonaphthols, or naphthol azo dyes, we find in all cases addition compounds of one molecule of bisulfite and one molecule of the original naphthol derivative. Here we definitely disagree with Bucherer who, on the basis of one incomplete analysis of the bisulfite compound of aminonaphthol, considers these compounds to be salts of acid esters of sulfurous acid and regards the reactivity of azo dyes with bisulfite from the point of view of Spiegel.[5]

Below we consider in greater detail the proof of the structure of the bisulfite compounds. Already in 1915, on the basis of the above-emphasized importance of the hydroxyl group in the reaction of the azonaphthol dye with bisulfite, it was suggested that dyes with one azo group and two hydroxyl groups can give compounds with bisulfite, containing two molecules of bisulfite and one molecule of dye.

This view has lately been disputed by A. King, an investigator who has contributed much interesting material in the field of bisulfite compounds of azo dyes.

King obtained the bisulfite compound of a dye obtained from diazotized 1,2-aminonaphthol-4-sulfonic acid and β-naphthol (I)

I



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[1] N. N. Woroshtzow, *J. Russ. Phys.-Chem. Soc.*, **43**, 771 (1911); *J. prakt. Chem.*, [2] **84**, 514 (1911).

[2] N. N. Woroshtzow, *J. Russ. Phys.-Chem. Soc.*, **47**, 1669 (1915); *Ann. chim.*, [9] **6**, 381 (1916); *ibid.*, **7**, 50 (1917).

[3] Woroshtzow, (a) *J. Russ. Phys.-Chem. Soc.*, **61**, 497 (1929); (b) *Ber.*, **62**, 57 (1929).

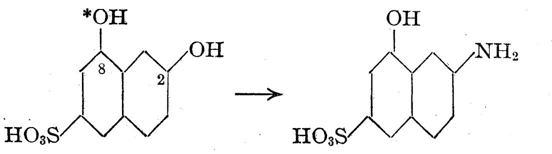
[4] N. N. Woroshtzow and A. G. Kassatkin, *ibid.*, **61**, 484 (1929); N. N. Woroshtzow and P. A. Bjelow, *J. Gen. Chem.* (*U. S. S. R.*), **63**, 39 (1931); *Ber.*, **64**, 77 (1931); N. N. Woroshtzow, *Bull. soc. chim.*, [4] **35**, 996 (1924).

[5] H. T. Bucherer, *J. prakt. Chem.*, [2] **69**, 49 (1904); H. T. Bucherer and M. Schmidt, *ibid.*, [2] **79**, 385 (1909); Bucherer and E. F. Sonnenborg, *ibid.*, **81**, 8 (1910); Bucherer and W. Zimmermann, *ibid.*, **103**, 285 (1921).

and found only one bisulfite group although the dye contains two hydroxyl groups.[6]

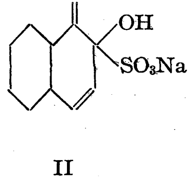
However, we do not see in King's experiment a refutation of our point of view, since the structure of this compound (I) has one peculiarity which allows us to foretell the inactivity of one of the hydroxyls, namely, the one present in the sulfonated nucleus.

It has long been known, from the work of Bucherer, that sulfo groups in the meta position to amino or hydroxyl groups in the naphthalene ring influence the bisulfite reaction unfavorably. It is possible, for example, using the ammonium salt of sulfurous acid, to exchange only one OH group for an amino group in 2,8-dihydroxynaphthol-6-sulfonic acid. Thus not diamino-

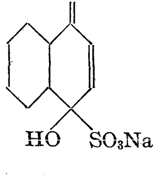


naphthalenesulfonic acid but aminonaphtholsulfonic acid is obtained, for the OH group in the 8-position marked by the star is paralyzed by the sulfo group in the meta position. Therefore we do not consider King's experiments final and have again taken up this work, formerly abandoned for various reasons, on the reactivity of monoazo dyes with two free auxochrome groups.

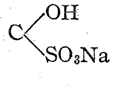
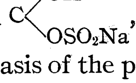
Before passing to a description of our experiments, we will attempt to give a short summary of the present state of the question of the structure of bisulfite compounds of azo dyes. Naphtholazo dyes give bisulfite compounds with the formula $HOC_{10}H_6N{=}NR\cdot NaHSO_3$. It is simplest to consider them according to the scheme corresponding to the quinoid (hydrazone) formula of azo dyes or the keto formula of naphthols, *e. g.*,

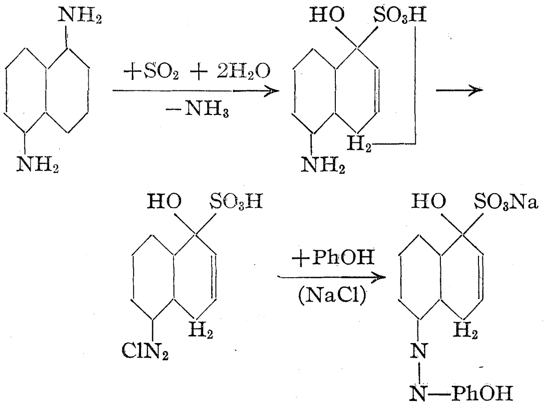


II



IIa

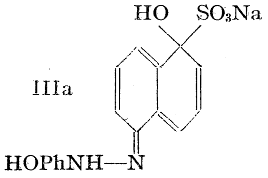
Here we employ the structure  $C\genfrac{}{}{0pt}{}{OH}{SO_3Na}$ and not the formerly used  $C\genfrac{}{}{0pt}{}{OH}{OSO_2Na}$, as better answering the facts on the basis of the proof of the structure of carbonyl bisulfite compounds by Raschig.[7] But earlier we saw that bisulfite compounds of azo dyes can be formed which do not differ in physico-chemical properties from the abovementioned compounds formed by introducing a bisulfite group into the diazo component before coupling, *e. g.*,

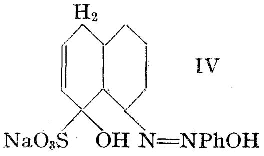


III

The compound III may be considered in its hydrazone form (IIIa) corresponding to ananaphthoquinone

IIIa

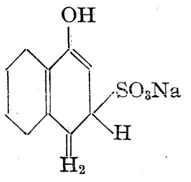




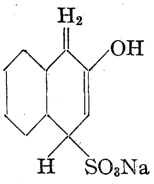
IV

But such a transformation cannot be allowed for the analogous 1,8-aminonaphthol derivative, *e. g.*, (IV) where the quinone-hydrazone structure is excluded by the impossibility of the existence of 1,8-naphthoquinone. Later investigation of the bisulfite reaction of nitroso-β-naphthol led S. W. Bogdanow to suggest another form for the structure of naphthol bisulfite compounds and hence for bisulfite compounds of azo dyes.[8]

Bogdanow considers these compounds of α- or β-naphthol to have the structures V and VI.



V



VI

In favor of this view we note the unfavorable influence of the sulfo group in the meta-position

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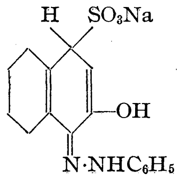
[6] A. King, *J. Chem. Soc.*, 1271 (1932).

[7] F. Raschig, *Ber.*, **59**, 859 (1926).

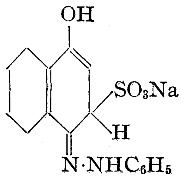
[8] S. W. Bogdanow, *J. Gen. Chem.* (*U. S. S. R.*), **64**, 9 (1932).

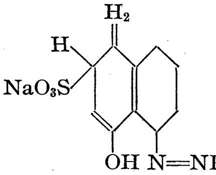
to the OH on the formation of bisulfite compounds, which can be explained by the comparative ease with which the sulfo group enters the 4-position in reduction reactions of bisulfite β-naphthol derivatives, *e. g.*, in the conversion of the bisulfite compound of nitroso-β-naphthol to 1,2-aminonaphthol-4-sulfonic acid.[9] According to Bogdanow the structures of the compounds II, IIa and IV are

VII



VIIa

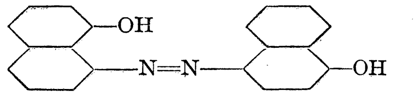




VIII

Thus, from the reactivity of the naphthalene component of azo dyes, with an OH group, we may consider permissible in various cases two different structural forms of bisulfite compounds of azo dyes—the hydrazone form in the quinoloid bisulfite (II, IIa) and hydroxyquinoidosulfonic acid (VII, VIIa) variants and the azoid form in the keto bisulfite (IV) and dihydronaphtholsulfonic acid (VIII) variants. A final choice of variants or determination of their stability under various conditions remains to be decided by further investigation.

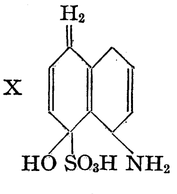
We set ourselves the task of studying the behavior of dyes with the structure IX in the bisulfite reaction. We shall also study mono-



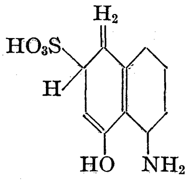
IX

bisulfite azo dyes obtained from the diazotized compounds of X or Xa and α-naphthol or α-

X

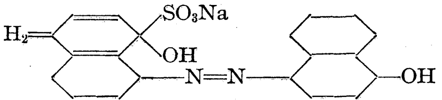


respectively



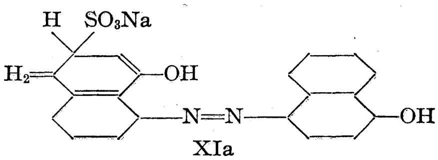
Xa

naphthylamine. The bisulfite compound of 1,8-aminonaphthol (X or Xa) was obtained by one of the authors in 1915 from 1,8-naphthylenediamine by Bucherer's method and its composition determined by analysis. Thus dyes which are derivatives of this bisulfite compound have the structure



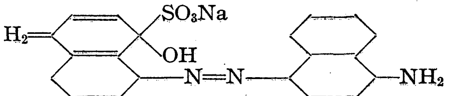
resp.

XI



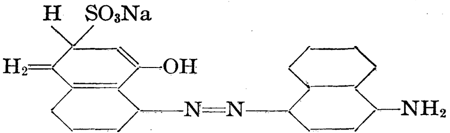
XIa

and



resp.

XII



XIIa

The diazotization of compound X takes place smoothly and quickly and requires no especially low temperatures since the diazo compound is stable. Coupling with α-naphthylamine to give the dye XII is carried out in an acid medium. An azo compound containing a bisulfite group (XII) is precipitated. On recrystallization, irregular reddish-violet needles are obtained. Coupling with α-naphthol to give the dye XI required a search for the proper medium since an alkaline soda medium affects the stability of the bisulfite radical. In an acid medium, coupling takes place very slowly. The best medium proved to be acetic acid to which a large quantity of sodium acetate was added. On recrystallization from alcohol, the orange-red dye XI precipitates in the form of fine, irregular needles. Both coupling products were treated with a 35% solution of bisulfite.

The aminoazo dye, XII, dissolves even in the cold in three to four times the theoretical amount of bisulfite solution, giving a yellow solution from which the new compound settles out in yellow crystals.

The hydroxyazo dye XI reacts only upon warming. In this case yellow crystals settle out more quickly.

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[9] Schmidt, *J. prakt. Chem.*, [2] **44**, 513 (1891); M. Boeniger, *Ber.*, **27**, 23, 3050 (1894).

The mother liquor obtained from the product prepared from the aminoazo dye contains an amount of ammonia corresponding to one molecule of ammonia for each molecule of aminoazo body.

The mother liquor from the product prepared from the hydroxyazo dyes does not contain ammonia. Therefore, the reaction of aminoazo dyes is accompanied by hydrolysis of the amino group in naphthalene dyes, in this case under extraordinarily mild conditions.

The compounds obtained from both dyes proved to be identical in composition and properties. The substance crystallizes in yellow, well-formed needles. It is soluble in water and alcohol.

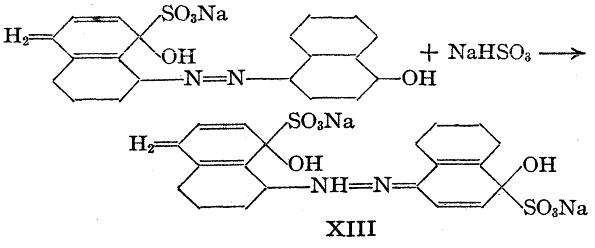
On diluting and warming the aqueous solution to 70°, the substance darkens and decomposes, giving off bisulfite. It is stable toward acids. Alkaline carbonate solutions decompose it, splitting off sulfur in the form of $SO_3^{=}$ ions, and a red substance is formed which crystallizes out when an excess of alkali carbonate is added. On heating the soda solution, the sulfur is completely split off as $SO_3^{=}$ ions, and a violet solution of a dye containing no sulfur is obtained. On treatment with caustic solutions, the substance decomposes rapidly, splitting off sulfurous acid. On heating with an excess of alkali or alkaline carbonates above 100°, a reddish-brown tarry mass is obtained.

The composition of the yellow bisulfite compound of both XI and XII is $HOC_{10}H_6N{=}NC_{10}H_6OH \cdot 2NaHSO_3$.

Thus the substance is an addition product of two molecules of bisulfite and one molecule of the dihydroxy dye.

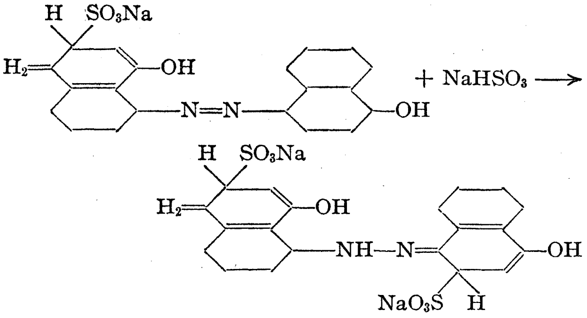
In favor of this theory we cite the yellow color of the new compound compared to the red color of the original monobisulfite compound and the increased solubility in water.

The formation of the dibisulfite compound according to the first variant may be represented as



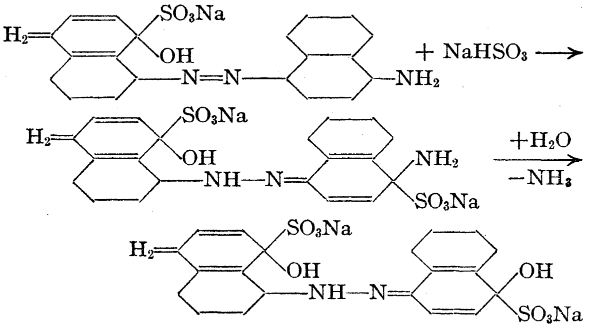
XIII

or according to the second variant (Bogdanow)



XIIIa

In the reaction between bisulfite and the aminoazo dye, according to the above scheme, in which the dibisulfite compound is formed, hydrolysis of the amino group either precedes or accompanies the reaction, for example (according to the first variant)



The possibility of obtaining from compounds XIII and XIIIa first the monobisulfite compound and then the dihydroxyazo compound, free of sulfur, by stepwise hydrolysis with alkaline reagents, is in agreement with this theory of the structure of XIII and XIIIa.

On treating the water solution of the yellow dibisulfite compounds with a soda solution at a temperature not greater than 40°, the solution turns red. On adding a large excess of saturated soda solution, orange-red, irregular needle-like crystals settle out. These proved to be the monobisulfite compound of the dihydroxyazo dye. Its properties did not differ from the above-mentioned original dye (XI). Evidently the molecule of bisulfite combining with the α-naphthol nucleus is less stable than that combined with 1,8-aminonaphthol.

If the product obtained by partial hydrolysis of the dibisulfite compound is treated with bisulfite, the yellow crystalline dibisulfite compound is obtained again.

When bisulfite is split off completely from the dibisulfite compound (or the monobisulfite compound XI) by treatment with an aqueous solution of soda above 70° or sodium hydroxide solution in the cold, the solution turns violet. On addition of excess concentrated sodium hydroxide solution, the monosodium compound of the dihydroxyazo dye, $NaOC_{10}H_6N_2C_{10}H_6OH$, settles out in beautiful violet needles.

It is interesting to note that it was not possible to recrystallize either the free dye or its sodium compound in sufficiently large quantities from organic solvents. As might be expected, the products obtainedf rom the dibisulfite compounds of both the aminoazo and oxyazo dyes proved to be identical.

When the sodium compound of the dihydroxyazo dye is treated with an alcoholic water solution of bisulfite, a mixture of the same yellow dibisulfite compound described above and the monobisulfite compound is obtained. At the same time reduction processes take place which greatly lower the yield of bisulfite compound. The products of reduction were not further investigated. The presence of ammonia and an aminohydroxy compound in the reaction mixture was confirmed.

On longer treatment of the dihydroxyazo dye with bisulfite, no bisulfite compound at all could be isolated because reduction processes dominate.

Experimental

The original product, the bisulfite compound of 1,8-aminonaphthol (X) was prepared as described in our second communication by treating 1,8-naphthylenediamine with bisulfite.

(1) **Aminoazo Dye (XII) (Monobisulfite Compound).**—Two grams of compound X was dissolved in 70 cc. of water at 70°. After filtering off the insoluble residue, the hot solution was cooled. Two cc. of hydrochloric acid (sp. gr. 1.19) was then added and the mixture treated with 3.6 cc. of a 16% solution of sodium nitrite. The solution of the diazo compound is brownish-red in color.

An alcoholic solution of 1.2 g. of α-naphthylamine was prepared separately and added with rapid stirring to the solution of the diazo compound at a temperature not exceeding 12°. Stirring was continued for three hours longer. The reddish-purple dye formed on coupling settles out completely on standing at 0°. The precipitate is filtered, washed free of excess chlorine ions with water and the paste treated with bisulfite (according to 4).

The dye dissolves poorly in water and rather well in alcohol. It is difficult to crystallize it from alcohol. Only 50 mg. of reddish-violet, irregular needles was obtained from alcohol. On treatment with sodium hydroxide solution, part of the precipitate dissolves, giving a reddish-violet color. On heating it dissolves completely in the alkaline solution.

Cold soda solution has no effect in the cold. On heating, a reddish-violet solution is formed.

The dye undergoes no change on treatment with hydrochloric acid.

(2) **Hydroxyazo Dye (XI) (Monobisulfite Compound).**—To the solution of diazo compound prepared in (1) from 2 g. of compound X a solution of sodium acetate was added to neutralize the hydrochloric acid. The solution was tested with congo red. Five cc. of acetic acid (80%) and 8 g. of crystalline sodium acetate were then added. A solution of 1.4 g. of α-naphthol in 12 cc. of water containing 0.4 g. of sodium hydroxide was added gradually, and an orange-red solution was formed. A crystalline dye settles out of the solution almost quantitatively on allowing to stand in the cold (−5°) for twenty-four hours and adding 10 g. of solid sodium chloride. The precipitate was filtered, washed with small portions of ice water and the paste treated with bisulfite. If coupling with α-naphthol is carried out in acetic acid solution without adding sodium acetate (or adding only a small amount of sodium acetate), the reaction is slowed up considerably and will go to an end on addition of an excess of α-naphthol. About four times the theoretical quantity of α-naphthol is required. However, the yield is small, and the product is contaminated by α-naphthol. On coupling with α-naphthol in sodium bicarbonate solution, the same results are obtained.

The dye dissolves fairly well in water, giving an orange-red solution. It dissolves readily in hot and cold alcohol. It does not crystallize well from alcohol. Only 30 mg. of pure substance was obtained in the form of fine, needle-like, reddish-orange crystals.

The dye does not dissolve in cold soda solution but gives a violet solution on heating. A deep violet solution is obtained on dissolving the dye in cold or hot sodium hydroxide solution.

On heating above 75°, the neutral aqueous solution darkens and becomes orange-brown in color. The dye is unchanged by hydrochloric acid.

Determination of sulfur in the bisulfite group of the dye is carried out in all cases in the following manner. A sample, weighed exactly, is dissolved in a definite volume of water so as to obtain a very dilute solution (0.005–0.01%) since at higher concentrations the violet color of the solutions makes it difficult to titrate with starch. A definite volume is treated with excess sodium hydroxide solution and heated for half an hour to 75°.

The sodium sulfite formed is titrated iodometrically. The solution containing the sulfite is added from a buret to a 0.01 *N* solution of iodine acidified with hydrochloric acid to disappearance of the blue color.

Anal. Calcd. for $C_{20}H_{15}N_2SO_4Na$: S, 7.65. Found: S, 7.24.

(3) **Dihydroxyazo Dye (IX) (1,5′-Dihydroxy-4,4′-azonaphthalene).**—Ten cc. of a solution of the diazo compound obtained according to (1) from 2 g. of compound X, was treated with an excess of alkali (5 cc. of a 30% sodium hydroxide solution). The solution turned deep red. The theoretical quantity of α-naphthol (1.2 g. of α-naphthol +0.34 g. of NaOH +10 cc. of water) was added gradually to the solution. Coupling takes place rapidly. However, the dye does not settle out quantitatively even after standing for twenty-four hours in the cold. When the mixture is treated with excess hydro-

chloric acid, the dye settles out quantitatively in the form of a reddish-violet powder, which gives with concd. sulfuric acid a bluish-green solution.

(4) **Dibisulfite Compound of the Dihydroxyazo Dye (XIII).** (a) **Preparation from the Aminoazo Dye (XII).**—A paste of the dye (prepared as in (1)) was shaken with 10 cc. of 35% sodium bisulfite solution at room temperature. The dye gradually goes into solution, and the color, which is orange-brown at first, turns orange-yellow. After eight to ten hours the dye is dissolved completely. On further standing, light yellow crystals of the dibisulfite compound settle out. When tests taken from the reaction mixture were observed under the microscope, the gradual disappearance of the reddish-violet crystals of monobisulfite compound and the precipitation of the yellow needles of dibisulfite compound could be followed. After three to four days the precipitation of the product is complete and the solution turns yellow. The crystals were filtered off, washed with small quantities of ice water and dried at room temperature over sulfuric acid in a desiccator. On drying with exposure to air above 40–50°, the product turns brown. When alkali is added to the mother liquor, ammonia is liberated.

The dibisulfite compound cannot be precipitated from the mother liquor by addition of sodium chloride. After half the water had been distilled off *in vacuo*, a mixture of crystals of sodium bisulfite and dibisulfite compounds settled out. When all the water had been distilled off at 35°, the residue was extracted with absolute alcohol to which 2 cc. of glacial acetic acid had been added. After filtering off the mineral salts, three-fourths of the alcohol was distilled off. On standing in the cold, orange-yellow crystals settled out of the remaining solution. These crystals were darker than those obtained in the first crop.

Quantitative Determination of the Ammonia Obtained by Hydrolysis of the Aminoazo Dye (XII) with Bisulfite.—A small quantity of thoroughly washed dye paste was dried to constant weight at 40° and a sample of the dry substance (0.5240 g.) mixed with 5 cc. of 35% sodium bisulfite solution and allowed to stand overnight. After twenty-four hours the mixture was treated with a large excess of sodium hydroxide solution and heated to boiling, the ammonia liberated being absorbed in 75 cc. of 0.04 *N* hydrochloric acid solution. The excess hydrochloric acid was titrated with 0.1 *N* sodium hydroxide solution. Calcd. for $C_{20}H_{14}N_2(SO_3Na)NH_2$: NH_3, 4.2. Found: NH_3, 3.9.

Iodometric Determination of Sulfur (see above).—Calcd. for $C_{20}H_{16}N_2S_2O_8Na_2$: S, 12.26. Found: S, 11.15.

(b) **Preparation from Hydroxyazo Dye (XI).**—To a paste of the dye (obtained from 2 g. of the bisulfite compound of 1,8-aminonaphthol according to (2)) was added 10 cc. of 35% sodium bisulfite solution and the mixture refluxed on a water-bath at 70°. After three hours the precipitate gradually dissolved.

After heating for twenty-four hours, the red crystals of the monobisulfite compound in the mixture disappeared, and their place was taken by pale-yellow crystals of the dibisulfite compound. The course of the reaction was followed under the microscope by observing test samples taken every hour.

The yellow crystals were filtered off, washed with a small quantity of ice-water, and dried at room temperature in a desiccator. On standing, a small quantity of yellow crystals settled out of the mother liquor. No ammonia was liberated on warming the mother liquor with alkali.

The dibisulfite compounds obtained according to (a) and (b) are absolutely identical. The compound is readily soluble in water, giving a yellow solution. It is readily soluble in alcohol. Its solubility in hot and cold alcohol is almost the same. It is difficult to recrystallize the compound from alcohol but it crystallizes from water in long pale yellow needles. The product was purified by recrystallization from small portions of alcohol. On cooling, only 60 mg. of pure substance was obtained.

Long boiling with alcohol or concentration of the alcohol solution of the product by distillation even *in vacuo* causes the product to darken and lose its crystalline form.

On heating with soda or sodium hydroxide solution, a violet solution is obtained. A solution of the dibisulfite compound does not change color on treatment with hydrochloric acid in the cold; on heating it reddens noticeably.

On heating 0.5–2% water solutions of the dibisulfite compound to 65°, the solutions redden.

Iodometric Determination of Sulfur.—Calcd. for $C_{20}H_{16}N_2S_2O_8Na_2$: S, 12.26. Found: S, 11.40.

(c) **Preparation from 1,5′-Dihydroxy-4,4′-azonaphthalene (IX).**—A paste of the dye obtained according to (3) undergoes no change when treated with bisulfite solution in the cold. On long heating at 70–95° the solution turns orange-brown, and the product is converted to a tarry mass. The reaction with sodium hydroxide indicates the presence of only traces of bisulfite compound. Ammonia was found in the reaction mixture. A solution of ferric chloride gives a dirty blue color with the reaction mixture.

Better results were obtained when four times the required amount of sodium bisulfite in alcoholic water solution (ratio of alcohol to water 3:2) was used and the mixture heated to 70° at a pressure of 100–120 mm.

After ten hours most of the dye had dissolved, giving a brown solution. Part remained in the form of black, tarry lumps. After filtering the cooled solution and allowing it to stand for twenty-four hours, a large quantity of orange-yellow crystalline bisulfite compound settled out. The course of the reaction was controlled by observing test samples of the reaction mixture under the microscope. The product was collected and dried as described above. It consisted of a mixture of mono and dibisulfite compounds.

(5) **Hydrolysis of the Dibisulfite Compound of 1,5′-Dihydroxy-4,4′-azonaphthalene.** (a) **Partial Hydrolysis.**—Two grams of dibisulfite compound prepared according to 4a and 4b was dissolved in 25 cc. of water, treated with 30 cc. of saturated soda solution in the cold and heated to 40°. The solution turns orange-red. After ten to fifteen minutes no further precipitation takes place. Sodium chloride and soda precipitate no more crystals from the filtrate. The crystalline precipitate is washed with ice water and dried as above.

The compound does not differ from the one described in (2) in crystalline form, solubility in water and alcohol, behavior toward alkalies and acids, behavior of its solutions on heating.

Iodometric Determination of Sulfur.—Calcd. for $C_{20}H_{15}N_2SO_8Na$: S, 7.65. Found: S, 7.31.

Two grams of the monobisulfite compound was treated with 10 cc. of 35% sodium bisulfite compound at 70°. After twenty-four hours the product dissolved completely. Yellow needles in all respects similar to those obtained in (4) settled out of the solution.

When treated with bisulfite in the cold, the monobisulfite compound is not converted to the dibisulfite compound even after forty-eight hours.

(b) **Complete Hydrolysis.**—The same results are obtained from hydrolysis of both the monobisulfite and dibisulfite compounds of 1,5′-dihydroxy-4,4′-azonaphthalene (XI).

One gram of the bisulfite compound was treated with 10 cc. of 25% sodium hydroxide solution. Very fine violet needles settled out in the cold, and on heating with excess sodium hydroxide, a violet solution was obtained. On cooling this solution, large violet needles with a metallic luster settled out. The product was recrystallized from hot alkali solution, washed with water to neutral reaction, and dried at 100°. According to the analysis, the product is the monosodium salt of the dihydroxyazo dye.

Analysis of the products obtained from the dibisulfite (1) and monobisulfite (2) compounds of the dihydroxyazonaphthalene: (1) Calcd. for $C_{20}H_{13}N_2O_2Na$: Na, 6.84; N, 8.5. Found: Na, 6.95; N, 8.3. (2) Calcd. for $C_{20}H_{13}N_2O_2Na$: Na, 6.84. Found: Na, 7.04.

On treating the hot (80°) alkaline solution of the dye with excess hydrochloric acid, all of the dye settles out in the form of reddish-violet powder which is absolutely identical with the product obtained in (3). The precipitate is washed thoroughly with water and dried at 100°.

The monosodium compound of the dye is insoluble in both hot and cold water, readily soluble in alcohol, ether, ethyl acetate and chloroform. It dissolves with difficulty in cold, better in hot benzene, toluene, nitrobenzene and glacial acetic acid. It is insoluble in cold alkalies but dissolves completely in hot alkalies. It is insoluble in both hot and cold soda solution.

The free dihydroxyazo dye behaves like the sodium compound toward solvents.

Summary

1. It has been shown, contrary to the statement of A. King, that it is possible to obtain addition products containing two molecules of bisulfite from monoazo dyes with two auxochromes. This proves the dominant importance of the auxochrome group (and the nucleus containing it) in the reaction of naphthaleneazo dyes with bisulfite and disproves Spiegel's theory.

2. The dibisulfite compound of the dye prepared from diazotized 1,8-aminonaphthol and α-naphthol may be obtained easily from the monobisulfite compound. Due to side reactions, a pure product cannot be obtained from the dye which contains no bisulfite group.

3. The formation of the dibisulfite compound from the monobisulfite compound of the α-naphthylamine dye is accompanied by hydrolysis of the amino group and the transition of the organic nucleus to the dihydroxy dye.

4. On hydrolysis of the dibisulfite compound of the dye in alkaline solution, stepwise decomposition takes place. First one molecule of bisulfite splits off, giving the monobisulfite compound. Then the second molecule splits off, forming the free dye.

5. The formation of bisulfite compounds corresponding to both the azoid and hydrazone forms is possible.

Moscow, U. S. S. R.

RECEIVED JULY 24, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF MERCK & CO., INC.]

Preparation and Properties of Xyloseen-(1,2) Tribenzoate

BY RANDOLPH T. MAJOR AND ELMER W. COOK

In the course of the investigation of various new syntheses of ascorbic acid an attempt was made to prepare xyloseen-(1,2) triacetate. Only a gum was obtained. The preparation of xyloseen-(1,2) tribenzoate was then undertaken in the hope that it might crystallize. This proved to be the case. Xyloseen-(1,2) tribenzoate was prepared by a procedure similar to that described by Maurer and Petsch[1] for the preparation of glucoseen tetrabenzoate.

Experimental

***d*-Xylose Tetrabenzoate.**—*d*-Xylose (50 g.) was added gradually to a mixture consisting of 190 cc. of benzoyl chloride, 200 cc. of anhydrous pyridine and 380 cc. of anhydrous chloroform, cooled in an ice-bath. The xylose soon dissolved and the solution was allowed to stand for twenty-four hours. Chloroform (600 cc.) was then added and the solution was washed successively with cold dilute sulfuric acid, sodium bicarbonate and water. After drying over calcium chloride the chloroform was removed by evaporation *in vacuo*. The crystalline residue of α-*d*-xylose tetrabenzoate was recrystallized from dioxane with the addition of methanol. It was also recrystallized either

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(1) Maurer and Petsch, *Ber.*, **66**, 998 (1933).

from absolute alcohol containing 10% pyridine or from benzene with the addition of petroleum ether; yield, 90%. The product was quite insoluble in water or petroleum ether and only slightly soluble in warm methanol. It was soluble in chloroform, dioxane and benzene; m. p. 115–116°; $[\alpha]^{20}D$ +115° in dry chloroform, $c = 2$.

Anal. Calcd. for $C_{33}H_{26}O_9$: C, 69.94; H, 4.63. Found: C, 70.15; H, 4.74.

***l*-Xylose Tetrabenzoate.**—α-*l*-Xylose tetrabenzoate was obtained in a similar manner; m. p. 115–116° and with the same rotation, but of opposite sign. However, on one occasion when crystallizing the reaction product from absolute alcohol containing 10% pyridine, the β-isomer was obtained; yield 29%; m. p. 173–174°; $[\alpha]^{20}D$ +44.5°, in dry chloroform, $c = 2$.

Anal. Calcd. for $C_{33}H_{26}O_9$: C, 69.94; H, 4.63. Found: C, 69.91; H, 4.64.

Benzobromo-*d*-xylose.—α-*d*-Xylose tetrabenzoate (25 g.) was dissolved in a mixture of anhydrous dioxane and chloroform. A saturated solution of hydrogen bromide in glacial acetic acid (50 cc.) was added and the whole allowed to stand for twenty-four hours. By this time benzobromo-*d*-xylose had precipitated. The mixture was cooled, filtered and washed with petroleum ether. The product was recrystallized from benzene by the addition of petroleum ether; yield 60%; m. p. 134–135°; $[\alpha]^{20}D$ +117°, in dry chloroform, $c = 2$.

Anal. Calcd. for $C_{26}H_{21}O_7Br$: C, 59.42; H, 4.03; Br, 15.22. Found: C, 59.62; H, 4.22; Br, 15.08.

The benzobromo-*d*-xylose was soluble in dioxane, chloroform, acetone and fairly soluble in methanol. It was insoluble in water, and only slightly soluble in petroleum ether.

Benzobromo-*l*-xylose.—Both α-*l*-xylose tetrabenzoate of m. p. 115–116° and β-*l*-xylose tetrabenzoate of m. p. 173–174° gave the same benzobromo-*l*-xylose of m. p. 134–135° and $[\alpha]^{20}D$ −116° in dry chloroform, $c = 2$.

***d*-Xylose Tribenzoate.**—Benzobromo-*d*-xylose (20 g.) was dissolved in 50 cc. of acetone and 0.8 cc. of water was added. The solution was cooled in an ice-bath and 12 g. of silver carbonate was added. After short stirring effervescence stopped. The mixture was then shaken an hour at room temperature. The insoluble silver salts were filtered and the filtrate evaporated *in vacuo* until a crystalline residue was left. The product was recrystallized from anhydrous benzene; yield, 98%; m. p. 188–189° (Pyrex capillary tube); $[\alpha]^{20}D$ +39.5°, in dry chloroform, $c = 2$.

Anal. Calcd. for $C_{26}H_{22}O_8$: C, 67.51; H, 4.80. Found: C, 67.54, 67.62; H, 4.85, 5.02.

Xyloseen-(1,2) Tribenzoate.—Benzobromo-*d*-xylose (20 g.) and anhydrous diethylamine (8.7 cc.) were dissolved in anhydrous benzene contained in a tightly capped bottle. The solution was heated at 55° for three hours, at the end of which time about 75% of the theoretical amount of diethylamine hydrobromide had precipitated. After cooling 150 cc. benzene was added and the mixture filtered. The filtrate was washed with iced dilute sulfuric acid and twice with ice water. The benzene extract was dried over calcium chloride and evaporated *in vacuo* to a gum. The gum was dissolved in 50 cc. of warm absolute ethanol and petroleum ether added to a faint turbidity. Upon allowing this to stand two to three days in an ice box, xyloseen-(1,2) tribenzoate precipitated. It was recrystallized from absolute ethanol; yield, 11%; m. p. 126–128°; $[\alpha]^{20}D$ −280°, in dry chloroform, $c = 0.5$.

Anal. Calcd. for $C_{26}H_{20}O_7$: C, 70.24; H, 4.54. Found: C, 70.34, 70.15; H, 4.80, 4.71.

Similarly *l*-xyloseen-(1,2) tribenzoate of the same melting point, and optical rotation, $[\alpha]^{20}D$ +280°, in dry chloroform; $c = 2$ was prepared.

Xyloseen-(1,2) Tribenzoate Dichloride.—*l*-Xyloseen-(1,2) tribenzoate (2.5 g.) was dissolved in 200 cc. of anhydrous benzene and chlorine was passed in until a permanent greenish-yellow color remained. After evaporating the solution *in vacuo* the gummy residue was crystallized from absolute ethanol. The 1-xyloseen-(1,2) tribenzoate dichloride was recrystallized from anhydrous benzene with the addition of petroleum ether; yield, 17%; m. p. 178–180°; $[\alpha]^{20}D$ +110°, in dry chloroform, $c = 1.5$.

Anal. Calcd. for $C_{26}H_{20}O_7Cl_2$: C, 60.57; H, 3.91; Cl, 13.77. Found: C, 60.70; H, 4.07; Cl, 13.26.

Summary

1. Dextro and levo xylose tetrabenzoate have been synthesized. The α form of the former has been isolated and both the α and β forms of the latter were made.
2. Benzobromo-*d*- and *l*-xylose have been made.
3. *d*-Xylose tribenzoate has been made from *d*-benzobromo-*d*-xylose.
4. Dextro and levo xyloseen-(1,2) tribenzoate have been synthesized.
5. *l*-Xyloseen-(1,2) tribenzoate dichloride was made by the addition of chlorine to *l*-xyloseen-(1,2) tribenzoate.

RAHWAY, N. J.

RECEIVED SEPTEMBER 25, 1936

NOTES

Polymorphism of Acetaldehyde 2,4-Dinitrophenylhydrazone

By W. M. D. Bryant

In two earlier papers the writer reported the melting point and optical crystallographic constants of acetaldehyde 2,4-dinitrophenylhydrazone.[1] It was shown in the second paper that this derivative exists in at least two distinct crystalline modifications designated as stable and metastable, respectively. Shortly afterward Ingold, Pritchard and Smith[2] reported two crystalline modifications and commented on their possible identity with the above polymorphs. Their "metastable" modification, however, melted at 146°, while only one melting point (168.5°) was obtained from both of the writer's products. Campbell has recently stated[3] that only one modification exists and that the writer's metastable modification was merely contaminated material. This statement is completely at variance with the writer's previous work and with experiments to be reported below. Further, Campbell has incorrectly quoted this modification as melting at 147° instead of 168.5°. He suggests crotonaldehyde 2,4-dinitrophenylhydrazone as a possible contaminant.

Extending the work reported earlier, it has been possible to duplicate the preparation of the low melting material obtained by Ingold, Campbell, and also by Purgotti.[4] This material recrystallized once from benzene is optically indistinguishable from the stable modification as judged by refractive indices, optic axial angle and the highly characteristic inclined dispersion, but is quite distinct from the writer's metastable form. The material melts fairly sharply at 147° and the melting point is not noticeably depressed on mixing with some of the higher melting stable material. No similar product was obtained on mixing a small amount of crotonaldehyde derivat
(m. p. 199.6°) with some of the stable mod
tion.

While it is not proposed that the low
material is necessarily pure, it appears lik

the contaminant is of a catalytic sort (perhaps a trace of sulfuric acid) and that the low melting point is due to an inhibition of the transition from the stable to the metastable form rather than contamination by another "hydrazone." The fact that the stable and metastable forms previously reported both melted at 168.5° suggests that the transition ordinarily occurs in the solid state prior to fusion in the case of the pure stable modification and that the observed melting point is in both cases really that of the metastable form. It may well be that 147° approximates the melting point of the unchanged stable form. According to this reasoning the two products described by Ingold and by Campbell would both be the stable variety, with the difference that the low melting samples may contain a trace of negative catalytic material.

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Received September 19, 1936

Kinetic Medium Effects in the Reaction between Bromoacetate and Thiosulfate Ions

By Sam Eagle and J. C. Warner

An examination of the results of recent
studies[1-3] on the rate of reaction of thi
ion with bromoacetate ion in water
solvents has led us to the co
facts are in better agreem
theory[4] than is implied i
La Mer and Kamner
tion is revealed by
either for our d
aqueous alco
constants
search
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(1) Bryant, This Journal, **54**, 3758 (1932); **55**, 3201 (

(2) Ingold, Pritchard and Smith, *J. Chem. Soc.*, 86 (19

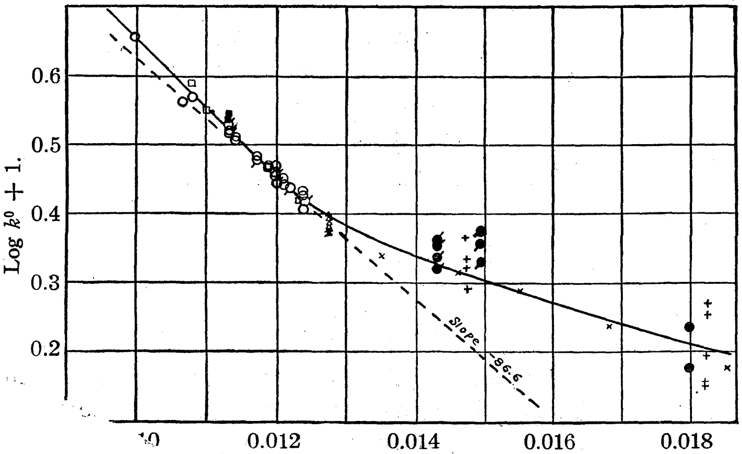
(3) Campbell, *Analyst*, **61**, 391 (1936).

(4) Purgotti, *Gazz. chim. ital.*, **24**, 569 (1894).

In testing the theory, La Mer and Kamner have used rate constants over the range $\mu = 0.002–0.05$. In most of their experiments in solvents of dielectric constant less than water, the primary salt effect is larger than the effect of decreasing the dielectric constant and as a consequence the experimental rates are higher in the mixed solvents than in water. It must be emphasized that the k^0s in equation (1) from Scatchard's theory are rate constants at zero ionic strength. We have calculated k^0 values from the data of the above investigators[1-3] by the well-known relation

$$\log k/k^0 = \frac{\epsilon^2 \mathbf{Z}_A \mathbf{Z}_B}{2.3D''k''T} \frac{\kappa}{1 + \kappa a} \qquad (2)$$

using Straup and Cohn's value, $a = 5.6$ Å. The rate constants at zero ionic strength (k^0) show a uniform decrease with decrease in dielectric constant. In the figure, we have plotted log k^0



Ac⁻ at 25°: Kappanna— + $C_2H_5OH-H_2O$, ●, Kamner— ▲, H_2O; ■, urea-H_2O, ●, glycerol- nd Cohn—△, H_2O, ○, glycine-H_2O, ○-, α-], urea-H_2O × $C_2H_5OH-H_2O$.

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and Kamner
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points to the inadequacy of equation (2) for extrapolating to zero ionic strength. The "theoretical" slope using $a = 5.6$ Å. in equation (1) is shown in the figure.

In mixed solvents of dielectric constant greater than water there is good agreement with the theory. The somewhat steeper experimental slope may be attributed to the "salting in" of the highly polar non-aqueous constituents of the solvent. In solvents of dielectric constant less than water, the rate decreases less rapidly with decrease in dielectric constant than required by the approximate equation (1). This deviation might be expected for a variety of reasons. It may be due to a "salting out" of the non-aqueous solvent so that the effective dielectric constant about the reacting ions is less than the dielectric constant according to solvent composition.[5] Since k^0 values are calculated from experimental values at finite ionic strengths, the influence of salting out will be to give calculated values which are higher than the true k^0. Scatchard[4] has already pointed out the limitations imposed upon equation (2) through the neglect of "higher terms" in its derivation. Due to these limitations, equation (2) becomes less adequate for calculating k^0 from an experimental k at constant dielectric constant as the dielectric constant of the solvent is decreased. Due to each of these causes, one would expect the true k^0 to be lower than any calculated by equation (2). This conclusion is supported by our calculations, especially those using Kappanna's data which cover a considerable range of ionic strength. Almost invariably, the lowest k^0 (calculated) is obtained from the experimental k at lowest ionic strength.

The difference in rate constants found by Straup and Cohn in isodielectric solvents is of the same order of magnitude as found by Warner and War-
ck[5] for the conversion of ammonium cyanate
urea in isodielectric mixtures of water and
alcohols. These differences might be
d whether the deviations for the simple
s were due to salting in and salting out or
nadequacy of equation (2). In addition
factors already discussed, one might at-

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rner and Warrick, THIS JOURNAL, **57**, 1491 (1935).

tempt to attribute deviations to a change in "a" with solvent or to ion associations which might change the factor $\mathfrak{z}_A\mathfrak{z}_B$ from 2 to 1. Considering all of the limitations imposed in obtaining equations (1) and (2) from the theory, one must conclude that the agreement is as good as could reasonably be expected.

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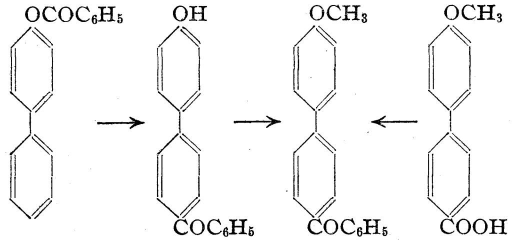
SCHENLEY PARK, PITTSBURGH, PA.
RECEIVED JULY 13, 1936

The Fries Rearrangement of 4-Benzoyloxydiphenyl

BY L. F. FIESER AND CHARLES K. BRADSHER

Having recently reported that the Fries rearrangement of 4-acetoxydiphenyl yields a mixture of 4-hydroxy-3-acetyldiphenyl and 4-hydroxy-4′-acetyldiphenyl,[1] we were interested to note that, in a paper published prior to ours but after the completion of our work, Hey and Jackson[2] obtained only 4-hydroxy-3-benzoyldiphenyl on heating 4-benzoyloxydiphenyl with aluminum chloride in tetrachloroethane solution at 140° and found no evidence of the heteronuclear migration of the benzoyl group. No trace of the alkali-soluble product, m. p. 193–195°, claimed by Blicke and Weinkauff[3] to be produced under identical conditions was observed. The latter investigators had assigned to their product, albeit without satisfactory evidence, the structure of 4-hydroxy-4′-benzoyldiphenyl and had regarded this as a case of heteronuclear rearrangement.

In view of the discrepancy in these two reports and the divergence of our results with the acetate from those of Hey and Jackson with the benzoate, we investigated the rearrangement of the latter ester under conditions similar to those employed with the former.[1] The reagents were brought together in the presence of carbon bisulfide, the solvent was distilled, and the residue heated at 160°. From the resulting mixture a substance identified as 4-hydroxy-4′-benzoyldiphenyl (II), m. p. 194–195° when pure, was isolated in 22% yield. As in other cases, the 4′-derivative is easily separated by virtue of its relatively low solubility. The structure of the substance was established by conversion to the methyl ether (III), which was compared with a sample synthesized by the condensation of the chloride of 4-methoxy-4′-carboxydiphenyl[1] (IV) with benzene. The two samples were found to be identical. The same substance resulted from the Friedel and Crafts reaction of 4-methoxydiphenyl with benzoyl chloride, as stated by Blicke and Weinkauff and by Hey and Jackson, but our results differed from those of the previous investigators in that we isolated not only the 4′-benzoyl derivative (37% yield) but also 4-methoxy-3-benzoyldiphenyl (39% yield).



I II III IV

We are in agreement with both pairs of investigators regarding the properties of the various compounds, and the differences in the results appear to be due to variations in the conditions of the reactions and the methods of separating the products. We are inclined to believe that the conditions for the Fries rearrangement specified by Blicke and Weinkauff are not very satisfactory, for although these workers undoubtedly obtained 4-hydroxy-4′-benzoyldiphenyl, we were no more able to duplicate their results, at least in one small-scale experiment, than were Hey and Jackson.

That under slightly different conditions the benzoyl group migrates to an appreciable and unmistakable extent to the 4′-position is consistent with the findings regarding the acetyl migration.[1] We do not, however, regard these examples of heteronuclear migration as having any great theoretical significance, for the evidence available indicates that the Fries reaction is not a true rearrangement but an intermolecular acylation.[4]

Experimental Part

Fries Rearrangement.—4-Benzoyloxydiphenyl (5 g.) was mixed thoroughly with finely powdered aluminum chloride (4.7 g.) and carbon bisulfide (25 cc.) and the solvent was removed by distillation from the steam-bath. The residue was heated for thirty minutes in an oil-bath maintained at 160°, and after cooling and adding ice and

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[1] Fieser and Bradsher, THIS JOURNAL, **58**, 1738 (1936).

[2] Hey and Jackson, *J. Chem. Soc.*, 802 (1936).

[3] Blicke and Weinkauff, THIS JOURNAL, **54**, 330 (1932).

[4] Rosenmund and Schnurr, *Ann.*, **460**, 56 (1928); Cox, THIS JOURNAL, **52**, 352 (1930).

dilute hydrochloric acid the product was taken up in ether. The ethereal solution was washed with dilute acid and with water and extracted with 2.5% sodium hydroxide, and on acidifying the alkaline extract there was obtained 4 g. of grayish material. On two crystallizations from benzene this afforded nearly pure **4-methoxy-4'-benzoyldiphenyl**, m. p. 193–195°, yield 1.1 g. (22%). A small amount of a highly colored impurity was removed on reprecipitation from an alkaline solution, and further crystallization from benzene gave round, faintly yellow crystal-clusters, m. p. 194–195°.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.18; H, 5.14. Found: C, 83.42; H, 5.14.

No pure products were isolated from the mother liquor. On conducting the rearrangement according to Blicke and Weinkauff[3] the alkali-soluble product amounted to only about 2% of the ester used and it consisted largely of 4-hydroxydiphenyl.

The acetate formed colorless plates, m. p. 127–128°, from methyl alcohol.

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.72; H, 5.09. Found: C, 80.00; H, 5.39.

The methyl ether, prepared with the use of dimethyl sulfate and alkali, crystallized from benzene as colorless needles, m. p. 165–166°. It was identified by comparison with the samples described below.

Friedel and Crafts Reaction.—A solution of 10 g. of 4-methoxydiphenyl and 6.9 cc. of benzoyl chloride in 130 cc. of tetrachloroethane was cooled to −10° and 8 g. of aluminum chloride was added all at once. The mixture was stirred mechanically and allowed to come to room temperature. After eighteen hours ice and acid were added, the solvent was removed with steam, and the moist product was taken up in benzene. On concentrating the solution to a volume of 50 cc. and cooling, 5.8 g. of nearly pure **4-methoxy-4'-benzoyldiphenyl**, m. p. 165–167°, crystallized. The mother liquor was concentrated to a volume of 25 cc. and treated with petroleum ether. The material which separated on one crystallization from methyl alcohol gave 6.1 g. of a product melting at 91–92° (flat needles). This substance is insoluble in alkali and depresses the melting point of 4-methoxydiphenyl; it is undoubtedly 4-methoxy-3-benzoyldiphenyl, which Hey and Jackson[2] prepared by a synthesis establishing the structure and for which they report the melting point 93°.

Synthesis of 4-Methoxy-4'-benzoyldiphenyl.—A solution of 0.5 g. of 4-methoxy-4'-carboxydiphenyl[1] in 10 cc. of thionyl chloride was refluxed gently for one hour and the excess reagent was removed at reduced pressure. The residue was dissolved in 25 cc. of thiophene-free benzene, 0.3 g. of aluminum chloride was added and the mixture was refluxed for one hour. The reaction product, recovered in the usual way, crystallized from alcohol or benzene as colorless needles, m. p. 165–166°. Mixed melting point determinations of this 4-methoxy-4'-benzoyldiphenyl with both of the samples obtained above indicated the identity of all three preparations.

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RECEIVED AUGUST 12, 1936

A New Synthesis of Morpholine

BY BURT L. HAMPTON AND C. B. POLLARD

Morpholine was first prepared by L. Knorr[1] by heating diethanolamine and an excess of concentrated hydrochloric acid in a sealed tube and then refluxing the reaction mass with potassium hydroxide. Because of low yields Knorr abandoned this method for the sulfuric acid method.[2] In both cases he failed to state his yields. However, Jones and Burns[3] have shown that morpholine is formed in about a 10% yield by the action of sulfuric acid on diethanolamine following the directions of Knorr. Therefore the yield using hydrochloric acid and potassium hydroxide must have been considerably lower. The only other methods for the preparation of morpholine are indirect ones and need not be reviewed here.

In his first preparation Knorr assumed the chlorohydrin of diethanolamine to be formed. Ring closure with loss of hydrogen chloride was then effected by refluxing in potassium hydroxide solution. He based this assumption on the fact that he was able to isolate the chlorohydrin of N-phenyldiethanolamine in a similar reaction; however, he was unable to isolate the chlorohydrin of diethanolamine because of its similarity in properties to the parent substance.

We have shown in this investigation that the chlorohydrin does not necessarily have to be formed and that no dehydrating agent other than that of heat on the hydrochloride is necessary for the formation of morpholine from diethanolamine. This was surprising in view of the work of Knorr.

Preparation.—Diethanolamine (2 moles) is placed in a round-bottomed flask fitted with a thermometer and an air-cooled condenser. Concentrated hydrochloric acid is added slowly until the solution is acid to litmus. The solution is then heated rapidly until the water is driven off, and the temperature of the solution is kept at 200–210° for fifteen hours. The reaction mass is now allowed to cool, an excess of calcium oxide is added, and the mixture subjected to dry distillation. The resulting liquid is dried over solid sodium hydroxide and refluxed over metallic sodium for thirty minutes; it is then subjected to fractionation. The entire product boils at from 126–129° and is practically anhydrous. The yield is around 48%. This procedure offers a rapid

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(1) Knorr, *Ber.*, **22**, 2081 (1889).

(2) Knorr, *Ann.*, **301**, 1 (1898).

(3) Jones and Burns, THIS JOURNAL, **47**, 2966 (1925).

method for the preparation of morpholine and obviates many steps necessary in other methods.

If instead of subjecting the mixture to dry distillation concentrated sodium hydroxide is added and the solution distilled with steam into hydrochloric acid, a yield of 65% of the hydrochloride of morpholine is obtained. This, when distilled over calcium oxide, gives about 45% of morpholine (based on diethanolamine).

If to the original reaction mass cold sodium hydroxide is added, and the resulting amine layer is extracted with ether, pure morpholine is obtained.

The picrate melts at 145–147°. Knorr gives the melting point of the picrate as 145–147°. N-(2-Chlorocinchoninyl)-morpholine was used for the analysis.

Anal. Calcd. for $C_{14}H_{13}ClN_2O_2$: N, 10.13. Found: N, 10.07.

ORGANIC CHEMISTRY LABORATORY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA
RECEIVED AUGUST 20, 1936

Alkylation of Aromatics with Olefins in the Presence of Boron Fluoride[1]

BY V. N. IPATIEFF AND A. V. GROSSE

In the course of our investigations on hydrocarbon reactions in the presence of metallic halides[2] the alkylation of aromatic hydrocarbons with olefins in the presence of boron fluoride was also accomplished. This fact is interesting in connection with recent similar work of Nieuwland[3] in which the addition of acids, especially sulfuric acid, was considered to play an important part in these condensations.

As has been recently shown in our laboratories[4] the sulfuric acid *per se* is an excellent alkylating catalyst under the conditions used by Nieuwland and the presence of boron fluoride is not necessary. On the other hand, boron fluoride *without acids* is *also* an alkylating catalyst.[5]

The alkylation of aromatic hydrocarbons with olefins, including ethylene,[6] takes place in the presence of boron fluoride in a *nickel-lined*[7] autoclave at room temperature and also at temperatures up to 250°.

In one particular experiment 250 cc. (219 g.) of benzene was treated in a rotating nickel-lined bomb with ethylene in the presence of 18.5 g. of boron fluoride and 2.0 g. of water for eight hours at 20–25°. The initial ethylene pressure was 20 atmospheres, which dropped readily to 10 atmospheres when fresh ethylene was pressed in. In all five refillings were made and 22 g. of ethylene was absorbed.

The reaction product, after washing and drying, was separated into the following fractions:

Charge, 250.0 cc.

Fraction	Boiling points at 760 mm., °C	Volume in cc.	% of total product	$n^{20.0}D$	Remarks: (All fractions water white and stable to $KMnO_4$ solution)
1	80 ± 1.5	180.0	72.0	1.5002	Pure benzene, solidifies in ice
2	81.5–135	1.0	0.4	1.4985	
3	136 ± 1	52.0	21.0	1.4960	Monoethyl benzene; $d^{20.0}_4$0.8674
4	137–182	3.5	1.5	1.4958	
5	183 ± 1	7.5	3.0	1.4974	Diethylbenzenes
Bottoms	>184	4.0	1.6	1.5032	
Losses		2.0	0.8		
Total		250.0	100		

As can be seen from these results over 25% of the benzene was alkylated to monoethyl-, diethyl and higher alkylbenzenes. The constants of our monoethylbenzene (see table) are in complete agreement with the values given in the literature (see "I. C. Tables," boil. point at 760 mm. 136°, $n^{20}D$ 1.4959, $d^{20.0}_4$ 0.8669). As a further check oxidation with boiling potassium permanganate solution gave only *benzoic acid*, melting at 122.0°, proving the absence of xylenes.

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(1) Announced by V. N. Ipatieff before the Organic Section of the American Chemical Society at the Kansas Meeting on April 22, 1936.

(2) V. N. Ipatieff, A. V. Grosse and co-workers, THIS JOURNAL, **57**, 1616, 1722, 2415 (1935); **58**, 913, 915 (1936); *Ind. Eng. Chem.*, **28**, 461 (1936).

(3) S. J. Slanina, F. J. Sowa and J. A. Nieuwland, THIS JOURNAL, **57**, 1547 (1935).

(4) V. N. Ipatieff, B. B. Corson and H. Pines, *ibid.*, **58**, 919 (1936).

(5) For alkylations of paraffins, see Ref. 1, p. 1616.

(6) As contrasted to the actions of sulfuric acid, see Ref. 3.

(7) For the role of nickel, see Ref. 1, pages 1617 and 1618.

UNIVERSAL OIL PRODUCTS CO.
RIVERSIDE, ILL.
RECEIVED JULY 22, 1936

Thermal Type Silver–Silver Chloride Electrodes

BY C. K. RULE AND VICTOR K. LA MER

In connection with an investigation of the temperature coefficients of the e. m. f. of quinhydrone-silver chloride cells in deuterium oxide, we have tested the reliability of silver–silver chloride electrodes made by a thermal method analogous to that recommended by Owen[1] and by Keston,[2] respectively, for the corresponding iodide and bromide electrodes. An electrode formed from a coil of platinum wire sealed into a tube of Jena normal glass was covered with a paste composed of seven parts of silver oxide and one part of silver chlorate and heated to decomposition in an electric furnace. No appreciable differences were observed when the percentage of silver chlorate was varied between 8 and 15.

Twelve electrodes immersed in 0.01 M hydrochloric acid solution exhibited ±0.02 mv. as the average deviation from the mean. After standing for six weeks this value increased to not more than ±0.04 mv. Freshly made electrodes agreed with the old within this limit.

A comparison of the "thermal" type electrodes with those made by decomposing a paste of silver oxide by heat and then electrolyzing for five hours in 0.2 M hydrochloric acid solution at 1.8 milliamperes per electrode showed that the electrolytic type tended to drift and were on the average about 0.04 mv. more positive.

CHANDLER LABORATORY
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NEW YORK, N. Y.

RECEIVED OCTOBER 6, 1936

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(1) Owen, THIS JOURNAL, **57**, 1526 (1935).
(2) Keston, *ibid.*, **57**, 1671 (1935).

The Heat of Fusion of Stannic Iodide

BY SAMUEL S. TODD AND GEORGE S. PARKS

The changes in heat content of stannic iodide were measured by us in 1928 for the temperature intervals between 27 and 80, 120, 155 and 171°, respectively. A method of mixtures was used with a water calorimeter, the details of the apparatus and experimental procedure being given in a previous paper by Parks and Todd.[1] The sample of stannic iodide studied had been kindly prepared for us by Professor J. H. Hildebrand.

Although the error in the calorimetric measurements themselves was within 1%, considerable uncertainty as to the premelting effect in the crystalline material precluded at that time a reliable calculation of the heat of fusion of stannic iodide from our heat content data. Recently, however, Negishi[2] has obtained accurate information concerning the heat capacities of solid and liquid stannic iodide over a range of temperatures. Using his data and taking the melting point as 144°, we have now calculated the following fusion values from our four determinations pertaining to the 27–155° range: 7.23, 7.19, 7.24 and 7.25 cal. per gram. The mean heat of fusion is 7.23 (±0.14) cal. per gram or 4530 cal. per mole.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY, CALIFORNIA

RECEIVED SEPTEMBER 2, 1936

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(1) G. S. Parks and S. S. Todd, *Ind. Eng. Chem.*, **21**, 1235 (1929).
(2) G. R. Negishi, THIS JOURNAL, **58**, 2293(1936). Prof. J. H. Hildebrand kindly sent us these essential data prior to publication.

NEW BOOKS

Physical Aspects of Organic Chemistry. By WILLIAM A. WATERS, M.A., Ph.D. (Cantab.), University of Durham. Introduction by Professor T. Martin Lowry, George Routledge and Sons, Ltd., Broadway House. 68–74 Carter Lane, London E.C., England, 1935. xv + 501 pp. 14 × 22 cm. Price, 25s.

The title of this book does not indicate very clearly the nature of its contents. Actually it is largely concerned with current electronic ideas of valence and their application to organic chemistry, especially to details of reaction mechanism. The chapter headings are: Chemical Affinity, Physical Theories of Molecular Structure, Valency, Electrical Dipoles, Chemical Reactivity, Unsaturation, Free Radicals and Their Non-ionic Reactions, Ionization and Ionic Reactions, Acidity, The Reactivity of Halogen Compounds, General Polarity, Hydrolysis and Esterification, Ionotropic Change, Molecular Rearrangement, Conjugation, Aromatic Compounds—I, Aromatic Compounds—II.

But this list does not furnish an adequate indication of the range of topics dealt with. Many of these subjects are exceedingly broad, have a lengthy and complicated history and even today have not reached any state of agreed opinion. One is therefore especially impressed with the skill of presentation. The author states in his preface: "The historical aspect of a rapidly developing subject has been kept continually in view, with the intention of giving a general outline of theoretical organic chemistry rather than one *ad hoc* point of view." In general, he succeeds admirably in this aim. Any final interpretations are usually those of the English schools, whose recent writings on electronic mechanisms have been so extensive and ingenious, though sometimes obscure and not always in mutual agreement. Here the obscurity is resolved or avoided, conflicting viewpoints are judiciously weighed, and the attempt to interpret is seldom pushed to such a degree of detail that it ceases to be profitable or becomes devoid of plausibility.

No book is perfect, and this one errs perhaps in a tendency toward excessive conciseness. Thus the discussion of atomic structure is probably too brief to inform anyone not already informed.

In so extensive an effort it is natural also to find some errors in apportioning or assigning credit. For example, the Diels–Alder reaction, which is neatly, if rather sketchily, summarized in about two pages was not first discovered by Diels and Alder in 1928, but by v. Euler and Josephson in 1920. Incidentally also, this reaction is not diagnostic of conjugated systems, since even apart from side reactions consisting of complex polymerization it sometimes fails.

Again it seems scarcely correct to state that what are here called stable mixed double bonds were first suggested by Lowry in 1922. It is no doubt true that he first called attention to some special implications of this type of structure. But the arithmetical existence of a charge on atoms having unconventional valences could hardly escape the attention of anyone making the count of electrons necessary to write the structure. Besides, Langmuir[1] had already in 1921 presented a generalized formula for the calculation of such residual charges.

No one will, however, deny that Professor Lowry has made important innovations in the application of electronic ideas to chemical structures and reactions. Moreover, he laid the foundation for this book, completed by Dr. Waters, which is the first clear and comprehensive summary in its field.

(1) Langmuir, *Science*, **54**, 62 (1921). In his original paper [*Trans. Faraday Soc.*, **18**, 285 (1923)] Lowry says "It is difficult to believe that Langmuir can have overlooked the fact ... that the nitrogen atom is positively charged ... but I cannot find in any of Langmuir's papers a clear recognition of the phenomenon of intramolecular ionization." Apparently then he had not noted the paper cited above.

W. H. Carothers

Die Bierhefe als Heil-, Nähr- und Futtermittel. (Beer Yeast as a Medicinal Agent, Food and Feeding Stuff.) By Dr. Julius Schülein, Munich. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1935. viii + 194 pp. 29 figs. 15 × 22.5 cm. Price, RM. 9; bound, RM. 10.

The author has brought together a large amount of widely scattered material dealing with the use of yeast as a food and as a medicinal agent. Much of this information has heretofore not been assembled. He has attempted to give a general view of the subject, and discusses the state of research in connection with this field. The subjects discussed are vitamins, the use of yeast as a therapeutic agent, the use of yeast and yeast extracts in human nutrition and as a food for animals. The work on vitamins is fairly comprehensive, but some of the conclusions are based on vitamin researches carried on a number of years ago, and consequently certain statements should be interpreted with this fact in mind. This also applies to some of the statements concerning yeast. The term yeast is used indiscriminately. It is not always clear whether he refers to baker's yeast or beer yeast.

The data given on page nine require correction. In paragraph three it is stated that McCollum designated the antirachitic vitamin as vitamin D in 1922, whereas in the tabulation following paragraph four the date is given as 1925. In a number of instances it is believed the author has been too brief, consequently the reader does not obtain a clear conception of the papers cited and of the subject under discussion.

The author discusses the value of vitamin B for the pregnant mother and for the child. He also discusses the vitamin B/2 complex. Whether or not vitamins A, C and D are present in yeast is taken up in considerable detail. Mineral salts, glutathione, amino acids, enzymes, hormones and choline are discussed. The therapeutic use of yeast is given considerable attention.

In describing the production of vitamin D milk by the yeast feeding method the type of yeast employed for irradiation is not given. Statements in regard to the quality of the mineral yeast and top yeast grown on molasses to which mineral salts are added, should be modified as they do not apply to modern conditions.

The author reviews some of the most valuable work pertaining to the use of yeast in animal nutrition, and the preparation of yeast extracts rich in vitamin B. Fortification of diets deficient in certain vitamins by means of yeast is also discussed.

It is believed that this work will stimulate research in the fields which the author has reviewed. 436 references are given. A complete author and subject index is included.

C. N. Frey
G. W. Kirby

Le Mêtabolisme de L'Azote, Physiologie des Substances Protèiques. I. Aliments, Digestion, Absorption, Enzymes Digestif. No. XX, Les Problèmes Biologiques. (Nitrogen Metabolism. Physiology of Protein Materials.) By Émile F. Terroine. Published by Les Presses Universitaires de France, 49 Boulevard Saint-Michel, Paris. Price, 80 francs.

This is the second book by the author on nitrogen metabolism. The first dealt with the excretion of nitrogen and the protein requirements of animals. The object of the book under review is to consider the physiological phases of the utilization of nitrogen and the changes that take place in nitrogenous substances from the time of ingestion through their utilization. The subject is discussed under four headings: (a) Protein foods and their digestibility; (b) The nature of nitrogenous substances absorbed by the body; (c) The processes of digestion and absorption; (d) The factors in digestion (enzymes), their respective roles, and conditions necessary for their activity.

The first part of the work discusses protein foods in general, followed by the consideration of digestibility, the effects of various factors, physical, chemical and physiological, on the digestion of proteins, and a table of digestion coefficients.

The second part takes up the question of absorption of unmodified protein, a short discussion of food sensitization, and the absorption of the intermediate and final products of protein degradation, including evidence for the presence of these products in the blood.

The third part of the book is devoted to the processes of digestion and absorption in the various parts of the alimentary tract with particular attention to the extent of digestion and absorption and the interrelationship of the processes in one portion of the digestive tract to those in another.

The last section of the book is concerned with enzymatic processes, the role of the gastric, pancreatic and intestinal juices, and the enzymes responsible for digestion, and their mode of action.

The style of the book is monographic. The author has gathered a wealth of material and presented it critically from a functional and dynamic point of view. The subjects are discussed by topics and often through the use of the question and answer method to focus the attention of the reader on a specific point.

PAUL E. HOWE

Röntgens Briefe an Zehnder. (Röntgen's Letters to Zehnder.) Edited by LUDWIG ZEHNDER. Rascher et Cie., Verlag, Limmatquai 50, Zürich 1, Switzerland, 1935. 198 pp. Illustrated. 16 × 23 cm. Price, Swiss fr. 5; bound, 7.50.

This is a collection of the more important and interesting letters written by W. C. Röntgen to Ludwig Zehnder. The first letter was written in 1887 shortly after the two men had become acquainted during a summer vacation at Pontresina. In this letter Professor Röntgen offered Dr. Zehnder a position as Assistant and Demonstrator in his Laboratory at the Realgymnasium in Mainz. Zehnder was only slightly Röntgen's junior and they became close friends, this friendship being terminated only by Röntgen's death in 1922.

The letters referring to Röntgen's epoch-making discovery of x-rays are of course of particular interest, but all of the letters are valuable in disclosing the vigorous, earnest and high-minded personality of Röntgen. Some of the important letters are reproduced in facsimile and Zehnder has interspersed a sufficient account of the circumstances, together with a few of his own letters, so that the subject matter of Röntgen's letters can be adequately appreciated.

This indirect biography of Röntgen is eminently satisfactory and the only item that leaves one dissatisfied is the inexplicable action of his executors, as reported by Dr. Zehnder, in destroying, apparently on their own initiative, all documents bearing on Röntgen's discovery of x-rays, including the letters of Zehnder to Röntgen during the period of 1889–1902.

Incidentally, this collection of letters depicts an almost ideal friendship between these two men and reflects the admirable though quite different personalities of each of them.

ARTHUR B. LAMB

Atomspektren und Atomstruktur. Eine Einführung für Chemiker, Physiker und Physikochemiker. (Atomic Spectra and Atomic Structure. An Introduction for Chemists, Physicists and Physical Chemists.) By Dr. GERHARD HERZBERG, Lecturer in Physics at the Technical Institute, Darmstadt. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1936. xvi + 188 pp. 79 figs. 15.5 × 22.5 cm. Price, RM. 13; bound, RM. 14.

This is the first of two monographs by the author on atomic and molecular spectra. The second, on molecular spectra, is in preparation.

As the title suggests, the book is intended primarily to serve as an introduction to atomic spectroscopy for those who wish to obtain a working knowledge of the subject which has, more than any other, thrown light on the extranuclear structure of atoms. No attempt is made to give a rigorous presentation of the theory of atomic spectra. Only an elementary physical description of the fundamental principles of the quantum mechanics is set forth, but brief descriptions of this method of treating certain problems, including the hydrogen spectrum, the Zeeman effect and the Pauli exclusion principle are given. The vector model is used in treating the main body of spectroscopic phenomena and the building of the periodic system of the elements. The last chapter gives an application of atomic theory in its discussion of valency and collision processes.

The author takes pains to explain clearly the fundamental spectroscopic terms and concepts. A feature of the book is the large number of term diagrams which are a great aid in visualizing spectroscopic phenomena.

ROBERT B. KING

Annual Tables of Constants and Numerical Data, Chemical Physical, Biological and Technological. Published under the patronage of the International Union of Chemistry. N. THON, Editor-in-Chief. The McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York, N. Y., 1936. 23 × 28.5 cm. Advance Reprints from Vol. XI. "Numerical Data on Rotatory Power," 1931–1934, by E. Darmois. 68 pp. $2.00. "Numerical Data on Radioactivity, etc.," 1931–1936, by I. Joliot-Curie, B. Grinberg and R.-J. Walen. 57 pp. $2.00. "Numerical Data on the Raman Effect, etc.," 1931–1934, by M. Magat. 112 pp. $3.00.

The Committee of Annual Tables, recently appointed by the International Union of Chemistry, announces that owing to the fact that Annual Tables has lagged behind its schedule of publication since Volume X (1930), the data for 1931 to 1936 are to be published in a more condensed form and more critically edited, in a series of fascicules by subjects, partly separately for 1931–1934 and 1935–1936, and partly for the wholly period 1931–1936. The full set of these fascicules will constitute Volumes XI and XII of Annual Tables. It is planned to complete this program in 1937, whereby the numerical material published by Annual Tables will then be brought strictly up to date.

In addition, an Index Volume by Substances for the Volumes VI–X (1923–1930), like the one published for the Volumes I–V (1910–1922), is to appear toward the end of

1936. A similar Index Volume will be prepared for the Volumes XI and XII, to be published in 1937.

The present three fascicules represent preprints from Volume XI. The section on Transmutations, in the fascicule by Joliot-Curie, giving a systematic, complete and critical account of the numerical data relative to nuclear reactions and artificial radioactive disintegrations, is particularly timely and noteworthy. The compilation of data on Rotatory Power, by Darmois, will be of great value to students of stereochemistry; while the compilation of data on the Raman Effect, by Magat, cannot fail to interest keenly those workers seeking a deeper knowledge of the structure of chemical compounds.

ARTHUR B. LAMB

Catalytic Reactions at High Pressures and Temperatures. By VLADIMIR N. IPATIEFF, Professor, Northwestern University, and Director of Chemical Research, Universal Oil Products Company. The Macmillan Company, 60 Fifth Avenue, New York, N. Y., 1936. xxii + 786 pp. 56 figs. 14.5 × 22.5 cm. Price, $7.50.

This book makes no pretense, except possibly in its title, of being a comprehensive survey of catalytic reactions at high pressures and temperatures. It is primarily a collection and review of the author's own researches in the field of catalysis. The author prepared this book because, as he expresses it: "Much of my published work is inaccessible"; a circumstance which probably explains why he has sometimes failed to receive the recognition which he so frequently in this book feels to be his due.

In the 700 odd pages of this book are disclosed the author's methods of work, his habits of thought, his concepts of catalytic reactions. These should be of interest to all workers in this field. The book is in every sense what the author intended it to be, namely, his "chemical autobiography." Accordingly, the presentation is more or less chronological, beginning with his early work on dehydration and dehydrogenation of alcohols and closing with his more recent work on destructive hydrogenation, polymerization and alkylation. In between, appear sections devoted to isomerization, condensation and pressure hydrogenation. A chapter is devoted to the author's theories of catalysis, particularly as applied to liquid phase hydrogenation. The book reports a very large number of experiments, the results of which are in many cases given in considerable detail. For the specialist, these should be of considerable interest. The arrangement is such, however, that the general reader will be able to maintain reasonable continuity.

One cannot read this book without a feeling of regret that the author's early researches were not more generally known by the other pioneer workers in the field of catalysis. The author was one of the first to appreciate that the material out of which the apparatus is constructed might have catalytic properties which must not be disregarded. His early experiences illustrate how equipment problems may determine the whole course of subsequent research. In studying the decomposition of alcohols he observed that considerable carbon was deposited when the reaction occurred in an iron tube. In order to determine whether the catalytic effect was due to the iron tube or to the carbon deposited, he lined the tube with graphite. The graphite contained kaolin as a binder, to which (so he states) he attached no catalytic significance. Why, is difficult to understand in view of his earlier observations that the material of the apparatus might have pronounced catalytic effects. Be that as it may, experiments with the new apparatus disclosed that iron and not carbon was the catalyst with which he had been dealing in his previous experiments. The carbon tube, however, gave an entirely different result than the iron, in that it produced almost exclusively ethylene and water. The author ascribed this reaction to the kaolin binder rather than the carbon. In his search for the active constituent of the kaolin, he discovered the catalytic properties of alumina. Then followed an extended study of alumina during which he disclosed that its catalytic properties were related in an important manner to its state of hydration which in turn could be controlled by its method of preparation. Likewise in his hydrogenation studies the author found that the method of preparation of metal and oxide catalysts was very important. For example, in the case of nickel, the state of oxidation, its previous heat treatment, rate of reduction—each of these had an influence on its catalytic properties. The author was one of the earliest, maybe the first, to recognize the so-called promoter action of certain substances which, by themselves, have no obvious catalytic effect and yet in contact with a catalyst do modify its properties favorably. There is frequent reference throughout the book to substances which have an adverse effect upon the catalyst, such as accidental impurities originally present in the catalyst or in the reactants involved. Since he recognized that certain substances could slow up a reaction, even stop it completely, it seems strange that he did not consistently avoid such materials in his own investigations. For example, on page 171, in referring to certain work of Sabatier and Senderens (whose investigations, by the way, receive considerable critical attention in this book), the author states: "Sabatier and Senderens were careful about the purity of the reduced nickel; I paid no attention to its purity." Again on page 182, referring to the work of Schröter, he states: "In my first experiments on the hydrogenation of naphthalene, I used the naphthalene as obtained from Kahlbaum, whereas Schröter paid serious attention to the purity of his naphthalene and was therefore able to hydrogenate it at a lower pressure."

In considering the mechanism of catalytic reactions the author feels that many investigators have been too much concerned with physical concepts. Catalysts, says he, must have very special chemical as well as physical properties. To understand a catalytic process one must consider the "mutual chemical action of the components participating in the reaction." In advancing theories explaining some of his own reactions he has adhered to the proposition that it is as impossible to formulate a single theory covering all catalytic reactions as it is to formulate a general explanation for all known types of chemical reactions. In the case of hydrogenation the author assumes a role for water which some investigators in this field may question.

Some readers may feel that the author has been a little too controversial at times. Some, that he has insisted too frequently upon the priority of his own investigations. On the whole, however, the book affords interesting and instructive reading. This reviewer believes it to be an important and timely contribution. Its reading and careful study are strongly recommended.

ALFRED T. LARSON

Die Fermente und ihre Wirkungen. (Enzymes and their Action), Supplement. Lieferung 2 (Bd. 1. Specieller Teil: Hauptteil VIII). By Prof. CARL OPPENHEIMER, Dr. Phil. et Med. W. Junk Verlag, Scheveningsche Weg 74, The Hague, Holland, 1935. 160 pp. 13 figs. 20.5 × 28 cm. Price, $6.80. Lieferung 3 Supplement (Bd. 1. Specieller Teil: Hauptteil VIII, IX). 1936. 160 pp. 25 figs. Price, $6.80. Lieferung 4 Supplement (Bd. 1. Specieller Teil: Hauptteil IX–XII). 1936. 160 pp. 10 figs. Price, $6.80.

Since the publication of Lieferung, or Part 1 dealing with the recent chemistry of the esterases [reviewed in THIS JOURNAL, **58**, 538 (1936)], three additional parts: 2, 3 and 4 have appeared. The same plan has been followed as in the first part. Parts 2, 3 and the first part of 4 are devoted to the chemistry of the carbohydrases and their substrates. The subject matter covered in Part 2 is chiefly the recent literature on the oligases, *i. e.*, enzymes specific to the hydrolysis of glycosidic linkages in the simpler sugars and glycosides. Part 3 takes up the chemistry of the amylases as well as some of the recent views concerning the constitutions of different starches as revealed by their enzymatic behaviors. The first part of Lieferung 4 also deals with the chemistry of poylases, although more particularly the glucanases, like cellulase, the fructanases, the polyuronidases and pectinases. The remainder of Part 4 takes up first nucleosidases, nucleic acids, aminases, acylic amidases, etc., followed by a discussion of some of the more recent views concerning the constitutions of proteins. The latter is intended to serve presumably as a background for a review of the more recent work in the field of proteolytic enzymes to be taken up in the next Lieferung.

As mentioned in the previous review of Part I, the author has succeeded in mentioning practically all of the large mass of literature which has appeared, in this part of enzyme chemistry, during the ten years elapsing since the publication of the original Hauptwerk. Although he has, by means of discussion in the text, tried to correlate and integrate as much as possible the more significant data contained in the literature, the supplement will be welcomed by chemists as an excellent and complete source of references, rather than as a critical review.

J. M. NELSON

Semi-Micro Qualitative Analysis. By CARL J. ENGELDER, Ph.D., Professor of Analytical Chemistry, University of Pittsburgh, TOBIAS H. DUNKELBERGER, B.S., University of Pittsburgh, and WILLIAM J. SCHILLER, Ph.D., Mount Mercy College, Pittsburgh, Pennsylvania. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, N. Y., 1936. x + 265 pp. 15.5 × 24 cm. Price, $2.75 net.

In the words of the authors, it has been their aim in this textbook "to apply the methods and technique of microanalysis to the ordinary (macro) schemes of qualitative analysis with the objects: first, of confining the operations to drops or, at most, to one or two cubic centimeters of solution; second, of developing a micro scheme which could be placed in the hands of undergraduate students taking their first course in qualitative analysis; and, third, by dispensing with the use of microscopes, of bringing the micro technique within practical pedagogic and economic reach of large laboratory classes of sophomore or even freshman students."

The book is divided into four parts: fundamental principles of qualitative analysis, reactions of the cations, reactions of the anions and systematic microanalysis. Approximately ninety pages are devoted to the fundamental theory of qualitative analysis, embracing the customary topics; there is a brief discussion of the Werner theory of valence, and of chelate compounds. The group separations of the cations follow the conventional macro scheme. The separations employed within the groups are again the usual ones in most instances. For the identification tests extensive use is made of the new spot reactions developed by F. Feigl and others, which are carried out on drop-reaction paper or a spot plate. In most cases two or three such tests are described for each cation, and in addition many other drop reactions are mentioned together with literature references. Inclusion of the sensitivities of the tests described would have added greatly to the practical value of the book.

Doubtless there will be a difference of opinion among teachers concerning the advisability of introducing the student to practical qualitative analysis via the semi-micro technique. The reviewer believes many will feel that the operations of qualitative analysis as ordinarily carried out are effected on an unnecessarily large scale, and that semi-micro and micro procedures have great advantages over the older technique in point of certainty and economy of time. To those favoring the new departure in analysis the present work is recommended.

E. B. SANDELL

Inorganic Chemistry for Colleges. A Textbook for Students who have had a Preparatory Course in Chemistry. Second edition. By WILLIAM FOSTER, Ph.D., Russell Wellman Moore, Professor of Chemistry in Princeton University. D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, N. Y., 1936. xi + 925 pp. Illustrated. 14 × 22.5 cm. Price, $3.90.

In this revised edition, the general plan of the former edition has been followed (confer the review on p. 1617 of THIS JOURNAL, 1931). Many of the sections of the book have been rewritten so as to incorporate any theories that have been enunciated.

An entire chapter is devoted to atomic structure, and the subject matter has been considerably extended along with many other things. This chapter contains a modified Bohr–Thomsen and Periodic Tables; the Electron Theory of Valence; the Main Facts Concerning Heavy Hydrogen and Heavy Water; A Discussion of the Transmutation of the Elements as well as a brief statement of the Quantum Theory. The chapters on Ionization have been thoroughly modified, and the new definitions of acid and base are given.

New problems and questions have been introduced; the reading references have been thoroughly revised, and extended; and the appendix enlarged. The Textbook has been modernized by an attempt not to include too large an amount of physical chemistry and physics, while at the same time, retaining an adequate amount of descriptive and industrial chemistry.

HERMAN SCHLUNDT

An Introduction to Organic Chemistry. By ALEXANDER LOWY, Ph.D., University of Pittsburgh, and BENJAMIN HARROW, Ph.D., College of the City of New York. Fourth edition. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, N. Y., 1936. xiv + 429 pp. 15.5 × 24 cm. Price, $3.00.

The fourth edition of this well known text follows closely early editions which have been reviewed in THIS JOURNAL, **47,** 900 (1925); **54,** 4468 (1932). Considerable additional material has been added including formulas proposed for certain of the vitamins and hormones.

R. R. RENSHAW

Allgemeine Untersuchungsmethoden. Erster Teil. Physikalische Methoden. (**General Research Procedures.** Part I. Physical Methods.) Edited by A. BÖMER. Vol. II, Bömer-Juckenack-Tillmans, "Handbuch der Lebensmittelchemie." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1933. x + 536 pp. 401 figs. 17.5 × 26 cm. Price, RM. 66; bound, RM. 69.

This volume, comprising approximately half of the second one of a series of eight which when completed will constitute an encyclopedic treatise on food chemistry, is devoted exclusively to comprehensive discussions of the underlying principles and descriptions of those methods and tools of the physical chemist which find application in this field as the Germans define it. Some eleven authors have contributed to the compilation of this volume of 21 chapters, each of which is practically a small monograph on the subject in hand.

The chapter headings and the author responsible for the contents are: specific gravity (16 p.), viscosity (12 p.), ultra-filtration (12 p.), dialysis and electrodialysis (16 p.) and surface tension, adsorption phenomena and capillary analysis (20 p.), by K. Täufel; solubility (11 p.), melting point and boiling point (23 p.), and heat of combustion (14 p.) by A. Bömer and R. Grau; cryoscopy (11 p.) by R. Strohecker; bathometry or measurement of *p*H (36 p.), indicators (22 p.) and electrolytic conductivity (28 p.) by A. Thiel; acidimetry and alkalimetry (20 p.) and oxidation–reduction potentials (17 p.) by P. Hirsch; refractometry (31 p.) by F. Löwe; spectroscopy and spectrophotometry (58 p.) by H. Ley; polarimetry (47 p.) and color measurement (20 p.) by F. Volbert; colorimetry and nephelometry (16 p.) by H. Freund; luminescence analysis (24 p.) by P. W. Danckwortt; and microscopy (74 p.) by C. Griebel.

The general treatment of the several subject matters is uniformly excellent. Illustrations have been generously used throughout this work. A few chapters follow somewhat the literature review pattern, yet this does not seem to detract from their interest or value. Some authors, as for example Täufel, Griebel, Freund and Volbert, have added to their literature citations brief references to the book literature for amplification, if the reader is so disposed. Danckwortt accomplishes this end by referring him to his larger work on luminescence analysis (1929). The field of micro-analysis has not been overlooked for included herein are its applications to cryoscopy, spectroscopy and the determinations of melting points and heats of combustion.

It is the opinion of the reviewer that this volume, perhaps under another less specialized caption and certainly enlarged as to make it more serviceable, by the addition of an index, would arrest the attention of others and serve them equally as well as the food chemist to whom it is obviously addressed.

H. A. SCHUETTE

Ebulliometry. By WOJCIECH ŚWIETOSLAWSKI, Professor of Physical Chemistry at the Polytechnic Institute of Warsaw. The Jagellonian University Press, Krakow, Poland, 1936. x + 196 pp., 52 figs. 18 × 25.5 cm.

In recent years ebulliometric technique has been improved in convenience and precision, as well as extended in its applications, by Professor Świetosławski and his coworkers. Modern methods and applications of ebulliometry are described comprehensively in this book, which is a revised and enlarged English edition of the monograph "Ebuljometrja" published in Polish in 1935. It is written in a straightforward and logical style. The description of experimental technique and the illustrations of apparatus are of such clarity and detail that the book serves as a laboratory manual as well as a text of principles and an interesting source of information, data, and references.

Perhaps the most important uses of Świetosławski's ebulliometers are the determination of exact boiling points (±0.002°), of dp/dt ratios, and the degree of purity of liquid substances. The last determination usually depends on the measurement of the difference between the boiling point and condensation temperature. For an absolutely pure liquid, these temperatures are, of course, identical, but in the presence of impurities their difference, and in many cases particularly the condensation temperature, changes markedly and uniformly with the quantity of the impurity. For example, by this method 0.002 per cent. of benzene is readily detected in toluene, and by similar measurements the moisture content of solids as well as of liquids can often be determined with high accuracy, even when of the order of only 0.001 per cent. In addition to measurements customarily classified as ebulliometric, many others, of which the following are noteworthy, can be made by these methods: the degree of thermal decomposition of substances, the solubilities of solids, the amounts of substances adsorbed on the surface of solids or occluded in crystals, the calibration of thermometers, esterification constants, deviations from Raoult's law, osmotic coefficients, the detection and analysis of azeotropic mixtures and the displacement of azeotropic points with change in pressure.

An excellent discussion is given of the phenomenon of azeotropy and its application to the purification of liquids, particularly with respect to the dehydration of liquids like toluene and ethanol by azeotropic distillation. Important data on accurate boiling points and dp/dt ratios of pure liquids are tabulated. A bibliography of the 64 references cited in the text is given at the end.

The increasing recognition in physical chemistry of the convenience and precision of comparative methods of measurement with the use of water as a primary standard may well lead to the universal adoption of Świetosławski's ebulliometric technique for the determination of many physical constants of liquid substances and mixtures as well as for the examination of their purity.

Edgar R. Smith

BOOKS RECEIVED

September 15, 1936–October 15, 1936

Otto Brunck. "Quantitative Analyse." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 223 pp. RM. 9.

A. H. B. Bishop and G. H. Locket. "An Elementary Chemistry." Oxford University Press, 114 Fifth Ave., New York, N. Y. 400 pp. $1.75.

Robert D. Coghill and Julian M. Sturtevant. "An Introduction to the Preparation and Identification of Organic Compounds." McGraw-Hill Book Company, Inc., 330 West 42d St., New York, N. Y. 226 pp. $1.75.

Robert Durrer. "Erzeugung von Eisen und Stahl." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 159 pp. RM. 10; bound, RM. 11.

Samuel Glasstone. "Recent Advances in General Chemistry." P. Blakiston's Son and Co., 1012 Walnut St., Philadelphia, Pa. 430 pp. $5.00.

Samuel Glasstone. "Recent Advances in Physical Chemistry." P. Blackiston's Son and Co., 1012 Walnut St., Philadelphia, Pa. 477 pp. $5.00.

L. A. Goldblatt. "Collateral Readings in Organic Chemistry." (Reprintings.) Lithoprinted by Edwards Brothers, Inc., Ann Arbor, Mich. 128 pp. $1.00.

Otto Hahn. "Applied Radiochemistry." The George Fisher Baker Non-Resident Lectureship in Chemistry at Cornell University, No. 14. The Cornell University Press, 124 Roberts Place, Ithaca, N. Y. 278 pp. $2.50.

Albert P. Mathews. "Principles of Biochemistry." William Wood and Company, Mt. Royal and Guilford Aves., Baltimore Md. 512 pp. $4.50.

William Buell Meldrum and Frank Thomson Gucker. "Introduction to Theoretical Chemistry." American Book Company, 88 Lexington Ave., New York, N. Y. 614 pp. $3.50.

N. F. Mott and H. Jones. "The Theory of the Properties of Metals and Alloys." Oxford University Press, 114 Fifth Ave., New York. 326 pp. $8.00.

Carl Oppenheimer. "Die Fermente und ihre Wirkungen." Supplement, Lieferung 5. W. Junk Verlag, Scheveningsche Weg 74, Den Haag, Nederland. 140 pp. Dutch fl. 10.00.

Keita Shibata and Yuji Shibata. "Katalytische Wirkungen der Metallkomplexverbindungen." Publication No. 2, Iwata Institute of Plant Biochemistry, Tokyo, Japan. 219 pp. $2.50.

"Annual Tables of Constants and Numerical Data, Chemical, Physical, Biological and Technological." Advance Reprints from Vol. XI. "Raman Effect," by M. Magat. "Rotatory Power," by E. Darmois. "Radioactivity," by I. Joliot-Curie, B. Grinberg and R.-J. Walen. Institut de Chimie, 11 Rue Pierre Curie, Paris 5^e, France. 112 + 68 + 57 pp. $3.00 + $2.00 + $2.00.

"Enzymologia." Carl Oppenheimer, Editor. Vol. I, Nos. 1–2. W. Junk Verlag, Scheveningsche Weg 74, Den Haag, Nederland. 96 + 64 pp. Per vol., Dutch fl. 15.00.

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[CONTRIBUTION FROM THE SIR WILLIAM RAMSAY LABORATORIES OF INORGANIC AND PHYSICAL CHEMISTRY, UNIVERSITY COLLEGE]

The Critical Concentration for Micelles in Solutions of Cetane Sulfonic Acid

BY G. S. HARTLEY

The existence of a fairly critical transition with change of concentration in solutions of some micelle-forming substances was first demonstrated by Bury and collaborators,[1] who explained the phenomenon by application of the mass-action law to the equilibrium between micelles and single ions or molecules. The critical phenomenon is strikingly apparent in the conductivity of unhydrolyzed higher paraffin chain salts, the equivalent conductivity showing a sudden fall when the concentration is increased beyond a certain value, as was first observed by Lottermoser and Püschel[2] in various salts of higher alkyl sulfuric acids and later by the author and collaborators in other salts.[3] Ekwall[4] found a sudden inflection in the equivalent conductivity–concentration curves for soaps in dilute solution, a phenomenon which has probably the same explanation, but is modified by the enhanced conductivity due to hydrolysis.[5] Murray and Hartley extended in some respects the theoretical treatment of Bury and applied it to the abnormal solubility–temperature curves of paraffin chain salts, and Murray[6] has also applied it to the surface tension data of Lottermoser and collaborators.

McBain's well-known theories of the constitution of soap solutions were based on data obtained at higher concentrations than those with which most of the work quoted above has been concerned. This work has necessitated a considerable modification of McBain's former conception of the nature of the dilute solutions, chiefly in that we now know colloidal aggregates to be formed in considerably lower concentrations than was previously thought to be the case. McBain and Betz,[7] in discussing their conductivity, f. p. and e. m. f. data on several paraffin sulfonic acids, have in part accepted the newer point of view, but they make no mention of the critical phenomenon, although such of their data as are given in detail are not inconsistent with its existence. McBain[8] now considers the "bulk of the transition from simple electrolyte to colloid" to take place between 0.05 and 0.15 N in the case of the C_{11} and C_{12} acids and at a still lower concentration in the C_{14} acid. From the results of earlier work on the C_{16} acid he previously concluded[9] that at so high a concentration as 0.1 N there was still less than 15% of the acid in colloidal form. The C_{16} acid is, however, almost certain to be more aggregated than the C_{14}.[10]

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(1) Jones and Bury, *Phil. Mag.*, **4**, 841 (1927); Grindley and Bury, *J. Chem. Soc.*, 679 (1929); Davies and Bury, *ibid.*, 2263 (1930).

(2) Lottermoser and Püschel, *Kolloid Z.*, **63**, 175 (1933).

(3) (a) Malsch and Hartley, *Z. physik. Chem.*, **170A**, 321 (1934); (b) Murray and Hartley, *Trans. Faraday Soc.*, **31**, 183 (1935); (c) Hartley, Collie and Samis, *ibid.*, **32**, 795 (1936).

(4) Ekwall, *Z. physik. Chem.*, **161**, 195 (1932).

(5) See Hartley, "Aqueous Solutions of Paraffin Chain Salts," Hermann, et Cie, Paris, France, 1936, p. 29.

(6) Murray, *Trans. Faraday Soc.*, **31**, 206 (1936).

(7) McBain and Betz, THIS JOURNAL, **57**, 1905, 1909, 1913 (1935).

(8) McBain, *ibid.*, p. 1916.

(9) See the diagrams in the "International Critical Tables," Vol. V, 1929, p. 448.

(10) Unless the difference is to be attributed to the effect of temperature, the diagram for the C_{16} acid being worked out from data at 90° and the recent work on the other acids referring to 0 and 25°. The influence of temperature is dealt with later in this paper.

The object of this paper is to present the results of a closer study than has previously been made of the conductivity in the immediate neighborhood of the critical concentration and of the influence on this concentration of changes of temperature and addition of other solutes. Since McBain (in a private communication) has suggested that the observations recorded on the critical phenomenon may have been due to incomplete solution at the higher concentrations, and Ekwall[4] made a similar suggestion with regard to his own work, particular attention has been paid to the question of reversibility.

Experimental

Cetane sulfonic acid was prepared by a modification of the method described by Murray.[11] Fifty grams of pure cetyl bromide[3c] was stirred for three hours at 60° with 1 liter of 0.5 *N* solution of caustic potash in 95% alcohol, previously saturated with hydrogen sulfide and kept saturated during the reaction. Sufficient strong hydrochloric acid was then added to drive off the hydrogen sulfide and solid iodine added till its color persisted in order to oxidize the mercaptan to the stable disulfide which is less soluble in alcohol. The mixture was cooled and filtered, the residue washed with hot water to remove salts and recrystallized from ethyl acetate, a yield of about 40 g. of disulfide melting at 54° being obtained. The disulfide was oxidized on the steam-bath with redistilled nitric acid and the product dried in a vacuum desiccator over solid caustic soda. The resulting solidified foam was recrystallized from redistilled (40–50°) petroleum. The warm solution (which goes brown if kept warm) deposits lustrous plates on cooling, but these are impossible to remove by filtration. Accordingly the warm solution was placed in warmed centrifuge cups and allowed to cool during centrifuging. A hard crust of crystals was obtained from which the mother liquor could be poured off fairly completely. The process was several times repeated, drying the product if necessary in between as it takes up water readily from the air and its solubility in petroleum ether may in consequence rise inconveniently high. The product, after drying *in vacuo* over anhydrous calcium chloride, was white in color and free from ash and from nitrate. It gave, however, a milky solution in hot water which became clear only if kept hot and concentrated for a long time. A clear solution, at temperatures above about 36°, was given more quickly by acid which had been fused and kept molten for some minutes, but the molten acid becomes rapidly brown.

A weighed sample of the product, which melted about 53–54°, was heated slowly in a high vacuum. It did not then melt till 74° and was found to have lost in weight by 5.8%. This is in good agreement with Noller and Gordon's[12] finding that the acids ordinarily obtained are monohydrates (theoretical loss on conversion to anhydrous form 5.5%). The fused anhydrous acid also went brown on continued heating, but without further loss of weight. Titration of a 0.01 *N* solution of the anhydrous acid with standard alkali, using brom cresol purple as indicator, gave the equivalent weight as 305 (theoretical 306). The anhydrous acid went into perfectly clear solution when kept at about 80° for three hours, initial opalescence gradually disappearing during this time, probably a similar phenomenon to that attributed by McBain and Betz to the slow solution of an anisotropic phase. Once the clear solution has been obtained, it may be allowed to form an opaque curd by cooling, but the curd, if stored in Pyrex or quartz vessels, will, no matter how old, always quickly become completely clear on warming. If stored in soft glass vessels, small crystals, presumably of alkali salt, are slowly produced and these require a higher temperature for solution. The color of the resulting solution at a concentration of *ca.* 0.3 *N* was about the same as that of *N*/300,000 methyl orange (alkaline).

As there seemed room for doubt, from the behavior described, about the purity of the resulting solution, stock solutions (*ca.* 0.01 *N*) were made up from the hydrated acid by four different methods. These stock solutions, all becoming clear above 35°, were standardized by titration with alkali and their conductivities were determined at different dilutions at 60°, the intrapolated values at two concentrations being given in Table I. Within experimental error the two different solutions gave the same results and we can conclude that no appreciable amounts of unstable impurities of a nature which might affect the conductivity are present. The concentrations as determined by titration with standard barium chloride solution (using the simultaneous disappearance of foaming power and coagulation of precipitate as end-point) agreed with those determined by alkali titration within the experimental error (±0.5%) of the former. The extrapolated value of the equivalent conductivity at infinite dilution was 543 ± 3, to which the hydrogen ion alone would, according to intrapolation of Johnston's[13] data, contribute 507. Johnston's figures however were calculated from conductivity data on the assumption that the potassium and chloride ions are equally mobile at higher temperatures. If the value of MacInnes and Longsworth[14] of 0.490 for the cation transport number in potassium chloride at 25° held good at 60°, we should have to reduce the hydrogen value to 504. The maximum probable value for the infinite dilution equivalent conductivity of the cetane sulfonate ion at 60° is thus seen to be 42. The value for the cetylpyridinium ion, which will have about the same mobility, was found[3a] to be 21 at 25°. Multiplying by the viscosity ratio, we should expect a value of 40 at 60°. There is therefore little room for the presence of other anions of higher mobility. The absence of

TABLE I

	Method of treatment of recrystallized acid	Equiv. cond. at 60° 0.0005 *N*	Equiv. cond. at 60° 0.003 *N*
I	80° in air for 5 minutes	535.3	225.0
II	80° in air for 10 minutes	534.3	255.5
III	Concd. soln. at 90° for 48 hrs.	535.1	255.0
IV	Dehydrated and melted *in vacuo* at 74°	535.0	255.2

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(11) Murray, *J. Chem. Soc.*, 739 (1933).

(12) Noller and Gordon, THIS JOURNAL, **55**, 1090 (1933).

(13) Johnston, *ibid.*, **31**, 1010 (1909).

(14) MacInnes and Longsworth, *Chem. Rev.*, **11**, 211 (1932).

sulfate, the most probable anion arising from oxidation of cetane sulfonic acid, was confirmed by addition of 0.1 N magnesium nitrate solution to an equal volume of 0.001 N cetane sulfonic acid, evaporation to 0.1 of the initial volume, cooling, filtering and testing the filtrate with barium chloride solution. No immediate precipitate resulted. A slight precipitate appeared slowly but similar behavior resulted when the magnesium cetane sulfonate on the filter was washed with N magnesium nitrate and was therefore considered due to the slight solubility of the magnesium cetane sulfonate itself. Addition of sulfate in amount equivalent to 0.3 equivalent % of the original sulfonate gave an immediate precipitate. It can be concluded that sulfate certainly is not present in greater amount than this.

Cetyl pyridinium chloride was prepared from the bromide[3c] by recrystallizing several times from hydrochloric acid and then drying the product *in vacuo* over solid caustic soda until a *ca.* 0.1 N solution was no longer appreciably acid to α-naphthylamine-azo-p-benzyltrimethylammonium nitrate[15] (*i. e.*, pH > 5). A 0.01 N solution was standardized by electrometric titration with standard silver nitrate solution (equivalent weight, found 359, calcd. for monohydrate 358).

Conductivity water, free from ammonia and collected in carbon dioxide-free air ($\kappa_{25°}$ 0.11–0.16 × 10^{-6} ohm^{-1} cm.$^{-1}$), was used throughout but no attempt was made to exclude atmospheric carbon dioxide from the conductivity cell as it is almost completely undissociated in the acid solutions examined.

Dilution was carried out by weight in a 250-cc. stoppered conical Pyrex flask. The densities of the solutions used are not appreciably different from that of water and no correction for this very small difference was made. Dilution was always made so as to have the flask nearly full and thus reduce the volume of froth formed on shaking, since otherwise considerable depletion of solute from the bulk of the solution was found to occur when dealing with very dilute solutions. All concentrations are expressed in gram equivalents per liter at the temperature studied, allowance being made for the expansion of water.

The conductivity cell used was of Jena 16 III glass, fitted with smooth platinum electrodes of about 1 cm. diameter, having a cell constant of 1.431 cm.$^{-1}$ and a capacity of about 25 cc. It was filled from the top by means of a pipet and closed by a ground stopper sunk within a protecting collar so that the cell could be placed in the thermostat with the ground neck below the level of the liquid without danger of contaminating the solution. At least three fillings at each concentration were measured and the solution heated above the temperature of the thermostat before filling to prevent formation of air bubbles on the electrodes. Water was used in all cases for the **thermostat** liquid, but for work at 60 and 80° was covered with a layer of paraffin oil.

Resistance measurements were made on a direct-reading Wheatstone bridge with 6-dial non-inductive decade resistance box and equal ratio, fed by a valve-oscillator giving three frequencies of about 1000, 1000 × $\sqrt{2}$ and 2000 cycles per second, detection being by tuned amplifier and telephones. The common point of the variable resistance and cell was directly earthed and error from capacitative coupling between oscillator and output coils was eliminated by commutating the leads from output coil to bridge, and taking the mean of the readings. Error due to non-ideal capacity between the leads to the cell was determined by calibration with a standard resistance box in the cell position. Error in measurement of high resistances due to resistance–capacity shunts in the cell was eliminated by extrapolation against square of frequency to zero frequency. Error due to polarization in measurement of low resistances was eliminated by extrapolation against inverse square of frequency to infinite frequency. Except for the polarization error, which amounted to only 0.3% in the lowest resistances measured, the error, for a given leads system, frequency and oscillator-bridge connection, is a single-valued function of the measured resistance and so, by previous calibration, the procedure was considerably simplified.

Results and Discussion

In order to decide whether cetane sulfonic acid is behaving as a strong electrolyte in dilute solution, it is necessary to know what fall of equivalent conductivity with concentration is to be expected. Owing to the absence of reliable data for the dielectric constant of water at higher temperatures, it is not possible to apply Onsager's equations directly. The behavior must therefore be compared with that of an acid known to be strong—*e. g.*, hydrochloric acid. Data for 100°

TABLE II

EQUIVALENT	CONDUCTIVITIES AT 60° IN WATER		
$C \times 10^3$	λ	$\lambda_0 - A\sqrt{C}$	Difference
	HCl, A = 250		
0.0000	640.0	640.0	0.0
.0939	637.4	637.6	+ .2
.2791	635.8	635.8	.0
.5708	633.8	634.0	+ .2
1.0870	631.5	631.7	+ .2
2.359	628.0	627.7	− .3
3.921	624.7	624.4	− .3
	$C_{16}H_{33}SO_3H$, A = 230		
0.0000	543.0	543.0	0.0
.0860	540.7	540.9	+ .2
.1132	540.5	540.6	+ .1
.1928	538.9	539.8	+ .9
.3187	538.2	538.9	+ .7
.5131	534.8	537.8	+ 3.0
.7410	526.4	536.7	+ 10.3
.831	512.6	536.4	+ 23.8
.8615	499.4	536.3	+ 36.9
.970	467.8	535.8	+ 68.0
1.184	416.2	535.1	+118.9
1.450	366.7	534.2	+167.5
1.899	315.2	533.0	+217.8
2.580	273.8	531.3	+257.5
3.098	251.3	530.2	+278.9

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[15] An indicator whose color change is associated with a change from a univalent to a divalent cation and is not therefore displaced by cationic paraffin chain salts; see Hartley, *Trans. Faraday Soc.*, **30**. 444 (1934).

already available[13] show that the relative fall of equivalent conductivity with concentration is not much greater than at room temperature, but no accurate measurements were available on very dilute solutions at intermediate temperatures. Accordingly measurements were made at 60°. The results of these, and of the measurements on cetane sulfonic acid (solution IV) at this temperature, are given in Table II. C is the concentration in gram equivalents per liter and λ the equivalent conductivity. In the third column are given the values calculated from the equation $\lambda = \lambda_0 - A\sqrt{C}$, λ_0 being the infinite dilution value of λ and A a constant. In the fourth column the experimental values have been subtracted from the values given by this equation.

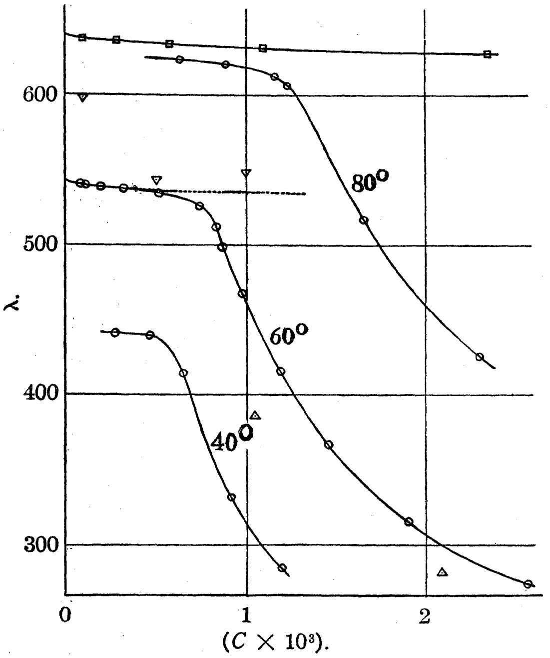

Fig. 1.—Equivalent conductivity of hydrochloric acid (□) at 60° and of cetane sulfonic acid (○) at 40, 60 and 80°. Dotted line represents approximate conductivity if cetane sulfonic acid behaved as a normal strong acid. (△), data of Reychler at 60°; (▽), data of McBain and Williams at 90°.

The data for hydrochloric acid are fitted, within the experimental error, by $\lambda_0 = 640.0$ and $A = 250$, except at the two highest concentrations. The value of λ_0 obtained by intrapolation of Johnston's[13] figures is 640.5. At 25°, where $\lambda_0 = 426$, Onsager's formulas give $A = 157$. A/λ_0 is thus, as expected, slightly greater at 60 than at 25°. It was assumed that the ratio of A for cetane sulfonic acid to A for hydrochloric acid would be the same at 60 as at 25°. Taking λ_0 for cetane sulfonic acid at 25° to be 371, we obtain $A = 144$, and therefore, at 60°, $A = 230$. Below 0.0003 N, the agreement is within the experimental error. At 0.0005 N the observed conductivity is appreciably smaller. At 0.00074 N the deviation amounts to 2% of the whole conductivity, increases to about 12% for a further increase of 30% in concentration, and is no less than 30% at twice this concentration. This behavior, almost equivalent to a sudden change of direction of the λ–c curve at about 0.0008 N, is to be expected if the deviation is due to the formation only of fairly large aggregates. That association is playing a considerable part in these low concentrations is now recognized by McBain, but his conclusion that, in sufficiently dilute solution, the behavior is that of a "simple partially dissociated electrolyte" could only be maintained if there were a range of concentration in which the deviation is proportional to concentration. The effect of aggregation extends to too low a concentration for it to be possible to separate a deviation proportional to the first power of concentration from that proportional (when small) to a much higher power. It is improbable that, in the lower sulfonic acids examined by McBain and Betz, it would be any more simple to separate these effects, because, although the region of great deviation is displaced to higher concentrations, it will also spread over a greater range of concentration, both absolutely, and, owing to the micelles being smaller, relatively. The experimental points of McBain and Betz are, in any case, insufficiently close together in the dilute solutions for this separation to be attempted.

That there is an appreciable formation of covalent acid, except in the aggregates, is extremely improbable from theoretical considerations[5] (p. 17). An experimental test was made by examining the behavior in a solvent appreciably less polar than water, namely, a mixture of glycerol and water. Simple dissociation will certainly be less complete than in water. Aggregation will probably also be less, since the solvent will have less tendency to expel the paraffin chains from solution. The conditions will therefore be more favorable for a separation of the two effects. It was found that the λ–C curve is of the same form as in water, but the critical concentration is increased some three times. Below

0.002 *N*, however, cetane sulfonic acid in the glycerol–water mixture is as strong as hydrochloric acid, *and apparently stronger than in water.* Since the solvent (water diluted to twice its volume at room temperature with ordinary "pure" glycerol, containing *ca.* 56.3% by weight of glycerol) had a considerable residual conductivity (17.1 ohm^{-1} cm.$^{-1}$ at 60°), the procedure adopted was to subtract the value of κ/C (*i. e.*, the equivalent conductivity without correction for solvent conductivity) for cetane sulfonic acid from that for hydrochloric acid at the same concentration. If the two acids have, at the same concentration, the same effect on the solvent conductivity,[16] this difference will be equal to that of the corrected λ values. The data are given in Table III and the difference plotted against concentration in Fig. 2.

TABLE III

EQUIVALENT CONDUCTIVITY OF CETANE SULFONIC ACID IN 56.3% GLYCEROL AT 60°

HCl		$C_{16}H_{33}SO_3H$			
$C \times 10^3$	κ/C	$C \times 10^3$	κ/C	κ/C for HCl	Diff.
5.615	180.8	5.886	96.6	181.4	84.8
5.590	180.9	5.870	96.8	181.4	84.6
3.460	182.4	4.490	112.7	181.7	69.0
2.150	183.9	3.394	132.6	182.4	49.8
1.374	186.4	2.964	142.3	182.9	40.6
1.135	187.8	2.486	151.6	183.3	31.7
0.422	202.4	1.800	156.1	183.8	27.7
.275	220.0	1.391	158.8	186.3	27.5
		0.665	166.7	194	27
		.332	182.9	210	27

Quite different is the effect of another nonelectrolyte, *n*-amyl alcohol, which, unlike glycerol, has a highly unsymmetrical distribution of affinity and will therefore tend to be sorbed by the aggregates and so, in sufficient concentration, will facilitate their formation. The concentration may be kept too low for there to be any possible effect on the unaggregated acid. In this case the additional solute was used at a constant concentration with respect to the cetane sulfonic acid, dilution being by addition of water only. The data are given in Table IV and plotted in Fig. 2. It will be seen that the effect is, as expected, to lower the critical concentration.[17]

The critical concentration is also lowered by the presence of another strong acid. In Table IV are given the results of measurements on a solution containing hydrochloric acid in about the same concentration as cetane sulfonic acid and on dilutions of this solution with water. From the observed conductivity was subtracted the product of the concentration of hydrochloric acid by its equivalent conductivity in a pure solution of concentration equal to the total acid concentration of the mixture. The quantity λ is the quotient of this difference by the cetane sulfonic acid concentration and is plotted in Fig. 2. The critical concentration of sulfonate[18] in this mixture is lower than in pure

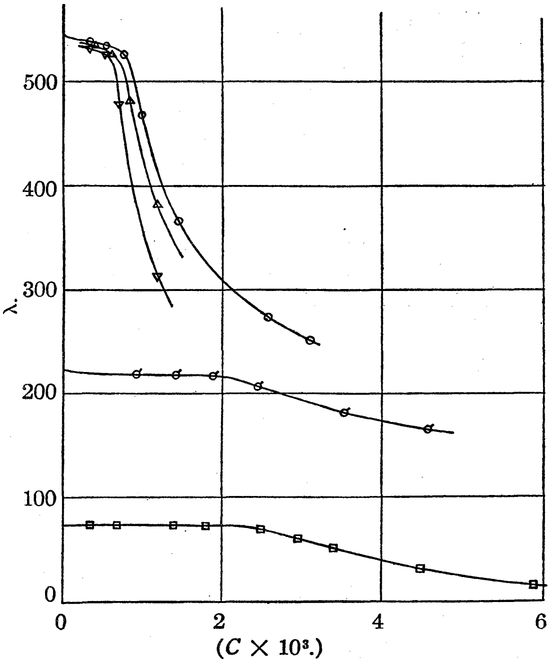

Fig. 2.—Equivalent conductivity of cetane sulfonic acid at 60°: (○), in water; (△), in dilute aqueous amyl alcohol; (▽), in dilute aqueous hydrochloric acid; (□), $\lambda_{C_{16}H_{33}SO_3H} - \lambda_{HCl} + 100$ in glycerol–water mixture. Also, (○-), equivalent conductivity of cetyl pyridinium chloride at 80° in water.

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(16) This is due *mainly* to a weak acid, as the λ values obtained by subtracting the whole conductivity of the solvent are too low in low concentrations, but not *entirely*, as κ/C curves sharply upward. The two acids will certainly have nearly the same effect below the critical concentration and above it the correction is in any case small.

(17) It is possibly this effect which may be responsible for the data obtained by Reychler [*Bull. soc. chim. Belg.*, **27**, 113 (1913)] being consistently lower than mine, as is seen in Fig. 1. Reychler's final stage of preparation was the evaporation of an alcoholic solution and his product (which was in any case only 90% pure) may have contained some ethyl ester, which, being far more absorbable than amyl alcohol, might have a profound influence on the conductivity when present in even small amount. The data for dilute solutions of McBain and Williams [THIS JOURNAL, **55**, 2250 (1933)] at 90° are also obviously not in agreement with mine, but their internal consistency is obviously not good. The neutralization by glass mentioned below may have played a part. The work here described was repeated on the other three solutions with results agreeing everywhere to within 0.5%. A measurement by Mr. C. S. Samis on solution III at a concentration of 0.02 *N* was in good agreement with McBain and Williams' data, if the latter's value at 0.047 *N* is set aside as being a misprint or otherwise in error.

(18) This result is not in conflict with that of McBain and Searles [*J. Phys. Chem.*, **40**, 493 (1936)], who found that the conductivity

cetane sulfonic acid solution, but that of total acid is greater, as is to be expected if the aggregates, primarily of cetane sulfonate ions, are partly neutralized by hydrogen ions, attached either electrostatically or by covalent linkage or even only forming a close "atmosphere."

TABLE IV

EQUIVALENT CONDUCTIVITY OF CETANE SULFONIC ACID AT 60° IN WATER IN PRESENCE OF HYDROCHLORIC ACID AND AMYL ALCOHOL

Concn. $C_5H_{11}OH$ = 8.4 × concn. $C_{16}H_{33}SO_3H$		Concn. HCl = 0.958 × concn. $C_{16}H_{33}SO_3H$			
$C \times 10^3$	λ	$C \times 10^3$	$\kappa \times 10^6$	λ_{HCl}	λ
0.000	543.0	0.000			543
.398	534.8	.306	348.7	636.6	532
.597	525.7	.511	577.8	631.8	526
.817	482.4	.680	735.2	630.7	478
1.180	382.6	1.172	1073.4	628.1	313

Measurements were also made on cetane sulfonic acid at 40 and 80° (Table V, Fig. 1) and on cetyl pyridinium chloride at 80° (Table V, Fig. 2). The curves for cetane sulfonic acid at the three temperatures are very similar. The critical concentration at 80° is about 1.5 times that at 60°, and that at 60° is 1.3 times that at 40°. The temperature coefficient of the critical concentration therefore increases with increasing temperature in this range and is about 2% per degree at 60°. This is more than twice as great as the coefficient for the higher alkyl sulfates obtained, though with less certainty, from the data of Lottermoser and Püschel.[2] That cetane sulfonic acid is at least not unique in having this high temperature coefficient is evident from the increase in the critical concentration of cetyl pyridinium chloride from 0.0009 at 25°[3a] to 0.0022 at 80°.

TABLE V

EQUIVALENT CONDUCTIVITIES AT OTHER TEMPERATURES

$C_{16}H_{33}SO_3H$ 40°		$C_{16}H_{33}SO_3H$ 80°		$C_{16}H_{33}NC_5H_5Cl$ 80°	
$C \times 10^3$	λ	$C \times 10^3$	λ	$C \times 10^3$	λ
0.263	440.9	0.628	623.4	0.906	218.8
.454	439.3	.884	620.2	1.411	217.9
.641	414.2	1.155	612.1	1.889	216.9
.902	331.5	1.224	606.6	2.455	206.1
1.178	283.6	1.647	517.7	3.536	182.1
		2.307	426.3	4.580	164.9

That the critical phenomenon is due either to supersaturation or to incomplete solution is extremely improbable since it is equally evident at 40, 60 and 80°, while the curd form of cetane sulfonic acid gives place to a perfectly clear solution some 4° below the lowest of these temperatures. Although the clear solution has not been examined in the ultramicroscope, that of cetyl pyridinium chloride, the macroscopic crystals of which dissolve at about 18°, showed no ultramicrons, yet it has a well-defined critical concentration, even at 80° (see Fig. 2).

In cetane sulfonic acid solutions, a slow increase of resistance of the solution in the glass cell was always found, greatest at the highest temperature and amounting in the most dilute solutions examined to some 3% in twenty-four hours. This drift was not peculiar to the colloidal electrolyte, being found to almost as great an extent in hydrochloric acid. It was undoubtedly due to slow neutralization of the acid by alkali from the glass, and, in the case of cetane sulfonic acid, minute crystals of the alkali salt became visible after about forty-eight hours at 60°. The solution attained a resistance, constant except for this steady drift, within ten minutes after introduction into the cell. All the results recorded were obtained from measurements made after this time, except in the work with glycerol, when twenty minutes was allowed. A sample of one solution, kept in a quartz vessel in the thermostat for twenty-four hours, had a resistance only 0.03% less than that of a sample freshly heated from room temperature.

In the case of the neutral salt, cetyl pyridinium chloride, the glass solubility introduces no disturbing effect, and a more satisfactory test of reversibility can therefore be made. A solution of concentration about 0.0014 *N* was cooled down slowly in the cell from 80°. At about 60° a fairly abrupt increase in the rate of change of conductivity with temperature indicated that below this temperature aggregates are formed. The bath was therefore kept constant at a somewhat lower temperature, 53.7°, where aggregated and unaggregated salt must exist in comparable amount, so that the resistance would be very sensitive to changes of aggregation. The cell was then maintained at 80° for half an hour, put back into the thermostat and the resistance measured at one-minute intervals. After eight minutes the resistance had reached a value which was constant to 1 part in 6000 for the next half hour. The cell was then cooled[19] to 20°, main-

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of soaps and a simple salt with common ion were approximately simply additive, because we are here dealing with the increased degree of aggregation of the partly aggregated acid, whereas McBain and Searles are dealing, in higher concentration, with an effect on the fully aggregated soap.

(19) The cell had been almost completely filled for this experiment, and the stopper was sealed with mercury before cooling, so that solution of air was prevented, a precaution rendered necessary because air bubbles, if formed, adhere very tenaciously to the electrodes in this solution.

tained at that temperature for half an hour, put back in the thermostat and resistance readings taken as before. In eleven minutes the resistance had fallen to identically the same steady value previously reached, and decreased by only 2 parts in 6000 during the next twenty-four hours.

The high temperature coefficient of the critical concentration in cetane sulfonic acid gives rise to the existence also of a fairly definite critical temperature at one concentration. In Fig. 3 is plotted the specific conductivity of a 0.00073 *N* solution as a function of temperature, obtained by allowing the bath in which the cell was contained to cool slowly (about 10° per hour). The temperature coefficient in the range AB is the normal one (*ca.* 0.7% per degree) for a fully dissociated acid, while in the range BC it is very much greater (*ca.* 1.7% per degree). At B, aggregation commences and increases as the solution is cooled further. Once in the AB range and once in the BC range the fall of temperature was arrested and in each case the conductivity remained constant, after a slight fall as the temperature of the cell, which was of course slightly higher than that of the bath during cooling, fell to bath temperature. Quite different is the behavior when the second break, at C, occurs. Here curd fibers form slowly in the supersaturated solution. By quick cooling, values irregularly spaced below the dotted extension of the BC curve were obtained, but these fell in about half an hour to approximately constant values lying on the full line CD. It is a discontinuity of this latter type, more pronounced in the higher concentrations examined, which has been described by Reychler[20] and by Laing and McBain.[21] It is quite distinct from the break at B, which is caused by the rapid reversible formation of amicroscopic aggregates.

The formation of large aggregates in equilibrium with the simple ions is the only satisfactory explanation[22] which has been advanced of the existence of a fairly well-defined critical concentration. I have in the foregoing avoided the use of the word "micelle" as it was presumably my previous use of this word which led McBain and Betz to consider that I regarded aggregates as containing paraffin chain ions only.[23] I do not identify the aggregates formed in these dilute solutions with either the "ionic micelle" or the "neutral colloid" of McBain, as I do not believe that the separate existence of these entities is established. Evidence of a more direct nature has been put forward elsewhere,[3,5] that, just above the critical concentration, what I have there called micelles do in fact exist, and their nature has also been discussed[5] as fully as our present knowledge permits.

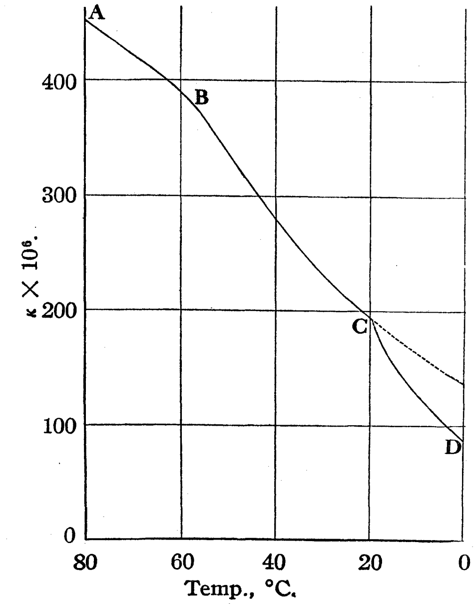

Fig. 3.—Specific conductivity of 0.00073 *N* cetane sulfonic acid on cooling.

It is reasonably certain that nearly all the paraffin chain ions in excess of the critical con-

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(20) Reychler, *Bull. soc. chim. Belg.*, **26**, 193 (1912); **27**, 113 (1913).

(21) Laing and McBain, *J. Chem. Soc.*, **117**, 1506 (1920).

(22) In a recent publication [*Proc. Roy. Soc.* (London), **155A**, 386 (1936)] Howell and Robinson have advanced an entirely different theory of the critical phenomenon. They believe that the paraffin chain ions, owing to their great "*rotational* volume," form a loose *network* which obstructs the passage of the small ions of opposite charge. They do not state how this theory can explain an *abrupt* change of properties, and the theory does not explain the observed increase of mobility of the paraffin chain ions when the critical concentration is exceeded,[3c] nor the increase of equivalent conductivity in high fields.[3c] Howell and Robinson's experimental data confirm the small temperature coefficient of the critical concentration in the case of the alkyl sulfates.

(23) McBain and Betz[7] (p. 1907) quote values for *A* in the equation $\lambda = \lambda_0 - A\sqrt{C}$ calculated by Mukherjee for uni-deci, and unicenti-valent electrolytes from Onsager's limiting formulas. They then combine these with the λ_0 value for the univalent acid and obtain λ values far lower than the experimental ones. They conclude that the ionic micelle does not behave as an "ordinary" polyvalent ion. Mukherjee's figures, however, were derived from formulas containing no term for the radius of the ion, and other simplifying approximations which made these formulas possible are certainly not applicable in solutions of very high-valent electrolytes in concentrations accessible to measurement. In an attempt, admittedly tentative, to estimate the real magnitude of effects of the Debye–Hückel type in colloidal electrolytes [*Trans. Faraday Soc.*, **31**, 55 (1935)], I concluded that the fall of conductivity in dilute solutions of paraffin chain salts could *not* be explained adequately in this way, and that the adherence of a considerable number of oppositely charged ions to the micelles must be assumed.

centration exist in micelles, and the concentration of single paraffin chain ions probably decreases absolutely.[24] By extrapolation of the figures given here, the critical concentration for cetane sulfonic acid at 90° will be about 0.0015 *N*. The aggregation will therefore be almost complete in a 0.01 *N* solution. According to McBain's diagram[9] it is only just appreciable at this concentration.

Summary

The critical fall of conductivity in dilute solutions of paraffin chain salts has been examined in considerable detail in the case of cetane sulfonic acid. A stable equilibrium has been shown to exist in the solution in the neighborhood of the critical concentration. The critical concentration, about 0.008 *N* in water at 60°, has been shown to increase with temperature by about 2% per degree. Addition of glycerol raises the critical concentration, while addition of amyl alcohol or hydrochloric acid lowers it.

The conductivity data lend no support to the belief that the acid is not a strong one in concentrations where it is not aggregated.

It is concluded that aggregation must be practically complete in a 0.01 *N* solution.

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[24] See refs. 3b, 5 (pp. 25–29), and, in particular, ref. 6.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Heat Capacities and Entropies of Organic Compounds. II. Thermal and Vapor Pressure Data for Tetramethylmethane from 13.22°K. to the Boiling Point. The Entropy from its Raman Spectrum

BY JOHN G. ASTON AND GEORGE H. MESSERLY[1]

The high symmetry of tetramethylmethane along with the absence of polarity makes this compound an inviting one for a comparison of the entropy calculated from its Raman spectrum and moments of inertia[2] and from calorimetric data using the third law of thermodynamics. In the present paper the necessary measurements are described and such a comparison is made.[3]

Tetramethylmethane.—The partially purified compound was kindly furnished by Dr. F. C. Whitmore and his students.[4] About 700 cc. was fractionally sublimed. The resulting material (freezing point about −23°) was twice distilled, at 370–400 mm., through an efficient glass fractionating column (packed with glass spirals) in which fractionation could be carried out in the absence of air in an all glass system.[5] The middle fraction was collected in a glass bulb. A 30-cc. middle portion was distilled from this fraction into a weighed 30-cc. sample bulb connected to the line by a ground glass joint. This sample was cooled to liquid air temperature and pumped out to less than 10^{-6} mm., melted, cooled again and repumped to remove the last traces of air.

The bulb was sealed off at a constriction below the ground glass joint and reweighed along with the joint. A correction to vacuum weights was made to ascertain the weight of tetramethylmethane. The sample bulb was equipped with a side arm closed by an inner-sealed capillary. For introduction into the calorimeter, the side arm was attached to the filling line which was evacuated to less than 10^{-5} mm. After cooling the tetramethylmethane to liquid air temperature the inner-sealed capillary was broken by a piece of iron sealed in glass and activated by a solenoid. The weight of sample was checked on removal from the apparatus. The impurity was 0.73 mole per cent. as estimated from the melting point range.

The Apparatus.—This was similar to that described by Giauque and Wiebe[6] except for details mentioned below. The calorimeter was made from 2.5-cm. copper tubing (0.025 cm. wall) and was 8 cm. long. Heat conduction was furnished by thirty-nine perforated disks (0.008 cm. thick) which made a spring fit with the walls and with a central tube, re-entrant from the bottom, which served as the well for the standard thermocouple.[7] The latter was fastened in with Wood's metal. A 3-mm. soft glass filling tube was sealed onto a short platinum tube brazed to the top. The whole was gold plated inside and out.

The calorimeter was wrapped with a gold resistance thermometer-heater (No. 40 B. and S. gage, double silk insulated annealed gold wire, containing 0.175% silver and drawn using only jewel dies). It was similar to that used by Giauque and Wiebe, except that a gap was left in the center in which a constantan resistance thermometer-heater for use below 25°K. was wound. It had a resistance at room temperature of 140 ohms, and 20 ohms at 25°K. The lower half, with a resistance of 81 ohms at room temperature, was used for heat of vaporization

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[1] Submitted in partial fulfilment of the requirements for the Ph.D. degree.

[2] (a) Kassel, *J. Chem. Phys.*, **3**, 115 (1935); (b) Eidinoff and Aston, *ibid.*, **3**, 379 (1935); (c) Kassel, *ibid.*, **4**, 276 (1936).

[3] For a report of the preliminary results of this comparison see Aston and Messerly, *ibid.*, **4**, 391 (1936).

[4] Whitmore and Fleming, THIS JOURNAL, **55**, 3803 (1933). These authors discuss the previous work on this compound.

[5] We wish to thank Professor J. H. Simons for the loan of the column and help in the purification.

[6] Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

[7] Parks, *ibid.*, **47**, 338 (1925).

measurements. The constantan resistance thermometer-heater, which was of No. 40 B. and S. gage double silk insulated thermocouple wire had a room temperature resistance of 114 ohms and below 25°K. an approximately constant temperature coefficient of 0.00145 deg.$^{-1}$. Both were wound as described by Ahlberg and Latimer,[8] and cooled several times to liquid air temperatures before use. However, both were continuously calibrated during the calorimetric measurements against the standard copper–constantan thermocouple S-2 whose calibration has already been described.[9a] The temperature scale was extended above 273°K. using carbon bisulfide vapor pressures.[9b]

The temperature head between the gold heater wire and the inside of the calorimeter was about 0.05°K. for a one cal. per minute energy input. In the case of the constantan heater below 25°K. it was several times this value.

The radiation shield together with the massive cylinder, which formed its top and with which the lead wires and the filling tube made good thermal contact, contained 1890 g. of copper and 4800 g. of lead.

The built-in hydrogen liquefier and cryostat were exactly as described by Latimer and Greensfelder.[10]

In cooling the calorimeter after filling it was found necessary to keep the entire filling tube hotter than the calorimeter at all times. Otherwise solid tetramethylmethane condensed in the tube as a solid plug which was very difficult to drive back into the calorimeter. A stream of warm air passing over the tube leading to the cryostat and onto the top of the cryostat allowed the temperature of these to be kept considerably above the temperature of the calorimeter, while allowing the cooling to proceed from the bottom. Liquid air was added at the bottom of the Dewar. In addition the tube and the heavy top of the radiation shield were electrically heated while cooling.

The Heat Capacity Measurements.—The electrical connections and method of measurement were as described by Giauque and Wiebe.[6,11]

The White potentiometer and standard resistances were calibrated by (or against standards calibrated by) the Bureau of Standards. The one-tenth second stop watch was calibrated frequently against an astronomical clock set with the Arlington time signals.

Three standard cells were constantly intercompared and frequently checked by the Bureau of Standards during the measurements. A thermometer current was chosen to give in most cases a sensitivity of 0.001° in reading the temperature rise.

The various corrections described by Giauque and Wiebe have been applied. In addition a correction was applied to the resistance for the temperature of the pair of 5-cm. leads from the terminals on the radiation shield to each of the resistance thermometers. This was taken as the mean of the shield and calorimeter temperatures. This correction was necessary because these leads formed part of the measured resistance, and during calibration the shield was at the same temperature as the calorimeter; it reduced the heat capacity by 0.14% at all temperatures above 60°K. For the calorimeter of G. and W. this correction was negligible (0.025%). The shield was kept above the calorimeter at all temperatures above 110°K. to prevent condensation. The vapor pressure measurements described later were used in correcting for material vaporized into the filling line, whose volume was determined accurately. In the calculation the density taken for the liquid was that given by Whitmore and Fleming[4]; that for the solid (0.73 g./cc.) was ascertained by the contraction on freezing.

The molal heat capacities are given in Table I and Fig. 1.

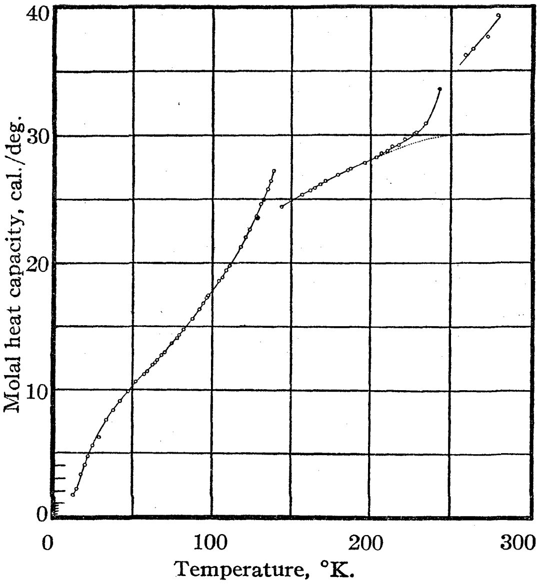

Fig. 1.—Heat capacity of tetramethylmethane.

In this and all other tables the molecular weight of tetramethylmethane was taken as 72.09, and the ice point as 273.16°K. One calorie (15°) was taken equal to 4.1852 absolute joules and one international joule to 1.00041 absolute joules.[12a] The present United States Standards were taken as yielding energy in international joules.[12b]

The error in these measurements from the various sources depends on the temperature. Below 25°K. the results may be in error by more than 1% due largely to the short range of calibration of the constantan resistance thermometer (10.9–26.2°K.) and the comparative insensitivity of the thermocouple in this range. Between 25 and 40°K. the lower points may be in error by about 1% due to the rapid change of derivative of the gold resistance thermometer. From 40 to 240°K. the error does not exceed a few tenths of a per cent. In the case of the points for the liquid the error may be somewhat above 0.5%. The error

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[8] Ahlberg and Latimer, THIS JOURNAL, **56**, 856 (1934).

[9] (a) Aston, Willihnganz and Messerly, *ibid.*, **57**, 1642 (1935); (b) Henning and Stock, *Z. Physik*, **4**, 226 (1921).

[10] Latimer and Greensfelder, THIS JOURNAL, **50**, 2202 (1928).

[11] See also Gibson and Giauque, *ibid.*, **45**, 93 (1923).

[12] (a) Birge, *Rev. Modern Phys.*, **1**, 30 (1929); (b) Vinal, *Bur. Standards J. Research*, **8**, 729 (1932).

TABLE I

HEAT CAPACITY OF TETRAMETHYLMETHANE

Molecular weight 72.09. 0°C. = 273.16°K.
Series I, 0.2419 mole; Series II and III, 0.2578 mole.

Temp., °K.	Rise, °K.	C_p, cal./deg./mole	Series number
13.14	0.453	1.688	I
15.24	2.244	2.134	I
18.05	2.042	3.281	I
20.28	2.206	4.061	I
22.40	2.615	4.734	I
25.22	3.873	5.583	I
29.12	3.160	6.203	I
33.83	4.695	7.579	I
38.12	3.852	8.380	I
42.28	4.951	9.087	I
47.30	5.170	9.854	I
52.11	4.407	10.544	I
57.45	6.244	11.190	I
59.29	3.377	11.403	II
62.72	5.138	11.946	III
63.17	5.336	11.965	I
64.19	5.891	12.126	II
65.56	4.849	12.303	I
68.03	4.572	12.696	I
69.69	5.125	12.906	II
70.05	4.183	12.918	III
70.86	5.454	13.043	I
72.90	5.111	13.336	I
74.70	4.560	13.623	II
74.81	4.780	13.615	III
78.12	4.569	14.009	I
79.47	4.965	14.266	II
82.13	4.079	14.712	III
82.50	4.163	14.673	I
87.12	5.327	15.623	I
87.34	5.263	15.501	II
87.81	3.615	15.632	III
92.20	4.838	16.407	I
92.21	4.629	16.287	II
94.57	4.561	16.772	III
96.70	4.445	17.191	I
97.39	4.283	17.372	II
103.89	5.280	18.488	I
104.14	3.842	18.514	III
106.53	5.326	18.808	II
108.95	4.846	19.350	I
111.14	4.516	19.711	III
118.22	4.035	21.20	III
121.35	7.441	21.96	II
124.00	3.686	22.53	III
128.07	3.453	23.59	III
128.84	3.571	23.40	IIIy
129.09	3.348	23.52	IIIx
130.87	6.376	24.53	II
132.87	3.200	24.90	III
135.50	1.533	25.72	III
137.06	1.485	26.36	III
138.81	1.438	27.15	III
140.02	"Transition"		
143.75	4.446	24.32	III
149.59	2.768	24.83	II
149.99	5.245	24.85	III
155.97	4.201	25.11	II
156.89	4.947	25.28	III
161.82	4.996	25.62	II
164.56	4.659	25.77	III
168.07	3.802	26.08	II
171.41	5.313	26.34	III
173.61	4.501	26.94	II
179.14	5.021	26.84	III
179.26	5.496	26.77	II
185.26	5.257	27.21	II
187.20	4.733	27.32	III
196.09	4.457	27.79	III
203.35	3.396	28.23	III
206.59	4.556	28.56	II
210.29	4.309	28.72	III
213.14	4.360	29.05	II
217.38	5.148	29.16	III
221.19	6.249	29.62	II
227.61	4.777	30.07	III
228.15	5.976	30.19	II
234.54	4.569	30.89	II
243.04	4.099	33.55	III
256.53	Fusion		
258.96	2.600	36.10	II
263.76	3.650	36.67	II
272.57	4.385	37.59	II
278.92	4.091	39.17	II
282.61	Boiling point		

due to the increased heat leak correction at the higher temperatures has been reduced by an accurate treatment of the drifts where these were non-linear.[13]

The High Energy Absorption near 140°K.—The abnormal rise in the heat capacity curve for the solid precedes what is perhaps an isothermal transition at 140.02°K.[14] However, the "transition" may be purely of the ammonium chloride type,[15] with very high heat capacities over a short range. In this connection it is noteworthy that up to almost 140°K. equilibrium was rapidly attained, whereas when energy was supplied in the neighborhood of 140.02°K. equilibrium was attained much more slowly (almost an hour). Table II records equilibrium temperatures at various fractions "transformed" as estimated from the fraction of the "transition" heat supplied, assuming this to be isothermal. The temperature at 80% transformed may be high due to difficulty in attaining equilibrium and less probably due to impurity.

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(13) See Keesom and Kok, *Comm. Phys. Lab. Univ. of Leiden*, 219c (1932).

(14) Wahl, *Z. physik. Chem.*, **88**, 135 (1914), states that solid tetramethylmethane is probably tetragonal (slightly birefringent) at low, and cubic (isotropic) at high, temperatures but no transition temperature is given.

(15) (a) Simon, *Ann. Physik*, **68**, 241 (1922); (b) see also Giauque and Blue, THIS JOURNAL, **58**, 833 (1936) for a very similar region of high energy absorption in the case of hydrogen sulfide between 126 and 127°K.

TABLE II

TEMPERATURES IN THE REGION OF HIGH ENERGY ABSORPTION

Per cent. transformed	Temp., °K. Thermocouple S-2	Temp., °K. Resistance thermometer
10	139.954	139.959
30	140.008	140.006
50	140.020	140.016
60	140.020	140.025
80	140.112	140.087
Mean	140.023	140.017
	Mean 140.020	

TABLE III

HEATS OF "TRANSITION" AND FUSION OF TETRAMETHYLMETHANE

(Mol. wt. 72.09; 0.25778 mole)

Temperature interval, °K.	Corrected heat input, cal./mole	$\int C_p dT$ cal./mole	Premelting, cal./mole	ΔH, cal./mole
"Transition" at 140.02° K.				
133.661–145.871	1054.5	438.6		615.9
135.534–146.911	1023.7	407.9		615.9
			Mean	615.9 ± 0.6
Fusion at 256.53°K.				
240.407–259.847	1609.9	854.1	23.5	779.3
240.913–261.442	1662.7	910.7	25.0	777.0
			Mean	778.2 ± 3.5

Table III contains a summary of data on the heat of "transition." For the calculation of $\int C_p dT$ the heat capacity curves on either side were extrapolated linearly to 140.02°K.

The two heat capacity measurements IIIx and IIIy recorded in Table I are lower than the best curve through the other series by 1.3%. This may indicate hysteresis in the neighborhood of the "transition" point. For this reason a history of the cooling for, and of the course of, the various series of heat capacity determinations is of interest. Before series I the solid material was heated until melting started and then cooled over two days to 10°K. Up to 70°K. the points were taken continuously. The apparatus was then cooled to 60°K. and the rest of the points of series I taken. Series II and III were taken on another filling from the same sample. In series II the cooling procedure was essentially the same except the calorimeter was cooled only to slightly below 60°K. Points were taken continuously to below the "transition" point; the material was carried through the transition with one application of energy. In series III the cooling to 60°K. occupied nine days. Points were taken continuously to just above the "transition" point. The calorimeter was then slowly cooled to obtain the point III_x, which was taken at the temperature where cooling stopped. The first heat of "transition" measurement was then taken. Point IIIy was taken after a similar cooling, and followed by the second heat of "transition" measurement. The rest of the points of series III were taken continuously to the melting point. Apparently hysteresis occurs only in the neighborhood of the "transition" point.

The Melting Point.—The equilibrium temperature of the system was observed with 50 and 97% of the sample melted as ascertained by measuring the heat required to melt the remaining solid as in a regular heat of fusion measurement. From the results and the heat of fusion the impurity present was found to be 0.727 mole per cent., assuming no solid solution. The melting point of pure tetramethylmethane calculated on this basis is 256.53 ± 0.10°K. (The freezing point of our sample was 255.31°K.) Previous melting points recorded in the literature[4] are: 253°K. (Lwow, 1871); 253.7°K. (Whitmore and Fleming, 1933).

Heat Capacities in the Premelting Range.—In the range between 200°K. and the melting point the tabulated heat capacities require correction for heat absorbed in fusion. The lower curve in Fig. 1 has been obtained from the upper one through the experimental points by subtracting this correction, obtained from the thermodynamic freezing point equation and the heat of fusion at the melting point without allowance for its change with temperature. (The heat capacity of the increasing quantity of liquid could be assumed equal to that of the solid without serious error.) This lower curve was extrapolated to the melting point as indicated by the extension to obtain heat capacities used in calculating the heat of fusion.

The Heat of Fusion.—The method described by Gibson and Giauque[11] was used. The results are recorded in Table III.

The correction for premelting (col. 4) is the area between the upper and lower curves (Fig. 1). The estimated error does not include the error due to our estimation of this correction. This may produce about 1% error in the heat of fusion, but does not seriously affect the entropy. Indeed if the whole fusion had been treated as a heat capacity in calculating the entropy, the effect on the final entropy would have been only to add the almost negligible entropy of mixing of the impurity—($-0.0073\ R \ln 0.0073 - 0.9927\ R \ln 0.9927 = 0.088$ e. u.).

The Vapor Pressure Measurements.—The measurements were made as already described.[9] The results for the liquid are given in Table IV. Column 1 gives the absolute temperature as read by the thermocouple; col. 2 gives the observed pressure, and col. 3 the pressure calculated from equation (1).

$$\log_{10} P_{\text{mm.}} = -1525.0/T - 2.16979 \log_{10} T + 13.59527 \qquad (1)$$

Column 4 gives the temperature deviation corresponding to the pressure difference. Since the boiling range of the sample used was about 0.1°, as ascertained by vapor pressure measurements on fractions distilled from it, these measurements should hold for pure tetramethylmethane to about 0.1° in the temperature. Vapor pressure data were also obtained on the solid, but are without significance as the partial pressure of impurity above the liquid is steadily increased as the solid crystallizes. For completeness we give equation (2), which represented our data on the solid between 230°K. and the melting point.

$$\log_{10} P_{\text{mm.}} = 11642.30/T + 258.6890 \log_{10} T - 0.241380\, T - 604.2570 \qquad (2)$$

The only other data on tetramethylmethane are the measurements of Whitmore and Fleming.[4] A comparison of their results on the solid with equation (2) shows that their material contained more impurity than ours, as does also the freezing point which they record for it. In col. 5 of Table IV are given the deviations (W. and F.–A. and M.) between the pressures observed by Whitmore and Fleming at their nearest temperature and those calculated from equation (1). From equation (1) the boiling point has been found to be 282.61°K. Previous boiling points recorded in the literature[4] are: 282.7°K. (Lwow, 1871); 282.6°K. (Whitmore and Fleming, 1933).

TABLE IV

VAPOR PRESSURES OF LIQUID TETRAMETHYLMETHANE

(g for State College, 980.124 ("I. C. T.")) (0°C. = 273.16°K.). Boiling point 282.61°K.

Temp., °K.	Pressure (obsd.) int. mm.	Pressure (calcd.) int. mm.	ΔT., °K. (calcd. − obsd.)	ΔP (mm.) (W. and F.–A. and M.)
258.036	283.71	283.64	−0.011	10.7
262.766	348.41	348.33	−.005	
267.847	430.66	430.46	−.009	8.1
272.292	515.02	514.48	−.021	9.0
277.865	637.77	637.70	−.003	4.7
280.396	700.30	700.82	+.017	
282.897	767.72	767.93	+.006	0.3

The Heat of Vaporization.—Our procedure differed from that described by Giauque and Wiebe (method II)[6] only in the method of collecting the vaporized material. A thin-walled glass bulb, connected to the line by a vaseline sealed glass joint, was used for this purpose. It was immersed in a well-stirred bath of benzene and benzene ice, along with excess water, contained in a silvered dewar. During vaporization the pressure remained constant to within a few millimeters except during the initial period required to build up the head necessary for heat transfer across the bulb, when it rose by about 20 mm. Before a measurement the calorimeter was brought to within a degree of the temperature of the bath of benzene–benzene ice. The surroundings were at such a temperature as to be above that of the calorimeter at all times during the vaporization. The drift of the calorimeter was observed with the resistance thermometer until a sudden decrease in its value indicated that material had started to condense in the bulb. The heater was then turned on. The energy for the vaporization before the heater was turned on was calculated from the heat leak. At the end of the measurement the heater was shut off at a predetermined time and a stopcock connecting the calorimeter to the rest of the line (manometer, condensing bulb, etc.) simultaneously closed. The drifts were followed until the calorimeter reached equilibrium. The correction for the varying pressure and hence temperature of the surface from which vaporization occurred was simply made as follows.

Consider n moles of liquid whose initial temperature is T' and whose vaporization temperature varies from T' to T. Let Q be the heat absorbed in heating the n moles from T' and vaporizing them. Let C_p be the heat capacity of the gas (assumed constant), and $\Delta H'$ the heat of vaporization at the temperature T'. Then

$$Q = \int_0^n [\Delta H' + C_p(T - T')]\, dn \qquad (3)$$

Over the small range of temperatures involved $(T - T') = k(P - P')$, where P and P' are the vapor pressures at T and T'. Substituting in (3) and integrating

$$Q = \Delta H'n - \alpha P'n + \int_0^n \alpha P\, dn \ (\alpha = kC_p) \qquad (4)$$

As the number of moles vaporized is proportional to the time of energy input

$$Q = \Delta H'n - \alpha P'n + \beta \int_0^t P\, dt \qquad (5)$$

where β is a new constant. If P had a constant value P_e

$$Q = \Delta H'n - \alpha P'n - \beta P_e t \qquad (6)$$

Comparing (5) and (6) it is seen that the vaporization may be considered as occurring at an effective pressure

$$P_e = 1/t \int_0^t P \, dt \qquad (7)$$

The integral (7) accordingly was evaluated graphically to obtain the effective pressure (and temperature) of the vaporization.

The number of moles of liquid vaporized was calculated from the increase of pressures in the line, and the weight of material condensed in the bulb. The pressure in the calorimeter line up to the closed stopcock was obtained from its equilibrium temperature at the end of the vaporization period; that in the manometer and bulb from the manometer reading when the bulb was sealed off.[16] The results are given in Table V.

TABLE V

HEAT OF VAPORIZATION OF TETRAMETHYLMETHANE

(662.2 int. mm. (278.59°K.)) (mol. wt. 72.09)

Moles vaporized	Time of energy input, min.	Total input, cal./mole	$\int C_p dT$, cal./mole	ΔH, cal./mole
0.05545	25.50	6281	797	5484
.06378	28.00	5980	447	5528[a]
			Mean	5506 ± 30
Corrected to one atm. (282.61°K.)				5438 ± 30
Calculated at one atm. from equation (1) and thermodynamics; Berthelot correction = 244 cal.				5490

[a] A correction of −5 cal. applied for difference in effective pressure.

The correction for raising the temperature of the liquid remaining in the calorimeter to the final temperature and the number of moles of liquid vaporized to the effective temperature of vaporization are given in col. 4. The mean value has been corrected to the boiling point using the measured heat capacities for the liquid and for the gas the heat capacities calculated by adding to 12/2 R (the translational and rotational heat capacity + $C_p - C_v$) the vibrational heat capacity calculated from the Raman spectrum using the equation

$$C_{\text{vib.}} = R \sum x_i^2 e^{x_i}/(e^{x_i} - 1)^2 \; (x_i = hc\tilde{\nu}/kT) \qquad (8)$$

with frequencies and constants discussed later. (The correction to the real gas state is here negligible.) It is of interest to compare the measured heat of vaporization with the one calculated from the vapor pressures (equation (1)) and thermodynamics using the modified Berthelot equation

$$PV = RT\,[1 - 9PT_c(1 - 6T_c^2/T^2)/128P_cT] \qquad (9)$$
$$T_c = 432°\text{K.}; \quad P_c = 33 \text{ atm.}^{17}$$

to calculate the volume of the gas. The heat of vaporization, thus calculated from the vapor pressures, at the boiling point, is included in Table V. The agreement justifies the equation of state chosen for the later correction of the entropy.

The Entropy.—Table VI summarizes the calculation of the entropy of the gas at the boiling point from the experimental data. The correction to the perfect gas state has been made using equation (9) and thermodynamics.[6]

TABLE VI

THE ENTROPY OF TETRAMETHYLMETHANE

(Mol. wt. 72.09)

	E. u./mole
0–13.14°K. Debye function $h\vartheta_m/k$ = 106.7 (six degrees of freedom)	0.56
13.14–140.02°K. graphical[a]	24.13
"Transition" 615.9/140.02	4.39
140.02–256.53°K. graphical[a]	16.55
Fusion 778.2/256.53	3.03
256.53–282.61°K. graphical[a]	3.63
Vaporization 5438/282.61	19.24
Entropy of actual gas at boiling point	71.53 ± 0.3
correction for gas imperfection	0.18
Entropy of ideal gas at boiling point	71.71 ± 0.3

[a] $\Delta S = \int C_p d \ln T$.

The classical rotational and translational entropy of the gas at 298.16°K. and one atm. has been calculated by Kassel to be 73.957 e. u.[2c] using 1.53 and 1.11 Å. for the C–C and C–H distances respectively. We have used 1.54 Å. for the former throughout, but have retained the latter.

The equation for the translational and classical rotational entropy, assuming zero potential associated with the rotation of the methyl groups, neglecting nuclear spin, and using 972 for the symmetry number, is then

$$S_{\text{T,R}} = 27.45011 \log_{10} T - 4.57504 \log_{10} P_{\text{atm.}} + 6.05751 \qquad (10)$$

The vibrational entropy has been calculated by the equation

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(16) To seal off the bulb a stopcock leading to it was closed before cooling in liquid air and sealing off at a constriction.

(17) T_c and P_c were ascertained as follows. An inspection of the data in the "I. C. T." reveals that for isomers of a given class P_c and T_c/T_b are respectively about the same (where T_b is the normal boiling point); *e. g.*, for *n*-pentane P_c = 33.0; T_c/T_b = 1.521, while for isopentane P_c = 32.8, and T_c/T_b = 1.529. For *n*-butane and isobutane P_c = 35.5, 37; T_c/T_b = 1.558, 1.546. With some confidence therefore we take P_c and T_c/T_b for neopentane the same as for isopentane.

$$S_{\text{vib.}} = R \sum x_i/(e^{x_i} - 1) - \ln (1 - e^{-x_i}) \; (x_i = hc\tilde{\nu}_i/kT) \quad (11)$$

using the Raman frequencies determined by Rank and Bordner.[18] These are, respectively, 335 (2), 414 (3), 733 (1), 925 (3), 1252 (4), and 1455 (8) cm.$^{-1}$, where the figures in parentheses give the multiplicities. For the first four frequencies which are due to the carbon skeleton this assignment is that of Rank and Bordner and is based on analogy with the Raman spectrum of carbon tetrachloride. The two higher frequencies, as Rank and Bordner point out, undoubtedly are due to deformation of the methyl groups, but they hesitate to estimate the multiplicity. Two similar frequencies appear in methyl chloride, namely, 1355 (1) and 1460 (2).[19] It seems justifiable to take four times these multiplicities in the case of tetramethylmethane where there are four methyl groups. The effect of the higher frequencies is negligible. In the calculation the constants R = 1.9869 cal.$_{15}$/deg./mole, hc/k = 1.4325 cm. deg., were used. A comparison of the calorimetric and spectroscopic values of the entropy is given in Table VII.

TABLE VII

COMPARISON OF CALORIMETRIC AND "SPECTROSCOPIC" ENTROPIES OF TETRAMETHYLMETHANE AT ONE ATMOSPHERE

	Temperature, °K.	282.61 E. u./mole	298.16 E. u./mole
I	Translational and rotational	73.34	73.98
II	Vibrational (carbon skeleton)	5.38	5.89
III	Vibrational (other modes)	0.17	0.25
IV	Absolute	95.42	96.65
V	Total (less nuclear spin)	78.89	80.12
VI	Calorimetric corrected to ideal gas state	71.71	
VII	Discrepancy	7.18	
		($5\,R \ln 2 = 6.89$)	

Discussion.—The spectroscopic entropy exceeds that calculated from the calorimetric data by $5\,R \ln 2$ within experimental error. The chief experimental errors lie in the heat of vaporization and in the extrapolation. That due to the former could hardly exceed 0.2 e. u. Any serious error in the extrapolation (on the basis of the actual crystal) is unlikely as the results fit a Debye function, calculated for six degrees of freedom, within experimental error.

The specific entropy of the impurity (probably isobutylene, $S_{298.1,\ 1\ \text{atm.}}$ = 67.3 e. u. per mole)[20] would be sufficiently similar so that the error on this account should be less than 0.1 e. u.; the entropy of mixing has already been eliminated without appreciable error as evident from its magnitude.

In the absence of any other calorimetric data on tetramethylmethane which might serve as an over-all check, we have made several isolated heat capacity measurements on methyl alcohol between 90°K. and room temperature, and the results have always been in agreement with those of Kelley[21] within the estimated accuracy of the respective observers.

An examination of the assignment of the four Raman frequencies due to the carbon skeleton also furnishes no obvious method of eliminating or materially reducing the discrepancy. Of the single frequency there is little doubt. Indeed this is true of the two highest pentatomic frequencies, of which the lower is a singlet and the higher a triplet, in the case of both methane and carbon tetrachloride. Inversion of the multiplicities of the two lower frequencies would raise the entropy calculated by 0.33 e. u.

If the above agreement of the discrepancy with $5\,R \ln 2$ is not fortuitous, it might be taken to indicate 2^5 possible arrangements in the crystal such as have been proposed by Giauque to explain discrepancies of a similar nature in the case of carbon monoxide,[22,23] and nitrous oxide;[24,25] and by Pauling for water,[26,27] although the possibility of rotation of the methyl groups in certain of the symmetry varieties must not be overlooked. A situation similar to the latter for the case of hydrogen has been discussed by Giauque and Johnston.[28,29]

In this connection it is to be noted that for methane the calorimetric and spectroscopic entropies are in agreement,[30] but there is a peak in the heat capacity curve at 20.4°K.[31]

The entropy corresponding to the area between the peak and the normal heat capacity curve is 1.78 e. u. This is close to the sum (1.63 e. u.) of the entropy of mixing of the degenerate lowest

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(18) Rank and Bordner, *J. Chem. Phys.*, **3**, 248 (1935).

(19) For discussion and references see Vold, THIS JOURNAL, **57**, 1192 (1935).

(20) Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932, p. 81.

(21) Kelley, THIS JOURNAL, **51**, 180 (1929).

(22) Clusius, *Z. physik. Chem.*, **B6**, 135 (1929).

(23) Clayton and Giauque, THIS JOURNAL, **54**, 2610 (1932).

(24) Clusius, *Z. Elektrochem.*, **40**, 98 (1935).

(25) Giauque and Blue, THIS JOURNAL, **57**, 991 (1935).

(26) Pauling, *ibid.*, **57**, 2680 (1935).

(27) Giauque and Stout, *ibid.*, **58**, 1144 (1936).

(28) Giauque and Johnston, *ibid.*, **50**, 3221 (1928).

(29) Giauque, *ibid.*, **52**, 4816 (1930).

(30) Giauque, Blue and Overstreet, *Phys. Rev.*, **38**, 197 (1932).

(31) (a) Clusius, *Z. physik. Chem.*, **B3**, 65 (1929); (b) Clusius and Perlick, *ibid.*, **B24**, 313 (1934).

rotational states of the triplet ($9/16\ R \ln 3 = 1.23$ e. u.) and the corresponding quantity for the quintet variety ($2/16\ R \ln 5 = 0.40$ e. u.) assuming the high temperature equilibrium mixture. It therefore seems probable that rotational states are present in methane down to this temperature and there rotation practically ceases. The energy differences between the orientations of minimum potential energy are then evidently sufficiently large compared with kT to cause a unique arrangement of all but a small fraction of the molecules.

It is likely that the abnormal heat capacity rise prior to the "transition" of tetramethylmethane is caused by rotation starting for at least one degree of freedom and perhaps not unreasonable that this is one of the angular coördinates for the carbon skeleton.

It would be of interest to investigate the heat capacity of methyl deuteride from 10 to 30°K. as the symmetry situation is changed and hence if the above interpretation for methane is correct it should present a peak of quite a different kind.

Data on the heat capacity of ethane[32] below 67°K. would make possible a third law comparison which might throw light on the tetramethylmethane discrepancy.

The apparatus for the investigation of both of these compounds down to 10°K. is now practically complete. It is also planned in the near future to investigate tetramethylmethane, and, if necessary, ethane, down to 1°K.

Acknowledgment.—We wish to express our appreciation of the assistance of Messrs. C. W. Siller and Maxwell Eidinoff with the experimental work. Mr. J. E. Key (late of the Department of Industrial Engineering), Messrs. G. F. Nelson and W. J. Cummings of the University of California are responsible for the excellent construction of certain parts of the apparatus essential to the work. The many suggestions of Professor W. F. Giauque have been invaluable. We wish to thank the National Research Council for Grants-in-Aid, without which this work would have been impossible.

Summary

1. The heat capacities of tetramethylmethane have been determined from 13°K. to the boiling point.

2. The vapor pressure of liquid tetramethylmethane has been determined from the melting point to the boiling point, and an equation derived to represent the data. An equation for the vapor pressure below the freezing point is given but not considered significant.

3. The melting point of tetramethylmethane is 256.53°K. (−16.63°C.) and the boiling point 282.61°K. (9.45°C.). There is an energy absorption which is perhaps isothermal at 140.02°K. (−133.14°C.) but which is preceded by an abnormal rise in the heat capacity.

4. The molal entropy of the ideal gas at the boiling point, calculated from the experimental data, is 71.71 ± 0.3 e. u. This value is, within experimental error, $5\ R \ln 2$ lower than the corresponding value of 78.89 e. u. calculated from the Raman spectrum and moments of inertia.

5. The "spectroscopic" entropy, calculated from the Raman spectrum and moments of inertia, is 80.12 e. u. per mole at 298.16°K. and one atmosphere neglecting nuclear spin.

STATE COLLEGE, PENNA. RECEIVED AUGUST 17, 1936

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[32] For data above 67°K. see Wiebe, Hubbard and Brevoort, THIS JOURNAL, **52**, 611 (1930).

[CONTRIBUTION FROM THE BIOLOGICAL LABORATORY, LONG ISLAND BIOLOGICAL ASSOCIATION]

A Vertical Microelectrophoresis Cell with Non-Polarizable Electrodes

BY HAROLD A. ABRAMSON, LAURENCE S. MOYER AND ANDR. VOET[1]

The measurement of the electric mobility of microscopic particles in horizontal electrophoresis cells may be complicated by the settling out of the particles under observation. It would be of advantage to have the cell constructed so that the same particle could be studied for periods even as long as one hour. Furthermore, it is of importance that non-polarizable electrodes be employed. An apparatus of this type in which the electrophoresis cell itself is *vertical* is described in this communication. It should not be construed from this paper that the vertical cell is more suitable for all systems, but it may be of advantage in the investigation of particles similar to those described here.

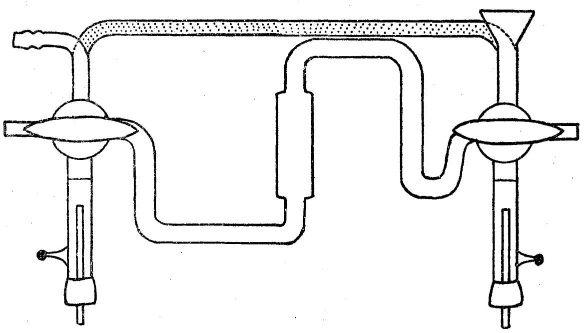

Fig. 1.

Description.—The instrument is constructed and calibrated similarly to that previously described by Abramson[2,3] (a modification of a type developed by Northrop and Kunitz) and discussed recently in some detail by Moyer.[4] As shown in Fig. 1, the apparatus is provided with the arrangement of electrodes developed for the horizontal cell. This arrangement combines the features of non-polarizability and use of plaster of Paris plugs designed to eliminate disturbances at the electrodes due to precipitation of sols. In addition, the instrument is constructed of one piece of glass with no rubber or other connections. This provides a device which may be fixed rigidly onto the stage of the microscope and hence eliminates completely the disturbing vibrations which are so commonly encountered in three-piece instruments. Cleaning is therefore facilitated and the cell may readily be removed for filling or for cleaning. For a detailed description of construction, electrical connections and calibration, see references 2, 3 and 4. The cell is used with the microscope tilted horizontally. The bar running across the top (Fig. 1) is fused onto the (L-shaped bore) stopcock sleeve. This bar (stippled) can then be suspended by hooks, made to fit from strap brass, in front of the objective and clamped to the stage by a spring brass clip. The clip can be adapted to the size and shape of the microscope stage and to glass microscope slides (not shown in the figure) which may be cemented to the horizontal bar and side arms to provide a flat resting surface for the cell against the stage of the microscope. The connections of the cell itself with the two electrodes may be altered to fit the needs of the investigator. Thus, the funnel may be made larger or replaced by other devices for filling; the side arms may be run directly to the cell from the stopcocks, etc. Both the horizontal and vertical instruments may be obtained from Mr. J. D. Graham of Haddonfield, New Jersey. Dimensions of the central chambers of the vertical and horizontal instruments used in these experiments are given in Table I.

TABLE I

DIMENSIONS OF CENTRAL CHAMBERS OF CELLS DISCUSSED

Dimension	Vertical cell, mm.	Horizontal cell, mm.
Length	42	37
Av. depth	0.615	0.795
Width	12.0	12.0
k	20	15

Use of the Cell.—Since the central chamber is of nearly rectangular cross section, the position of the stationary levels may be calculated. Calculation of the stationary levels from Komagata's equation[5] (which has been checked by Komagata as well as more recently by van Gils[6])

$$y_{(v_w = 0)} = \pm b[(1/3) + (128/\pi^5 k)]^{1/2} \qquad (1)$$

where y is the level measured from the central axis, k is the ratio of half the width to half the thickness, b (see Table I for values of k), yields levels which do not differ significantly from 0.2 and 0.8 of the total depth.

Any difficulties encountered in finding the true focus of the ceiling and floor may be obviated by filling the cell with powdered glass or quartz suspended in water and laying it flat for a sufficient time to permit a few particles to stick on both walls.

Since the electrical and gravitational forces operating on the particle are superimposed, the

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[1] Research Fellow, Netherland-American Foundation.

[2] H. A. Abramson, *J. Gen. Physiol.*, **12**, 469 (1929); H. A. Abramson and E. B. Grossman, *ibid.*, **14**, 563 (1931).

[3] H. A. Abramson, "Electrokinetic Phenomena," Chemical Catalog Co., New York, 1934.

[4] L. S. Moyer, *J. Bact.*, **31**, 531 (1936).

[5] S. Komagata, *Researches Electrotech. Lab. (Tokyo)*, No. 348 (1933).

[6] G. S. van Gils, "Electrophorese metingen." Thesis, Utrecht, 1936.

particle, although falling, tends to remain in the same level of the cell with respect to its thickness. If it is at the stationary level it will remain there and may be kept under observation for long periods of time. However a correction must be made for gravitational forces. This is done by timing the particle while moving it in one direction and then reversing the electrical field and timing for the same distance in the opposite direction. The effects of small convection currents, if not large enough to produce turbulence, are apparently also canceled out by this method, although such forces may be largely eliminated at the start by carefully equilibrating both the instrument and solutions to room temperature before filling the cell. Particles which move too rapidly under gravity may set up local turbulence which disturbs the normal mobility of smaller particles in their neighborhood. When such effects occur, letting the apparatus stand for a time without applying the field frequently eliminates the difficulty by allowing the large particles to settle out. Water-cooled lighting devices should be used, of course, for illuminating the sol.

In a given medium large particles are affected more by gravity than small particles of the same substance, even when both have the same electric mobility, so that the electric mobility *appears* to be dependent on size. However, when large and small particles are timed over the same distance, it is found that the differing effect of gravity cancels out and the resultant electric mobilities are not dependent upon size and shape. This is similar to the effects noted by Mooney.[7] Hence it is not sufficient to time a series of particles moving in one direction and then a series in the other and average, but each particle should be timed over the whole distance. For long observation where the eye is kept constantly at the microscope, a metronome may be used instead of a stop watch.

Interesting observations of these effects were made in a system consisting of gelatin-coated collodion particles (about 0.5 μ) and gelatin-coated, long asbestos needles (up to 50 μ). In the horizontal cell, both collodion particle and needle under these conditions migrate with the same mobility in either direction. On the other hand, in the vertical cell the long needles are operated on by a greater gravitational component which increases the observed mobility to such an extent, when particles are falling, that they migrate faster than the collodion particles. On reversing the current, however, so that the particles now migrate against gravity, the asbestos needles experience greater retardation and both particles are thus made to travel over the total distance in the same time.

Table II gives comparative measurements made on a mixed suspension of gelatin-coated collodion and asbestos particles in 0.01 *M* acetic acid. It will be noted that both types of particles move with the same mobility, irrespective of size, shape or orientation.

Table II

Times Required for Gelatin-coated Particles of Different Sizes to Travel a Fixed Distance in a Constant Electric Field

	Collodion particles, sec.		Asbestos needles, sec.	
	12.5	11.6	11.8	12.6
	12.3	12.2	12.1	11.8
	11.8	11.2	12.0	12.6
	13.4	12.5	12.2	12.1
	12.3	12.5	12.9	12.5
Average	12.23		12.26	

Comparison with Other Cells.—As far as the writers are aware, the instruments under discussion here are the only ones which have been shown to yield values comparable with those obtained in U-tubes (although Bull[8] checked his cell against streaming potential) and therefore may well be used as standards in measurements of this kind.

The recent measurements of Howitt[9] of the electric mobility of mammalian red blood cells by a moving boundary method in a U-tube afford an additional direct comparison of the validity of the entire method. It had been shown[3] previously that the mobility of various mammalian red blood cells is constant for each species investigated. For instance, the human erythrocyte exhibits the same mobility in isotonic phosphate buffer at *p*H 7.4 independent of sex, blood group, age or race of the individual. Table III presents data obtained on the red cells of different mammals, suspended in 0.067 *M* phosphate buffer at *p*H 7.4. Note the agreement, well within the usual limits of error of the methods concerned.

To demonstrate the symmetry and flatness of the vertical cell, collodion particles were coated with 1% Coignet gelatin, which was also used to coat the walls of the cell. The gelatin was then

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[7] M. Mooney, *Phys. Rev.*, **23**, 396 (1924).

[8] H. B. Bull, *J. Phys. Chem.*, **39**, 577 (1935).

[9] F. O. Howitt, *Biochem. J.*, **28**, 1165 (1934).

TABLE III

COMPARABLE MOBILITIES (μ/SEC.) OF RED BLOOD CELLS, FOUND BY DIFFERENT OBSERVERS WITH SEVERAL TYPES OF INSTRUMENTS

	Man	Rat	Rabbit	Mouse	Guinea pig
Moving boundary[9]	..	1.45	0.60	1.42	1.16
Horizontal[3]	1.31	1.45	.55	1.35	1.11
Horizontal[4]	1.30	..	..	..	..
Vertical	1.25	..	..	..	..

diluted to 0.1% by adding acetic acid so that its final concentration was 0.01 M. While keeping the field strength constant, mobilities were determined at various levels in the cell. It is clearly seen in Fig. 2 that no significant differences were observed between measurements made in the two instruments (vertical, open circles, and horizontal, closed circles). The smooth curve has been drawn from the equation

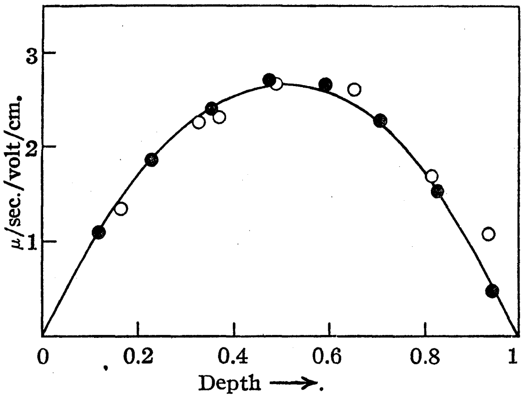

Fig. 2.

$$V(x) = 10.65\ (x - x^2) \qquad (2)$$

where V is the mobility at any depth, x, after a plot of the data in the form of a straight line, as discussed in a previous paper,[10] showed that the intercept was not significantly different from 0 (*i. e.*, the ratio of the electroösmotic to the electrophoretic mobility was 1.0). It may be observed that the electrophoretic mobility (at the 0.2 and 0.8 levels, = 1.70 μ/sec.) agrees with that found for the asbestos needles in the previous experiment.

Discussion

It is of some importance that the needle-shaped particles such as the asbestos ones investigated here assume a position with both ends of the needle at the same electroösmotic level. This is not found in the horizontal cell where needles are frequently observed with one end in one level and the other end at another level. The fact that the needles in the vertical cell thus assume a position with practically no velocity gradient acting upon them makes the vertical cell more suitable for investigations of this type of particle. It should be emphasized, however, that within the limits of time ordinarily adopted for a single experiment and within the. limits of the field strengths employed, little or no orientation of these rod-shaped particles occurs. It is very remarkable indeed to see asbestos needles up to 50 microns in length migrate independently of their orientation under these new and more favorable conditions, thus confirming previous experiments.[3] In accord with our previous results[10] on the ratio of electroosmosis to electrophoresis, recently confirmed independently by van Gils,[6] a ratio of 1.0 was found for gelatin-coated surfaces in dilute solutions (here at an ionic strength of about 3 × $10^{-4}\,M$). Under the seconditions, no motion was ever observed near the wall in either cell.

Summary

The horizontal microelectrophoresis cell has not been adapted to the measurement of particles which settle out of suspension. A vertical cell has been devised which embodies all of the useful characteristics of the one-piece glass cell described previously by Abramson and discussed more recently by Moyer. This vertical cell has been checked by comparing measurements on protein-coated collodion particles, asbestos needles, and blood cells with measurements obtained in a calibrated horizontal cell and a U-tube. Agreement within the usual limits of experimental error was obtained. The advantages and disadvantages of the vertical cell are discussed.

COLD SPRING HARBOR
LONG ISLAND, N. Y.
RECEIVED SEPTEMBER 21, 1936

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[10] L. S. Moyer and H. A. Abramson, *J. Gen. Physiol.*, **19**, 727 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HARVARD MEDICAL SCHOOL]

Studies in the Physical Chemistry of Amino Acids, Peptides and Related Substances. VIII. The Relation between the Activity Coefficients of Peptides and their Dipole Moments

BY EDWIN J. COHN, THOMAS L. MCMEEKIN, JESSE P. GREENSTEIN AND JOHN H. WEARE

Whereas the activity coefficients of ions depend upon their valence, those of dipolar ions depend largely upon their dipole moments. This had been suggested on the basis of theoretical considerations,[1,2] but further development of the field had to await more detailed experimental studies.

For ions, the effect of electrostatic forces can be distinguished from that of non-electrical forces since the former varies as the square root of the concentration, whereas the latter varies as the concentration. This distinction cannot be so readily made for dipolar ions because the effect of electrostatic forces is linear with the concentration and does not vary as its square root. It follows that even in very dilute aqueous solutions of amino acids and proteins the forces are not necessarily purely electrostatic in nature.

Electrostatic forces due to dipolar ions increase not with the quantity κ of Debye's theory,[3] but with κ^2. κ^2 increases not only with increase in concentration but with decrease in temperature and in dielectric constant. Electrostatic forces thus become more important the lower the temperature and the lower the dielectric constant.

The study of the influence of neutral salts upon glycine in ethanol–water mixtures demonstrated that at sufficiently low dielectric constants the logarithm of the solubility ratio multiplied by the dielectric constant ratio $(D/D_0) \log N/N_0$ was a function of κ^2. So plotted measurements in 60, 80, 90 and 95% ethanol containing neutral salts essentially coincide suggesting that under these conditions the activity coefficients of the amino acids studied were largely ascribable to electrostatic forces.[2,4]

These preliminary experiments on amino acids led to the choice of conditions for the studies of peptides here reported. The solvent employed was 80% ethanol containing varying concentrations of sodium chloride. At this alcohol concentration sodium chloride solutions up to 0.25 molar can be prepared, and the solubility of glycine in this most concentrated salt solution was 3.73 g. per liter, or approximately one-fourth the concentration of salt. In the absence of salt glycine is soluble only to the extent of 2.00 g. per liter in 80% ethanol. It is this solvent action associated with change in ionic strength with which we are here concerned, and not with the effect of change in medium which reduces the solubility of glycine in 80% ethanol one hundred-fold from its solubility in water of 216.6 g. per liter at 25°.

The peptides of glycine have been chosen for comparison rather than aliphatic amino acids of long dipole moment because of their far lower solubility in both water and alcohol–water mixtures. This is related to the far greater density of glycine peptide crystals.[5] As a result, although β-alanine and ϵ-aminocaproic acid are far more soluble than the corresponding α-amino acids (though they have closely the same densities in the solid state), the tightly packed glycine peptides are progressively less soluble in water the longer their molecules, despite their larger dipole moments. This is not true, as Fischer[6] pointed out, of certain peptides with paraffin side chains.

Lysylglutamic acid is extremely soluble in water. Its solubility in 80% ethanol is none the less very low, the very rapid falling off of solubility with dielectric constant depending upon its multipolar nature. In this its behavior resembles to a considerable extent proteins such as egg albumin, with which it is compared in a subsequent communication. The solubility of all of the peptides studied is so small in 80% ethanol that the composition of the solutions approaches closely those of the pure solvents.

I. Methods and Materials

Solubility has been determined by methods that have been described previously.[7,8] Fresh

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(1) Scatchard and Kirkwood, *Physik. Z.*, **33**, 297 (1932).

(2) Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

(3) The term proportional to κ has been shown by Scatchard and Kirkwood[1] to vanish when the net charge is zero.

(4) Cohn, *Naturwissenschaften*, **20**, 663 (1932).

(5) McMeekin, Cohn and Weare, THIS JOURNAL, **57**, 626 (1935).

(6) Fischer, *Ber.*, **36**, 2982 (1903).

(7) Cohn, McMeekin, Edsall and Weare, THIS JOURNAL, **56**, 2270 (1934).

(8) McMeekin, Cohn and Weare, *ibid.*, **58**, 2173 (1936).

aliquots of solvent were repeatedly saturated with the solute. It was demonstrated that solubility was independent of the amount of saturating body and the time of equilibration. The temperature for these experiments was 25.00 ± 0.05°.

Glycine and its peptides were prepared and purified by the methods that have been described previously.[5,7] Lysylglutamic acid was prepared by the method of Bergmann, Zervas and Greenstein.[9]

The hydantoic acids of glycine and of diglycine were the same preparations as were studied in the previous paper.[8] The heptyl esters of the hydantoic acids were prepared by the method described by Fischer for the preparation of the ethyl esters of hydantoic acids.[10]

Hydantoic Acid Heptyl Ester.—The heptyl ester hydrochloride of glycine was dissolved in water and an equivalent of potassium cyanate was added. On standing, the heptyl ester of hydantoic acid crystallized out. After recrystallizing from benzene, it melted at 98–99°.

Anal. Calcd. for $C_{10}H_{20}O_3N_2$: N, 12.96. Found: N, 12.80.

α-Aminocaproic Hydantoic Heptyl Ester (α-Uramidocaproic Acid Heptyl Ester).—The substance melted at 70–71°.

Anal. Calcd. for $C_{14}H_{28}O_3N_2$: N, 10.29. Found: N, 10.10.

Glycylglycine Hydantoic Acid Heptyl Ester (Uramido Glycylglycine Heptyl Ester).—The substance melted at 123–125°.

Anal. Calcd. for $C_{12}H_{23}O_4N_3$: N, 15.39. Found: N, 15.12.

II. Composition of Solvents

The three-component solvents employed in this investigation are most conveniently characterized by first considering the ethanol–water mixture and then the changes in the properties of the ethanol–water mixture brought about by the neutral salt.

The densities of ethanol–water mixtures are reported in the "International Critical Tables." Over the range in the neighborhood of 80% ethanol, they are given by the relation

$$\rho_0' = 0.85510 - 0.1672\ (N_2 - 0.5197)$$

where 0.5197 is the mole fraction of ethanol, 0.85510 the density of 80% ethanol and ρ_0' that of some other mixture of not very different mole fraction, N_2.

The addition of sodium chloride to an 80% ethanol–water mixture increases its density. The weight of ethanol in such mixtures is 628.05 g. per liter. In a subsequent paper in this series, we shall compare the results when the ratio of the weight of water to alcohol is retained constant with those here reported in which the weight of water is diminished as the concentration of salt increases. Solubility in solvents defined in either way may be computed from both sets of measurements, and yield the same result. In many of the experiments recorded in this paper, especially those with the peptides, it proved convenient to prepare the large volumes of solvent required by weighing the salt and ethanol into volumetric flasks, and then adding water to volume. All weights were corrected for air buoyancy.

TABLE I

Concn. of NaCl, C	Water g. per liter, g.	Density of solvent, ρ	$\frac{\rho - \rho_0'^{a}}{C}$	Apparent molal volume of NaCl,[a] Φ
0.00	227.04	0.85510		
.05	225.92	.85690	0.0408	20.7
.10	224.75	.85864	.0402	21.3
.15	223.52	.86033	.0398	21.8
.25	220.97	.86364	.0393	22.5

[a] The values of ρ_0' calculated from "International Critical Tables" for the weight per cent. of alcohol and water in the mixture were, respectively, 0.85486, 0.85462, 0.85436, 0.85382.

Since dielectric constant measurements cannot be made in the presence of electrolytes, it remains an open question whether solutions would be more nearly isodielectric where the volume occupied by the salt is considered to have the same properties as the water replaced, or whether the effect of the salt on the dielectric constant should be considered negligible.

III. Apparent Molal Volumes

When the apparent molal volumes of the sodium chloride in these solvents were at first calculated, we questioned the results since they were so much higher than those in water, defined by Gucker[11] by the equation

$$\Phi_{NaCl} = 16.28 + 2.22\sqrt{C}$$

For this reason a 25-cc. pycnometer was constructed which was employed in most of the above measurements. The remaining density determinations were carried out with 10-cc. pycnometers. The more accurate results confirm the order of those calculated from our routine density determinations, and indicate a higher apparent molal volume in 80% ethanol than in water, although the reverse might have been ex-

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(9) Bergmann, Zervas and Greenstein, *Ber.*, **65**, 1692 (1932).

(10) Fischer, *ibid.*, **35**, 1095 (1902).

(11) Gucker, *Chem. Rev.*, **13**, 111 (1933).

pected as a result of increased electrostriction of the solvent. These measurements as well as those to be reported subsequently may tentatively be defined by the equation

$$\Phi_{\mathrm{NaCl}} = 19.5 + 6\sqrt{C}$$

Solubilities in these solvents of all of the peptides are smaller than those of glycine, and the densities of the solutions deviate appreciably therefore from those of the solvent only in the case of glycine and the hydantoic acids. The densities of these saturated solutions are given in Table II and apparent molal volumes in 80% ethanol calculated.

TABLE II

APPARENT MOLAL VOLUMES IN 80% ETHANOL

Concn. of NaCl in solvent	Density of solvent	Density of solution	Soly., g. per liter	Apparent molal vol., Φ
		Glycine		
0.05	0.85690	0.85801	2.34	46.0
.15	.86033	.86175	3.00	46.0
.25	.86464	.86537	3.73	46.6
		Hydantoic acid		
.05	.85690	.86392	15.42	74.9
.15	.86035	.86823	16.44	71.5
.25	.86364	.87145	17.09	74.4
		α-Aminocaproic hydantoic acid		
.05	.85690	.86148	15.52	143.4
.15	.86035	.86500	16.24	144.2
.25	.86364	.86831	16.83	145.8

IV. Solubility Measurements

The solubilities in the various solvents are reported in Table III, as well as the ratio of solubility, expressed as mole fraction, in systems containing salt to that in the salt-free ethanol–water mixtures. The results would be essentially the same if the solubility ratios were calculated as volume concentrations, S/S', since the very large medium effects considered in the previous communications[7,5,8] are retained as nearly constant as possible in this study in which we are concerned only with the influence of salts upon amino acids, peptides and their derivatives.

The logarithm of the solubility ratio is plotted as ordinate in Fig. 1 and the concentration of sodium chloride as abscissa. The curves appear to belong to the same family and reveal effects of two kinds. In the first place the longer the peptide the greater the solvent action of the neutral salt. In the second place the larger the peptide the more this solvent action diminishes with increasing salt concentration. The solvent action of sodium chloride upon the hydantoic acids studied is far smaller than that upon these dipolar ions. It is greatest for the hydantoic acid of diglycine, which has two peptide linkages, and smallest for the hydantoic acid of α-aminocaproic acid which contains a larger number of nonpolar CH_2 groups.

TABLE III

INFLUENCE OF NaCl UPON THE SOLUBILITY OF GLYCINE, PEPTIDES AND HYDANTOIC ACIDS IN 80% ETHANOL AT 25°

Concn. of NaCl, C	$(D_0/D)C$	Solubility: Moles per liter, S	Solubility: Mole fraction, N	Logarithm of soly. ratio, $\log N/N'$	$(D/D_0) \log (N/N')$
		Hydantoic acid			
0.00		0.126	0.00485		
.05	0.110	.131	.00511	0.0227	0.0103
.15	.330	.139	.00538	.0451	.0205
.25	.550	.145	.00561	.0633	.0288
		Hydantoic acid of α-aminocaproic acid			
.00		.0867	.00337		
.05	.110	.0891	.00346	.0115	.0052
.15	.330	.0933	.00364	.0335	.0152
.25	.550	.0966	.00378	.0499	.0227
		Hydantoic acid of diglycine			
.00		.0220	.00084		
.05	.110	.0247	.00945	.0506	.0230
.15	.330	.0269	.00103	.0880	.0400
.25	.550	.0294	.00113	.128	.0584
		Glycine $\delta = 22.6$			
.00		.0267	.00102		
.05	.107	.0312	.00119	.0682	.0316
.10[a]	.213	.0361[a]	.00138	.123	.0576
.15	.321	.0400	.00153	.177	.0824
.25	.532	.0497	.00190	.272	.127
		Diglycine $\delta = 70.6$			
.00		.00374	.000143		
.05	.109	.00500	.000191	.126	.0579
.10	.217	.00650	.000248	.236	.109
.15	.325	.00780	.000298	.319	.147
.25	.539	.01060	.000406	.454	.211
		Triglycine $\delta = 113.3$			
.00		.000608	.0000231		
.05	.110	.000899	.0000343	.171	.0780
.10	.219	.00129	.0000492	.328	.150
.15	.328	.00180	.0000687	.473	.216
.25	.545	.00278	.000106	.661	.303
		Lysylglutamic acid $\delta = 345$			
.00		.0000778	.00000296		
.05	.110	.000137	.00000522	.247	.113
.10	.219	.000210	.00000801	.433	.197
.15	.329	.000288	.0000110	.570	.260
.25	.547	.000531	.0000203	.837	.383

[a] Calculated.

Hydantoic acid contains one less CH_2 group than diglycine and the hydantoic acid of diglycine one less CH_2 group than triglycine. Additional CH_2 groups might be expected to decrease slightly the solvent action of neutral salts. The far greater influence of sodium chloride upon the peptides may be ascribed, therefore, to their dipolar ion structure.

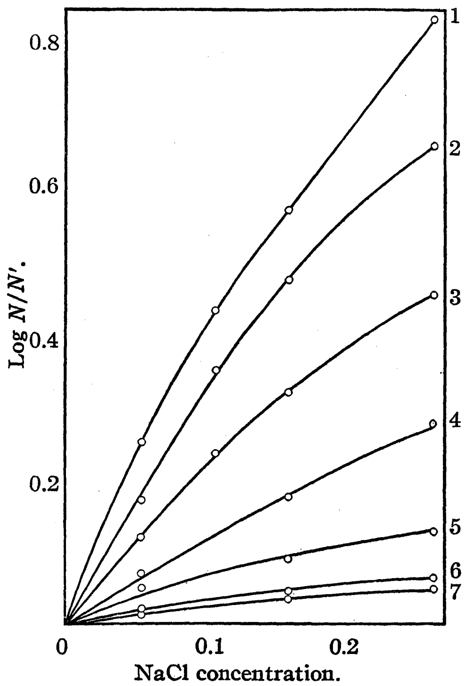

Fig. 1.—Solubility in 80% ethanol containing NaCl of 1, lysylglutamic acid; 2, triglycine; 3, diglycine; 4, glycine; 5, diglycyl hydantoic acid; 6, hydantoic acid; 7, α-aminocaproic hydantoic acid.

The logarithm of the activity coefficient varies as the reciprocal of the second power of the dielectric constant in Debye's theory. The dielectric constant of 80% ethanol is 35.72 and of water 78.54 at 25°.[12] The logarithm of the solubility ratio is therefore multiplied by D/D_0 in the last column of Table III. The concentration of salt, multiplied by D_0/D, given in the second column yields a quantity proportional to κ^2 in Debye's theory. The dielectric constants of the solvents are corrected in this calculation for the influence of glycine and the peptides. The values of δ tentatively adopted are those for water. The only amino acid sufficiently soluble to be studied thus far in 80% ethanol, α-aminobutyric acid, has a value of 24.0 in this solvent as compared with 23.5 in water.[13] Although the dielectric constant increments, δ, also given in Table III[14] are greater the longer the peptide, the solubility of all the peptides studied is so small in these solvents that the correction is appreciable only in the case of glycine. Correction for difference in volume between solvent and solution is negligible in 80% ethanol, though not in the lower ethanol–water mixtures subsequently to be reported. In order to facilitate comparison the hydantoic acids are also multiplied by the dielectric constant ratio of the solvent. Their own contributions to the dielectric constant of solutions is still in doubt.

Although it is certain that the longer peptides have the greater dipole moments, no satisfactory method is available for estimating the moments of dipolar ions. In a recent discussion of the problem two approximations were compared.[15] In the one, the molecules are considered extended in solution, as in the solid state, and the increment in the distance separating successive peptides taken as 3.5 Å. Structural considerations suggest that the dipole distance of glycine lies between 3 and 3.3 Å. The intermediate value of 3.17 Å. estimated by Kirkwood[2] from our solubility studies may be tentatively adopted. The ratio $[(D/D_0) \log N/N']/R'$, where R' represents the dipole distance estimated in this way, is calculated in Table IV. This ratio is plotted against $(D_0/D)C$ in Fig. 2. The agreement at low concentrations of salt indicates that *the logarithms of the activity coefficients of amino acids and peptides are, as a first approximation, proportional to their dipole moments.* At higher concentrations the influence of the larger molecules in diminishing their activity coefficients is reflected by the greater curvatures in Fig. 2.

Table IV

Influence of the Moments of Dipolar Ions on Their Activity Coefficient

Concn. of NaCl	Glycine	Diglycine	Triglycine	Lysylglutamic acid
		$[(D/D_0) \log N/N']/R$		
0.00	0.00	0.00	0.00	0.00
.05	.0100	.0105	.0111	.0092
.10	.0182	.0197	.0214	.0161
.15	.0260	.0267	.0308	.0212
.25	.0402	.0383	.0432	.0312
		$[(D/D_0) \log N/N']/R'$		
.00	.00	.00	.00	.00
.05	.0100	.0087	.0077	.0063
.10	.0182	.0163	.0147	.0111
.15	.0260	.0221	.0213	.0147
.25	.0402	.0316	.0298	.0216

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[12] Wyman, This Journal, **53**, 3292 (1931).

[13] Wyman, *ibid.*, **56**, 536 (1934).

[14] Wyman and McMeekin, *ibid.*, **55**, 908 (1933).

[15] Cohn, "Annual Review of Biochemistry," Vol. IV, Stanford University, California, 1935, p. 93.

The dipole distances of lysylglutamic acid have been estimated from structural considerations by Greenstein, Wyman and Cohn.[16] The longest dipole is 14.23 Å. The shorter dipole, which has the same configuration as glycylglycine, has a length in the direction of the chain of 3.5 Å. The logarithm of the solubility ratio divided by the vector sum, 17.73 Å., also is plotted in Fig. 2.

These estimates of R' may be considered maximal. Presumably there is at least some bending around the free bonds in these molecules, resulting in smaller dipole moments than those estimated from structural considerations. As a lower limit we may tentatively adopt the square root rule proposed by Werner Kuhn[17] for very long hydrocarbon chains. Assuming again the dipole distance of glycine to be 3.17 Å. and that of the peptides to increase as the square root of their dielectric constant increments, values of R have been calculated for these peptides.[15] The ratio $[(D/D_0) \log N/N']/R$ is also given in Table IV.

The results in Fig. 2 and Table IV suggest that in dilute solution, as a first approximation, the logarithms of the activity coefficients of dipolar ions increase as the concentration of the salt, and the dipole distance, R or R', of the peptides. The limiting slopes $[(D/D_0) \log N/N']/(D_0/D)C$ are 0.30 to 0.32 for glycine, 0.57 to 0.59 for diglycine, 0.75 to 0.80 for triglycine and 1.12 to 1.2 for lysylglutamic acid. These slopes will be proportional to the first term of any equation for the change in free energy of dipolar ions with change in ionic strength. They are approximately one-tenth the dipole distances estimated as proportional to the square root of dielectric constant increments and taken as 3.17 for glycine and 12.25 for lysylglutamic acid.

Kirkwood has developed an equation for this effect for spherical molecules and applied it to glycine.[2] The first term for this equation is $0.125\ R^2/a$, where a is the sum of the radii of ion and dipolar ion. The peptides that have now been studied cannot be considered spherical. Rather they are cylindrical or ellipsoidal, depending on whether they are stretched or somewhat constricted in solution as a result of rotation around free bonds. Kirkwood has now calculated the effect for an elliptical model[18] and finds that under these circumstances the first term in the free energy equation is proportional to R, as indicated by these experiments.

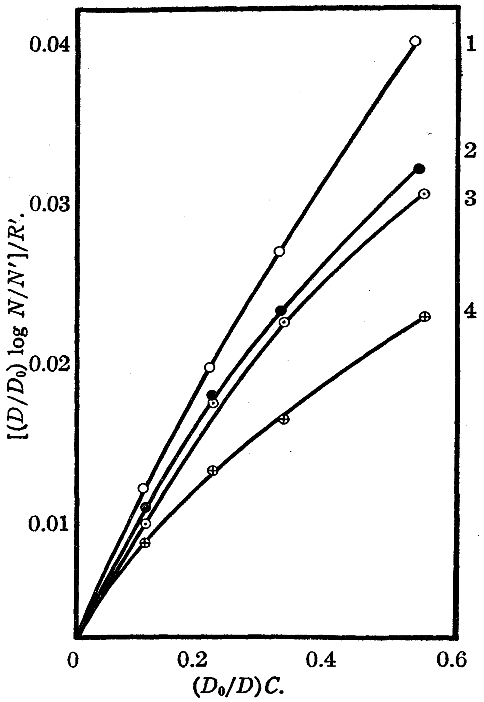

Fig. 2.—Solubility ratios of amino acids and peptides in 80% ethanol, containing sodium chloride, divided by their dipole distances as estimated by structural considerations: 1, glycine; 2, diglycine; 3, triglycine; 4, lysylglutamic acid.

The dipole moments of dipolar ions may be estimated by multiplying these distances by the charge on the electron. On this basis the moment of glycine is 15×10^{-18} e. s. u., and that of diglycine between 26 and 32×10^{-18} e. s. u. These moments are far greater than those due to the polar groups of these molecules. The moment of the ethyl ester of glycine, and those of other α-amino acids have been studied in benzene by Wyman and McMeekin[19] and estimated to be 2.1×10^{-18} e. s. u. That of the ethyl ester of diglycine they estimated to be 3.2×10^{-18} e. s. u.

Hydantoic acids terminate in NH_2 and COOH groups. That is to say, their structure is that classically ascribed to amino acids before the studies of Adams and of Bjerrum. With the exception of the movement of a proton, hydantoic acid differs from diglycine by possessing one less CH_2 group. The ester of hydantoic acid and of hydantoic α-aminocaproic acid might therefore

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[16] Greenstein, Wyman and Cohn, THIS JOURNAL, **57**, 637 (1935).

[17] Kuhn and Martin, *Ber.*, **67**, 1526 (1934).

[18] Personal communication. These results will be recalculated by Kirkwood in terms of this equation in another place.

[19] Wyman and McMeekin, THIS JOURNAL, **55**, 915 (1933).

be expected to have moments close to that of diglycine. Their heptyl esters have therefore been prepared and measured in benzene and found to have moments of 3.6 and 3.5 × 10^{-18} e. s. u., respectively.[20] The moments of these larger molecules in benzene fall off rapidly with concentration. They suggest a value of 1.4 or 1.5 × 10^{-18} e. s. u. for the peptide linkage, whereas the dipole moment of the amide group has been estimated to be 3.2[21] in the gaseous state and 3.6 to 3.8 in non-polar solvents.[22,23] The solvent action of neutral salts upon the hydantoic acids studied also suggests higher moments than are indicated by the measurements in benzene.

The moments of the esters of amino acids, peptides and of their hydantoic acids are, however, small in comparison with the superimposed effects due to dipolar ionization, and it is for the most part the latter which are responsible for the very large activity coefficients of peptides in salt solutions in regions of low dielectric constant. In regions of high dielectric constants, where the solubilities of amino acids and peptides are relatively high, the same contributions of Coulomb forces to activity coefficients presumably obtain, but are there supplemented by forces other than those due to the purely electrostatic interaction of ions and dipolar ions.

Summary

1. The interaction between ions and dipolar ions has been studied in regions of low dielectric constant in order to estimate the electrostatic forces involved.

2. Solutions of sodium chloride in 80% ethanol at 25° were employed as solvents, and glycine, diglycine, triglycine and the tetrapole lysylglutamic acid as solutes.

3. Hydantoic acids prepared from glycine and diglycine were studied in the same solvents in order to estimate what proportion of the effect was due to the dipolar ion structure of amino acids and peptides and what to the polar groups of these molecules.

4. The solvent action of neutral salts upon amino acids and peptides in dilute solution appears, as a first approximation, to be a function of their dipole moments.

BOSTON, MASS. RECEIVED AUGUST 8, 1936

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[20] We are indebted to Dr. Wyman for making these measurements.

[21] Zahn, *Trans. Faraday Soc.*, **30**, 804 (1934).

[22] Devoto, *Gazz. chim. ital.*, **63**, 491 (1933).

[23] Kumler and Porter, THIS JOURNAL, **56**, 2549 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HARVARD MEDICAL SCHOOL]

Studies in the Physical Chemistry of the Proteins. XIII. The Solvent Action of Sodium Chloride on Egg Albumin in 25% Ethanol at −5°

BY RONALD M. FERRY, EDWIN J. COHN AND ETHEL S. NEWMAN

Introduction.—The relation of the properties of amino acids and peptides to their chemical structure, and to the number and distribution of the electrostatic charges which they bear, has been considered in recent investigations.[1–3] Even when they have no net charge, these molecules, by virtue of their dissociated ammonium and carboxyl groups, have large electric moments and contribute markedly to the dielectric constants of their aqueous solutions, thereby diminishing electrostatic forces. The solubility of these dipolar ions diminishes, however, with diminution of the dielectric constant of the solvent, and under these conditions the properties of the solutions approach those of the pure solvents, and the effects of electrostatic forces are more readily observed.

It is of interest to extend these investigations to more complex dipolar and multipolar ions.[4] We have, accordingly, studied the solubility of isoelectric egg albumin in 25% ethanol–water mixtures at −5°. Egg albumin is a well-defined, easily purified, protein. Its molecules are roughly spherical with a radius of about 22 Å.[5] Early estimates revealed twenty-seven dissociable acids and the same number of dissociable basic groups,[6] whereas a recent study suggests a slightly higher number of dissociable groups.[7] Albumins are de-

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[1] Cohn, *Naturwissenschaften*, **20**, 663 (1932).

[2] Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

[3] Cohn, McMeekin, Greenstein and Weare, THIS JOURNAL, **58**, 2365 (1936).

[4] Such amino acids as cystine, such peptides as lysylglutamic acid, and all proteins are in reality multipoles. None the less they have an effective resultant dipole moment.

[5] Svedberg, *Kolloid Z.*, **51**, 10 (1930).

[6] Cohn, *Physiol. Rev.*, **5**, 349 (1925).

[7] Cannan, *Biochem. J.*, **30**, 227 (1936).

fined as proteins "soluble in pure water and coagulable by heat." Aqueous solutions containing 40% of egg albumin are readily prepared, but in the experiments reported in 25% ethanol the solubility of egg albumin was only 0.13 g. per liter, and neutral salts increased its solubility many fold, as they do with globulins in aqueous solution.

Although knowledge of their chemical structure is incomplete, it appears possible from this study and those subsequently to be reported that proteins may be completely characterized in terms of their size, shape, the length of their paraffin side chains, and the number and distribution of their polar, and especially of their charged, groups.

Methods and Materials.—The egg albumin used in these experiments was crystallized five times from ammonium sulfate solutions according to the procedure described by Sørensen.[8] Subsequently it was dialyzed in cellophane membranes against distilled water until the dialysate gave a negative sulfate test. In our early experiments it was then concentrated in negative pressure dialyzers[8] and dialysis continued until heat coagulated albumin yielded no sulfate or chloride to large volumes of hot water, even after its concentration from a volume of about 300 to 1-2 cc.

Our early experiments suggested that the saturating body contained traces of protein salt as well as uncombined isoelectric protein. Electrodialysis was therefore also used. The material obtained after dialysis in cellophane membranes was placed in a Pauli electrodialysis apparatus with a potential of 110 volts between electrodes. The contents of the cell were stirred at intervals, and dialysis continued against conductivity water, until the current passing through the cell became constant. A very small amount of insoluble material often appeared during this process and was filtered off. The soluble material was readily crystallizable.

After electrodialysis the egg albumin was concentrated in negative pressure dialyzers as before, where it reached a concentration of about 40% by weight. It was next dried according to the method of Adair[9] at about 2° in a vacuum over phosphorus pentoxide. The dry material was ground to a fine powder in a porcelain mortar and stored in vacuum desiccators over phosphorus pentoxide. It was readily soluble and crystallizable from ammonium sulfate solutions. Of the crystal forms figured by Sørensen and Hoyrup[10] the rhombic plates, rather than the needles, were most often observed.

The solvents employed were made up to contain 25% ethanol by volume at 20° and varying amounts of C. P. sodium chloride. The systems containing most salt therefore contained slightly less water. It may ultimately be desirable to calculate solubilities in systems having the same ethanol–water composition.[3]

The thermostat employed was maintained at $-5 \pm 0.05°$, and contained kerosene. Weighed amounts of dry powdered egg albumin were placed in double stoppered Pyrex centrifuge bottles. One of these is shown in Fig. 1. These were placed in a holder in the bath and completely filled with solvent which already had been cooled to $-5°$. The outer caps (B) were well greased, but not the inner ground glass stoppers (A). The bottles were slowly rotated in a horizontal position until equilibrium was attained.

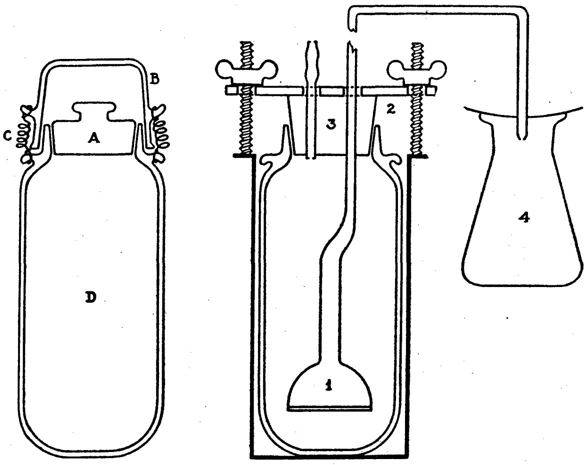

Fig. 1.—A, ground glass stopper; B, outer ground cap; C, springs; D, Pyrex bottle; 1, sintered filter; 2, yoke to hold stopper; 3, rubber stopper; 4, weighing bottle.

Although ninety hours of rotation apparently sufficed for saturation, rotation was continued for five to seven days. At the end of this time, rotation was stopped, the bottles were placed in a vertical position, and undissolved egg albumin allowed to settle. Sintered Jena glass filters (porosity G 4)—previously cooled to $-5°$—were then introduced into the equilibrium bottles without removing the latter from the bath (see Fig. 1). The supernatant fluid was filtered under 15 lb. (1 atm.) pressure of nitrogen gas into glass-stoppered weighing bottles, and the content of protein in the weighed sample determined.

After removing the supernatant fluid as completely as possible from the equilibrium bottles, they were again filled with solvent at $-5°$ and again equilibrated. Equilibrium was always approached by the saturation of solvents, the operation often being repeated as many as twelve times with a single sample of egg albumin. Even at the end of months of rotation in the thermostat by far the greater part of the undissolved material remained soluble and crystallizable. The small amount of denatured protein had no marked influence on these experiments. The solubility of egg albumin, denatured in 25% ethanol at room temperature, did not exceed 0.004 g. for 1000 g. solution under the conditions of our experiments, a quantity small in comparison with the solubilities here reported. Moreover, under these conditions, no solvent action of salt on the denatured egg albumin was detected.

Two different analytic procedures were employed. In case the solvent contained no salt, egg albumin was estimated gravimetrically. Weighed aliquots were dried to constant weight in an oven at 95°.

In the case of solutions containing salt the alcohol was first evaporated. A few cubic centimeters of acetate buffer of *p*H 4.85 and about 0.5 g. of potassium sulfate were

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[8] Sørensen, *Compt. rend. trav. lab. Carlsberg*, **12**, 1 (1917).

[9] Adair, *J. Physiol.*, **72**, 2P (1931).

[10] Sørensen and Hoyrup, *Compt. rend. trav. lab. Carlsberg*, **12**, 164 (1917).

then added in order to ensure complete coagulation of the protein over the steam-bath. The coagulated protein was transferred quantitatively to weighed sintered glass crucibles, of porosity G4, and washed until the filtrate gave a negative sulfate test. The crucibles and contents were dried to constant weight at 95°. The results obtained accorded satisfactorily with those based on Kjeldahl nitrogen analysis. Aliquots containing from 0.02 to 0.6 g. of dry protein were analyzed. Duplicate analyses accord within 0.3 to 0.4 mg. The errors due to change in weight of crucibles and losses in transfer did not exceed 0.5 mg., or at most 3%. Other factors not so well defined, such as variation in *p*H, presence of traces of protein salt, etc., gave rise to larger discrepancies and will be discussed subsequently. Change in the apparent dissociation constants of buffer acids in alcohol rendered their use undesirable as solvents in these investigations. The *p*H of each solution was, however, colorimetrically estimated at room temperature against standard buffers—0.05 *N* in acetate—in 25% ethanol.[11] The apparent isoelectric point of egg albumin in 25% ethanol is presumably increased by something less than one *p*H unit, the estimated values being more acid the larger the concentration of salt and protein in the systems.

Solubility Measurements.—The solubility of the first preparation studied diminished with each successive equilibration with solvent. An experiment of this kind is reported in Table I. Often more than a month would elapse until solubility became constant in successive solvents. Since the saturating body always contained egg albumin, which was both soluble and crystallizable, the slow diminution in solubility was believed to be due to the washing out of a more soluble impurity, and not to denaturation of the protein. Accordingly electrodialysis was resorted to in order to reduce the conductivity of the preparations as far as possible, even at the risk of denaturating some of the egg albumin. The electrodialyzed material generally exhibited constant solubility, as is indicated by the experiment reported in Table I. Thus prepared egg albumin had from the beginning the same solubility as was ultimately reached by the earlier preparation.

TABLE I

COMPARISON OF DIALYZED AND ELECTRODIALYZED EGG ALBUMIN IN 25% ETHANOL CONTAINING 0.005 *N* NaCl AT −5°

Hours of equilibration	Estimated *p*H	Soly., g./1000 g. soln.
Preparation CVB		
89	5.63	0.358
93	5.69	.269
112	5.75	.234
212	5.80	.209
259	5.87	.228
162	5.67	.268
498	5.70	.253
185	5.74	.166
233	5.74	.175
282	5.72	.165
Preparation CVI, electrodialyzed		
138	5.68	0.157
210	5.90	.173
191	5.86	.157
209	5.86	.175
188	5.84	.151
254		.174

In Table II are reported solubility measurements upon four egg albumin preparations, the last of which, on which most measurements were

TABLE II

THE INFLUENCE OF NaCl ON THE SOLUBILITY OF EGG ALBUMIN IN 25% ETHANOL AT −5°

Concn. of NaCl moles/liter	Egg Albumin Preparation CVB	CVA	CVB_2	CVI^a	Average
	Solubility: g. per 1000 g. of solvent				
0.0	0.119		0.109	0.151	
	.129		.147	.123	
	.118		.112	.114	
			.148	.128	
				.138	
				.149	
				.109	
				(.063)	
				.110	0.13
.00505	.166		.174	.157	
	.175		.146	.173	
	.165		(.210)	.157	
			.150	.175	
			.151	.151	
				.174	
				(.125)	.16
.0101	.224		.200	.203	
	.222		.153	.199	
	.222		(.128)	(.324)	
			.194	.225	
			.221	.176	.20
.0202				.292	
				.293	
				.244	
				.223	
				.243	
				.233	.26
.0505		0.527	.569	(.649)	
		.504	.523	.519	
			.497	(.684)	
				.509	
				(.632)	
				.556	
				.535	
				.461	.52
.101				1.32	
				1.04	
				1.20	
				1.28	1.2
.201				4.11	
				4.10	4.1
.349				18.5	
				18.2	18.4
.489				38.9	
				43.8	41.4

[a] Electrodialyzed.

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[11] Michaelis and Mizutani, *Z. physik. Chem.*, **116**, 135 (1925).

made, was electrodialyzed. In the case of the earlier series in which non-electrodialyzed material was used we have tabulated only those values which indicated that a reasonably constant solubility had been attained. In later experiments with electrodialyzed material at low salt concentrations a few points, which were clearly discordant, are given in parentheses and not included in the averages. These were probably due to temporary failure in the thermoregulator, a source of trouble only recently overcome by removing the relay from the cold room. At the highest salt concentrations only the first value for solubility is given, since at such high solubilities it was difficult to provide sufficient saturating body for repeated equilibration.

The deviations are far greater than in most studies from the laboratory, because of the difficulty of achieving equilibrium and of controlling small deviations in *p*H and in alcohol concentration. None the less, because of the very large solvent action at low sodium chloride concentrations, these determinations yield a very satisfactory estimate of the influence of salt on the solubility of egg albumin. Average values of solubility, expressed as grams per 1000 g. of solution, are given in the last column of Table II. Taking the density of the solvents as given by the approximate relation

$$\rho = 0.9761 + 0.043\ C$$

and the apparent specific volume of egg albumin as 0.75[12] and its molecular weight as 34,000, its solubility has been computed as moles per liter at −5° and mole fraction in Table III.

TABLE III

THE INFLUENCE OF NaCl ON THE SOLUBILITY OF EGG ALBUMIN IN 25% ETHANOL AT −5°

Concn. of NaCl C	$(D_0/D)C$ −5°	*p*H at 20°C.	Soly. of egg albumin Moles $\times 10^5$ per liter	Soly. of egg albumin Mole fraction $N \times 10^7$	(D/D_0) log N/N'
0.0	0.00	5.9	0.374	0.788	0.00
.00505	.0058	5.8	.460	.969	.08
.0101	.0116	5.7	.573	1.21	.16
.0202	.0231	...	.745	1.57	.26
.0505	.0578	5.6	1.49	3.15	.53
.101	.116	5.5	3.44	7.26	.84
.201	.230	5.4	11.9	25.3	1.31
.349	.399	5.3	53.7	115.0	1.89
.489	.559	5.3	122.0	266.0	2.21

Results.—The influence of neutral salts on each other increases with the square root of the ionic strength of the solvent, and with the valence type of the salt.[13,14] A tenth molal solution of potassium nitrate increases the solubility of thallous chloride approximately 20%,[15] of barium iodate 80%.[16] The solubility of luteo-hexacyanocobaltiate, a tri-trivalent electrolyte studied by Brönsted and Peterson,[17] is increased over ninefold by 0.1 mole of potassium chloride. Only an electrolyte of such high valence type approximates the behavior of proteins[18] at finite concentration.

The influence of neutral salts upon dipolar ions is not identical with that upon ions. Dipolar ions in the isoelectric condition have no net charge. In an extension of Debye's theory to the interaction between ions and dipolar ions, Scatchard and Kirkwood[19] have shown that the first term in the equation for the logarithm of the solubility ratio is proportional to the ionic strength, and not to its square root. The results upon egg albumin reported here are consistent with this prediction.

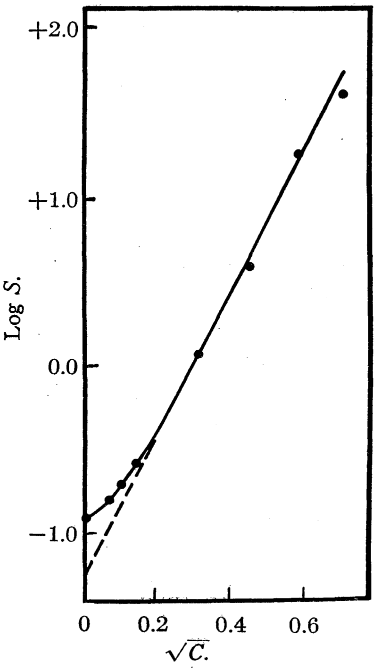

Fig. 2.—The influence of NaCl on the solubility of egg albumin in 25% ethanol at −5°.

In Fig. 2 the logarithm of the solubility is plotted against the square root of the concentration of

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[12] Svedberg and Nichols, THIS JOURNAL, **48**, 3081 (1926).

[13] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[14] Debye, *ibid.*, **25**, 97 (1924).

[15] Bray and Winninghoff, THIS JOURNAL, **33**, 1663 (1911).

[16] Harkins and Winninghoff, *ibid.*, **33**, 1827 (1911).

[17] Brönsted and Peterson, *ibid.*, **43**, 2265 (1921).

[18] Cohn and Prentiss, *J. Gen. Physiol.*, **8**, 619 (1927).

[19] Scatchard and Kirkwood, *Physik. Z.*, **33**, 297 (1932).

sodium chloride. The logarithm of solubility does not appear to be proportional to $\sqrt{C}$ when the latter is less than 0.1. In high concentrations of salt, where Debye's law for ions would not be expected to hold, however, the points so plotted apparently fall on a straight line as noted in an earlier study.[18]

Cystine, a tetrapole, is the least soluble of the naturally occurring amino acids. Its solubility also demonstrates that the logarithm of the activity coefficient is not linear in the square root, but is a function of the concentration (see Fig. 2, ref. 20).[20] Although the solubility of cystine is only increased 10% by 0.1 mole of sodium chloride, the same concentration of salt increases the solubility of egg albumin almost ten-fold.

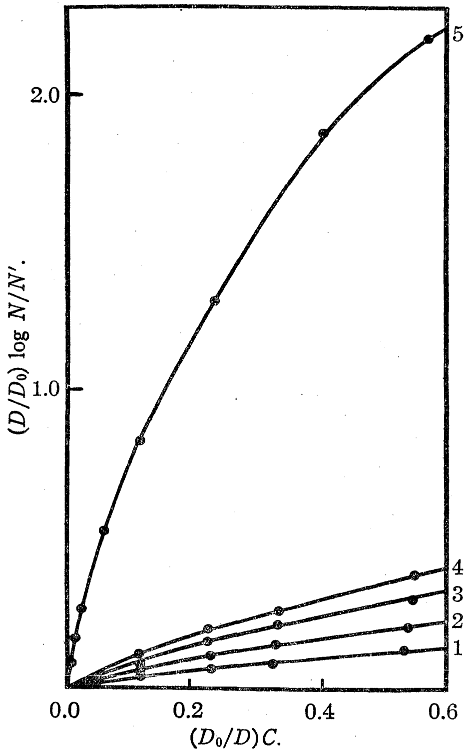

Fig. 3.—Solvent action of NaCl on: (1) glycine; (2) diglycine; (3) triglycine; (4) lysylglutamic acid and (5) egg albumin.

Many amino acids and peptides are so soluble in water, and increase the dielectric constant of the solutions to such an extent that electrostatic forces due to the interaction between ions and dipolar ions cannot be studied in this medium. They have accordingly been studied in alcohol–water mixtures in which their solubility was reduced and electrostatic forces due to this interaction increased. Under these circumstances it has been demonstrated for glycine that as a first approximation the logarithms of the solubility ratio increase as the second power of the reciprocal of the dielectric constant, as demanded if the effect is due primarily to Coulomb forces. Measurements made in from 60 to 95% ethanol, and plotted with (D/D_0) log N/N_0 as ordinate, and $(D_0/D)\Gamma_2$—a quantity proportional to κ^2 in Debye's equation—as abscissa, fall on the same curve.[1,2]

The measurements on egg albumin in 25% ethanol are plotted in this manner in Fig. 3. This method of plotting has the advantage that it presumably yields that part of the activity coefficient due to Coulomb forces that also obtain in aqueous solution. The dielectric constant of 25% ethanol at −5°, obtained by interpolation from Wyman's data,[21] is taken as 78.6. That of water at −5° was estimated by Wyman by extrapolation to be 90.0.[21] Accordingly the value 0.874 for D/D_0 has been employed tentatively in our calculations without any correction for the influence of salt or of egg albumin on the dielectric constant. It is conceivable that measurements upon egg albumin at still lower dielectric constant would reveal even greater changes in solubility with change in ionic strength, and that the maximum slope has not been attained even in 25% ethanol at −5°. The solubility of egg albumin falls off so rapidly with further decrease in dielectric constant, however, that the accuracy of the measurements would be still further reduced, and it seemed preferable therefore to study another protein, hemoglobin, in a series of alcohol–water mixtures. This study will be reported subsequently.

The curve for egg albumin is compared in Fig. 3 with that of the peptides of glycine and with the tetrapole lysylglutamic acid that has been studied in 80% ethanol at 25°.[3] The solvent action of neutral salts on these molecules is in the order of their influence on the dielectric constant of solutions, and presumably of their electric moments. The shapes of the curves suggest that the general phenomenon is the same for amino acids, peptides and proteins, and the far greater influence of salts upon the latter suggests that they have far greater dipolar and multipolar moments. Their size is also far greater and this presumably accounts for the very rapid falling off of protein

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(20) Cohn, "Annual Review of Biochemistry," Vol. IV, Stanford University, California, 1935, p. 93.

(21) Wyman, THIS JOURNAL, 53, 3292 (1931).

solubility curves from their limiting slopes with increase in salt concentration.

This phenomenon is more readily analyzed if we plot some function of change in solubility with change in concentration against some function of concentration. This has been done in Fig. 4. The forces which lead to the salting out of proteins are clearly manifest even in dilute solutions of protein and salt at low temperature. Whereas the measurements upon glycine fall on an essentially straight line, when plotted as in Fig. 4, and those upon lysylglutamic acid show some curvature; the curvature in the case of egg albumin is far greater.

There is no uncertainty in determining the limiting slope of glycine to be 0.30 to 0.32 by this method, or of lysylglutamic acid to be 1.1 to 1.2. The estimate for egg albumin, however, is not independent of the method of extrapolation. The average values of (D/D_0) log N/N' in Table III appear to be linear in $(D_0/D)C$ for values of the latter less than 0.02, and to yield 14 for the limiting slope.

The study of peptides[3] led to the conclusion "that, as a first approximation, the logarithms of the activity coefficients of dipolar ions increase as the concentration of the salt, and the dipole distance." Assuming the same rule to hold for egg albumin, and the dipole distance, R, of glycine[2] to be 3.17, would yield 140 Å. The peptides studied were, however, roughly rod shaped, whereas glycine and egg albumin are roughly spherical. Kirkwood has developed a theoretical equation for the activity coefficients of dipolar ions considered as spheres,[2] the first term of which gives the limiting slope for a single dipole as proportional to R^2/a. For egg albumin a, the sum of the radii of the protein and salt, may be taken as 23 Å. On this basis R would be 52 Å. or only slightly greater than the diameter of the molecule. Although the large number of charges involved precludes a unique solution of the distribution of the charges on the surface of the vast protein molecule, a preliminary study[22] suggests that egg albumin should not be treated as a single dipole, but that the quadropole and octopole moments dominate the interaction with salts.

The influence of dipolar ions on the dielectric constant of solutions may also be considered, as a first approximation, a function of the electric moment, presumably of its second power.[23] In the case of peptides, plotting the limiting slope against the square root of the dielectric constant increment, δ, yields a roughly linear relationship.[3] Errera[24] reports dielectric constants from which values of δ can be calculated of 10,000 and Shutt[25] of 4000. Assuming δ proportional to 2.3 $R^{2,20}$ yields values of R of 42 Å. and 66 Å. on the basis, respectively, of Shutt's and Errera's dielectric constant measurements. This result is in as good agreement as can be expected with the value 52 Å. on the basis of our solubility studies and the first term of Kirkwood's equation. There is thus little doubt that it is the distribution of charges and the effective electrical moments of the molecule that determine both its influence on the dielectric constant of solutions and on the interaction with ions and other dipolar ions.

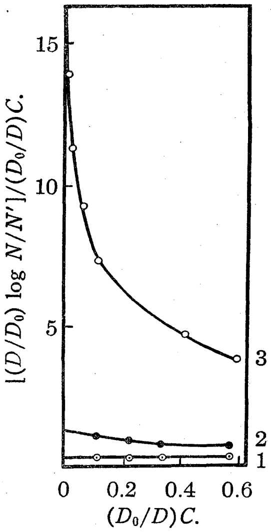

Fig. 4.—Diminution of solvent action of NaCl with increase in concentration upon: (1) glycine; (2) lysylglutamic acid; (3) egg albumin.

Summary

1. The solubility of egg albumin has been studied in 25% ethanol at −5°. Under these conditions denaturation was slight and the solubility of the albumin so low, 3.7×10^{-6} mole per liter, that its contribution to the dielectric constant of the solution was neglected.

2. Neutral salts increased the solubility of egg albumin under these conditions much as they do the solubility of globulins in water.

3. The solvent action of the neutral salt has been considered a measure of the electrostatic forces between the ions and the protein and compared with the comparable forces between ions, amino acids and peptides.

BOSTON, MASS. RECEIVED AUGUST 8, 1936

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(22) Kirkwood, personal communication. The analysis of these results in terms of this theory will be presented elsewhere.

(23) Wyman, THIS JOURNAL, **56**, 536 (1934).

(24) Errera, *J. Chim. Phys.*, **29**, 577 (1932).

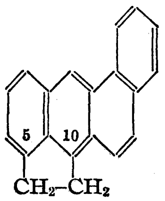
(25) Shutt, *Trans. Faraday Soc.*, **30**, 893 (1934).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Synthesis of 1,2-Benzanthracene Derivatives Related to Cholanthrene

BY LOUIS F. FIESER AND MELVIN S. NEWMAN[1]

Of the various hydrocarbons known to possess cancer-producing properties, the most potent are methylcholanthrene and cholanthrene (I).[2] In the regularity and rapidity with which they produce tumors in experimental mice these substances so far outshadow all of the many other derivatives of 1,2-benzanthracene thus far investigated (largely by Cook and co-workers[2]) that it is a matter of considerable interest to attempt to define the features of structure responsible for their striking activity. Clearly the methyl group present in methylcholanthrene in the 6-position of the 1,2-benzanthracene nucleus is relatively unimportant, for cholanthrene is as active, or very nearly as active, as methylcholanthrene.[2] Of other carcinogenic derivatives of the itself inactive 1,2-benzanthracene the 5-methyl compound is weakly active, the 5,6-dimethyl and 5,6-trimethylene derivatives are slightly more so, and the 8,9-dimethylene compound shows some activity,[3] but none of these hydrocarbons is comparable with cholanthrene (I) in potency. It should be possible to determine whether the special activity of cholanthrene is associated with the presence of the five-membered ring including carbon atoms 5 and 10, or merely with the presence of alkyl substituents at these positions, by investigating the biological actions of 5,10-dimethyl-1,2-benzanthracene, II. With this end in view we undertook the synthesis of the latter hydrocarbon and of the likewise interesting 10-methyl-1,2-benzanthracene.



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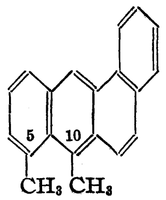
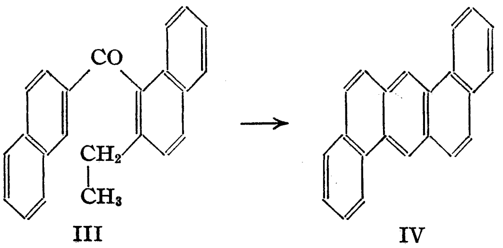


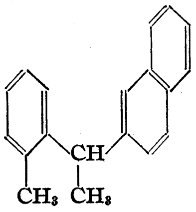
II

Considering the success of the modified Elbs reaction developed by one of us with Seligman[2b] for the preparation of cholanthrenes, it seemed possible that 10-methyl anthracenes or benzanthracenes might be obtainable by the pyrolysis of suitable *o*-ethyl diaryl ketones, for example 2-ethyl-3-methylphenyl-α-naphthyl ketone. As a preliminary trial of the reaction in a simple case, the ketone (III) from α-naphthoyl chloride and β-ethylnaphthalene was submitted to pyrolysis, but the resulting hydrocarbon, obtained in a yield quite good for such reactions, proved to be identical with 1,2,5,6-dibenzanthracene (IV), indicating the loss of a methyl group from the 10-position. Similarly the ketone from 2,5-dimethylbenzoyl chloride and β-ethylnaphthalene gave in small amounts an unidentified hydrocarbon having the composition of a monomethyl rather than a trimethyl 1,2-benzanthracene. This type of reaction was therefore abandoned, although from more recent work in this Laboratory (A. M. Seligman) it appears that in some cases the condensation proceeds without degradation of an *n*-alkyl group.



III IV

As another possible approach we investigated a method used by Cook and Haslewood[4] for the synthesis of cholanthrene. α-(*o*-Tolyl)-α-(2-naphthyl)-ethane, V, was prepared by the addition of *o*-tolylmagnesium bromide to methyl β-naphthyl ketone, dehydration of the resulting carbinol, and hydrogenation of the olefin. Attempts were made to introduce a carboxyl group in the 1-position of the naphthalene nucleus by the bromination of the hydrocarbon and carbona-



V

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(1) Lilly Research Fellow.

(2) For reviews and references, see (a) Cook, *Ber.*, **69A**, 38 (1936); (b) Fieser, "The Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, 1936, pp. 81–110.

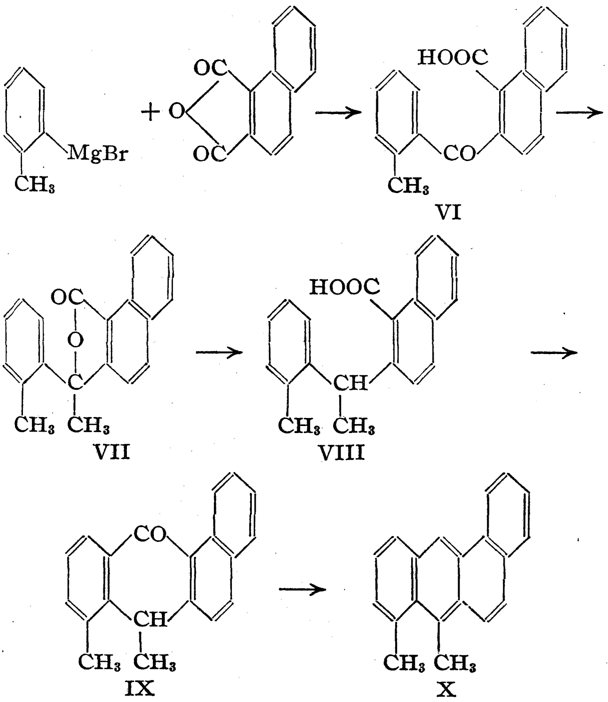
(3) Shear, *J. Biol. Chem.*, **114**, lxxxix (1936).

(4) Cook and Haslewood, *J. Chem. Soc.*, 770 (1935).

tion of the Grignard reagent, and by the hypochlorite oxidation of the (crude) acetyl derivative obtained by the Friedel and Crafts reaction, but a crystalline acid was not isolated. On submitting the acid mixture obtained by the first procedure to cyclization and reduction, there was isolated in very small amount through the picrate a hydrocarbon having the expected composition of a dimethylbenzanthracene, but the substance did not have the properties of a pure individual.

Following these unpromising results a successful synthesis was developed starting with 1,2-naphthalic anhydride (naphthalene-1,2-dicarboxylic anhydride), a compound easily prepared synthetically in any desired quantity.[5] On reaction with one mole of *o*-tolylmagnesium bromide this gave a mixture from which the desired keto acid VI was easily isolated in 40% yield. Reaction at the more hindered carbonyl group took place to a less extent, only about 3% of the isomeric 2-*o*-toluyl-1-naphthoic acid being isolated. The structures of the acids were established by decarboxylation to the known *o*-tolyl α- and β-naphthyl ketones.[6] 1,2-Naphthalic anhydride thus behaves in the Grignard reaction[7] much as it does in the Friedel and Crafts condensation with hydrocarbons.[8] On condensing the anhydride with cumene, Cook[9] isolated the keto acids resulting from condensation at the β- and α-carbonyl groups, respectively, in 23 and 10% yields.

The addition of the methyl Grignard reagent to the ketonic group of 2-*o*-toluyl-1-naphthoic acid (VI) was at first accomplished by using the ester, but about 20% of the keto acid usually was recovered unchanged and no more than 50% of the material utilized was converted into the desired reaction product, 2-(α-hydroxy-*o*,α-dimethylbenzyl)-1-naphthoic acid lactone (VII). The yield was considerably improved by treating the keto acid (VI) itself with two moles of methylmagnesium iodide, and when methylmagnesium bromide was employed no appreciable amount of acid was recovered and the yield of good product rose to 86%. The lactone VII exists in two apparently polymorphic modifications. Attempts to prepare 2-(*o*,α-dimethylbenzyl)-1-naphthoic acid (VIII) by the reduction of the lactone with zinc dust and alkali were unpromising, but as Martin[10] has shown recently that γ-phenylbutyrolactone can be reduced to γ-phenylbutyric acid with amalgamated zinc and hydrochloric acid, this method was tried. The desired acid was obtained in this way in excellent yield (76%) and purity and the reaction proceeded particularly smoothly in acetic acid solution. The acid VIII was cyclized with concentrated sulfuric acid at room temperature to an anthrone (IX) which was not isolated in a pure condition but reduced with zinc dust and alkali to the desired 5,10-dimethyl-1,2-benzanthracene (X). The hydrocarbon was obtained in good yield and was easily purified.



10-Methyl-1,2-benzanthracene was prepared by using phenylmagnesium bromide in the first step of the synthesis and proceeding as above. The free 2-benzoyl-1-naphthoic acid gave a good yield in the Grignard reaction and the normal ester, prepared with the use of diazomethane, gave a moderately satisfactory result. It was observed that the substance obtained by esterifying the acid with alcohol–hydrogen chloride and described in the literature[8] as methyl 2-benzoyl-1-naphthoate does not react with methylmagnesium iodide, except possibly to undergo hydrolysis.

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[5] Fieser and Hershberg, THIS JOURNAL, **57**, 1851 (1935).

[6] Fieser and Martin, *ibid.*, **58**, 1443 (1936).

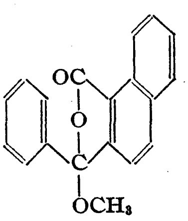
[7] The preparation of *o*-aroyl carboxylic acids by the addition of Grignard reagents to symmetrical aromatic anhydrides has been investigated recently by Weizmann, E. Bergmann and F. Bergmann, *J. Chem. Soc.*, 1367 (1935); see also Weizmann and E. Bergmann, *ibid.*, 567 (1936).

[8] Waldmann, *J. prakt. Chem.*, **127**, 195 (1930); **131**, 71 (1931).

[9] Cook, *J. Chem. Soc.*, 456 (1932).

[10] Martin, THIS JOURNAL, **58**, 1438 (1936).

The substance is thus regarded as the lactol ether XI. The formation of such a compound in the Fischer esterification reaction is in striking contrast to the behavior of *o*-benzoylbenzoic acid.[11]



XI

In the hope of introducing a long aliphatic chain in the 10-position, the keto acid VI or its methyl ester was treated with octadecylmagnesium bromide, but the only product isolated proved to be the lactone of the hydroxy acid resulting from the reduction of the carbonyl group of VI to a carbinol group by the reagent. This was reduced further with zinc and acid to 2-*o*-tolylmethyl-1-naphthoic acid, and the identical substance was obtained by the action of the same reagents on the keto acid VI. This acid was put through the remaining steps of the synthesis and afforded the known 5-methyl-1,2-benzanthracene.[12] A reducing action also was noticed in a preliminary study of the reaction of ethylmagnesium bromide with 2-*o*-toluyl-1-naphthoic acid (VI), but in this case some addition also occurred.

While the reducing action of at least certain alkyl Grignard reagents imposes some limits on the synthetic method, it may be possible to avoid this difficulty by reversing the order of the two Grignard reactions. We hope to investigate this possibility and to explore other applications of the synthesis.

The new hydrocarbons are being tested for carcinogenic activity by Dr. M. J. Shear, and although the experiments have been in progress only for a comparatively short time the preliminary results are of considerable interest. 5,10-Dimethyl-1,2-benzanthracene was injected subcutaneously into mice, using approximately 10 mg. of the crystalline material per animal. Severe ulceration at the cite of injection was noted in all of the mice after the first month. After three and one-half months tumors had been produced in seven of fifteen mice, the first two tumors making their appearance at the end of two and one-half months. From these results it appears that the new hydrocarbon is at least roughly comparable in carcinogenic activity with the most potent of the compounds previously investigated, namely, methylcholanthrene, cholanthrene and 3,-4-benzpyrene,[13] and that it is considerably more powerful in its action than any of the known monomethyl or dimethyl derivatives of 1,2-benzanthracene.[2] 5-Methyl-1,2-benzanthracene, injected subcutaneously into twenty mice in 5-mg. dosages, produced no noticeable effect in thirty-seven days, while 10-methyl-1,2-benzanthracene in the same dosage produced either ulceration, thickening of the tissue, or both, in thirteen of twenty mice during the same period.

From the present indications, it appears that the five-membered ring characteristic of the cholanthrene system is of importance in contributing to the carcinogenic potency of hydrocarbons of this type only in that it includes carbon substituents at the 5- and 10-positions. The presence of the intact ring is by no means essential, for simple alkyl groups at these positions produce nearly the same effect. Substitution at the meso position 10 seems to be particularly important, and it is interesting to note that 3,4-benzpyrene may be regarded as a 1,2-benzanthracene derivative with a carbon substituent at one of the meso positions (9). Heretofore the hypothesis that cancer-producing hydrocarbons may be formed in the organism by the abnormal metabolism of cholesterol or of bile acids has found support in the demonstration that two different bile acids can be transformed by chemical means into methylcholanthrene,[2] and in the striking circumstance that this outstandingly potent hydrocarbon carries as a mark of its possible origin the cyclopenteno ring characteristic of the sterols. While the possibility of the biological formation of methylcholanthrene remains undisputed, if, to be sure, quite unestablished, the observation that comparable activity is exhibited by a simpler hydrocarbon lacking both the C_{20}-methyl group and the cyclopenteno ring characteristic of the sterols, and of a type not likely to arise in the process of metabolism, weakens somewhat the circumstantial evidence favoring acceptance of the hypothesis.

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(11) H. Meyer, *Monatsh.*, **25**, 475 (1904); **28**, 1231 (1907).

(12) Cook, *J. Chem. Soc.*, 1592 (1933).

(13) In previous publications from this Laboratory the carcinogenic hydrocarbon isolated from coal tar by J. W. Cook, C. L. Hewett and I. Hieger has been referred to as "1,2-benzpyrene," in accordance with the system of numbering originally employed by the discoverers of the substance. Following a plea for unanimity from the editor of "Beilstein," and in agreement with Dr. J. W. Cook, we will employ hereafter the numbering system for pyrene favored in Germany and used in *Chemical Abstracts*, according to which the carcinogenic hydrocarbon becomes 3,4-benzpyrene.

Experimental Part[14]

Pyrolysis of 1-(2-Naphthoyl)-2-ethylnaphthalene (III).–β-Ethylnaphthalene, b. p. 122–125° (14 mm.), picrate, yellow needles, m. p. 76.5–77° from alcohol, was prepared in 52% yield by the Clemmensen–Martin procedure[10] and condensed with β-naphthoyl chloride with aluminum chloride in carbon bisulfide solution. The crude ketone, b. p. 235–240° (2–2.5 mm.), resulted in 91% yield but did not crystallize, and on pyrolysis at 425–430° for one and one-half hours 6 g. of the material gave 1.3 g. (23%) of a hydrocarbon melting at 261–262° and identified by analysis and mixed melting point determinations as 1,2,5,6-dibenzanthracene.

Pyrolysis of 1-(2,5-Dimethylbenzoyl)-2-ethylnaphthalene.—2,5-Dimethylacetophenone was prepared more satisfactorily than previously reported[15] by adding 45 g. of aluminum chloride during one and one-half hours to a stirred solution at 0° of 31 g. of *p*-xylene and 25 g. of acetyl chloride in 450 cc. of carbon bisulfide. After three hours at 0° with stirring, twelve hours at 0–5°, and one to two hours at 25°, the light yellow complex was collected with suction, washed with carbon bisulfide, and decomposed with dilute hydrochloric acid. A small additional amount of the ketone was recovered from the filtrate and the combined product distilled at 106.2° (14 mm.), yield 40.8 g. (95%). The ketone was converted to 2,5-dimethylbenzoic acid, m. p. 132–133°, with potassium hypochlorite from the commercial calcium salt in 93% yield by the general procedure reported.[16] The acid chloride (b. p. 101.5° at 11–12 mm.), prepared with thionyl chloride, was condensed with β-ethylnaphthalene as above and the ketone, b. p. 188–192° (2 mm.), yield 84%, was pyrolyzed at 450–455° for fifteen minutes. From 5.9 g. of the ketone 1.3 g. of hydrocarbon, m. p. 124–126°, was obtained after two crystallizations from alcohol. This yielded a picrate which after two crystallizations from benzene–ligroin formed red needles, m. p. 155–156°, and had the composition of a methylbenzanthracene picrate.

Anal. Calcd. for $C_{19}H_{14}\cdot C_6H_3O_7N_3$: C, 63.68; H, 3.64. Found: C, 63.93, 63.86; H, 3.80, 3.60.

Attempted Synthesis from α-(*o*-Tolyl)-α-(2-naphthyl)-ethane, V.—The Grignard reagent from 94 g. of *o*-bromotoluene, 13.4 g. of magnesium, and 500 cc. of ether was added to 85 g. of methyl β-naphthyl ketone in 225 cc. of benzene during one and one-half hours and after distilling the ether the benzene solution was refluxed for one hour. After hydrolysis with dilute hydrochloric acid the carbinol was heated at 200–250° to effect dehydration and the resulting **α-(*o*-tolyl)-α-(2-naphthyl)-ethene** was distilled at 2 mm., giving 83 g. (68%) of a colorless oil which immediately crystallized. Recrystallization from alcohol gave colorless prisms, m. p. 66–66.5°.

Anal. Calcd. for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.51; H, 6.57.

Hydrogenation of the olefin proceeded smoothly in glacial acetic acid solution with Adams catalyst and the resulting liquid hydrocarbon boiled at 177–179° (1.5–2 mm.), yield 86%. In attempted Friedel and Crafts condensations of the hydrocarbon with acetyl chloride under various conditions, naphthalene was always obtained as a fore-run, there was much resinous material, and the portion boiling in the range 160–200° (1.5–2 mm.) yielded no appreciable amount of acid on hypochlorite oxidation in aqueous medium or in pyridine,[17] or by other methods.[18] Chloroacetylation was also unsuccessful.

In other experiments the hydrocarbon V was brominated according to Cook and Haslewood[4] and the product was treated with pyridine, converted into the Grignard reagent, and this was carbonated and submitted to hydrogenation, as described by these authors. The acidic material obtained did not crystallize, even when seeded later with the pure acid VI. After several preliminary tests, cyclization was effected by warming the crude acid mixture for one-half hour with 90% sulfuric acid at 40°. The solid material which precipitated on treatment with ice was boiled with zinc dust and alkali for ten hours with added toluene. The resulting product yielded a picrate which after repeated crystallization formed apparently homogeneous, red needles, m. p. 152–153°, but the hydrocarbon recovered from it, although it formed excellent pale yellow needles from alcohol, melted over the range 149–168°.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.70; H, 6.30. Found: C, 93.56; H, 6.53. Picrate, calcd.: C, 64.32; H, 3.95; N, 8.66. Found: C, 64.56; H, 4.08; N, 8.53.

The product does not correspond at all with the pure 5,10-dimethyl-1,2-benzanthracene described below and as the yield was very poor the substance was not investigated further.

Synthesis of 5,10-Dimethyl-1,2-benzanthracene

Reaction of 1,2-Naphthalic Anhydride with *o*-Tolylmagnesium Bromide.—The 3,4-dihydronaphthalene-1,2-dicarboxylic anhydride was prepared with the use of sodium ethylate as described by Fieser and Hershberg[5] and with the same yield (81%) when employing as much as 254 g. of ethyl γ-phenylbutyrate. With large quantities it was found convenient to powder the sodium under xylene by simply agitating the mixture with a Hershberg wire stirrer.[19] The dehydrogenation was conducted as described,[5] using 213.5 g. of material. The product twice distilled and once crystallized from benzene was sulfur-free and suitable for the Grignard reaction; yield 163.5 g. (77.5%). The mother liquor afforded 11.5 g. of anhydride of the same melting point but giving a slight test for sulfur.

After a number of trials and variations the following procedure for the addition reaction was adopted as the most satisfactory. The Grignard reagent prepared from 19 g. of *o*-bromotoluene, 3.5 g. of magnesium, and 100 cc. of ether was filtered through a plug of glass wool under nitrogen pressure and forced *all at once* under pressure of the gas into a well-stirred (Hershberg stirrer) solution of 20 g. of sulfur-free 1,2-naphthalic anhydride in 400 cc. of warm thiophene-free benzene. A yellow complex

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[14] All melting points are corrected unless otherwise noted, using the precision apparatus of Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 312 (1936). Analyses by Mrs. G. M. Wellwood.

[15] Claus and Wollner, *Ber.*, **18**, 1856 (1885); Freund, Fleischer and Gofferje, *Ann.*, **414**, 1 (1916).

[16] Fieser, Holmes and Newman, THIS JOURNAL, **58**, 1055 (1936).

[17] Fuson, Lewis and DuPuis, *ibid.*, **54**, 1114 (1932).

[18] Babcock, Nakamura and Fuson, *ibid.*, **54**, 4407 (1932); Kröhnke, *Ber.*, **66**, 604 (1933).

[19] Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

separated immediately. The mixture was heated with stirring, the ether was allowed to distil, and the benzene was then kept refluxing for two hours. After cooling and treating with dilute hydrochloric acid, the benzene layer was diluted with 200 cc. of ether and extracted thoroughly with potassium carbonate solution. The residual ether–benzene solution contained no easily recovered products (some anhydride was obtained in early runs with less efficient stirring). The combined carbonate extracts were acidified and the keto acid mixture was taken into ether and the solution was washed with saturated sodium chloride solution and evaporated. A solution of the residue in 150 cc. of hot benzene was treated with 20–30 cc. of warm hexane to produce a saturated solution, and the crystalline material (m. p. 130–145°) which separated on standing overnight was taken up in 50 cc. of glacial acetic acid. After standing for twelve to sixteen hours (no longer) the dense, diamond-shaped prisms of **2-*o*-toluyl-1-naphthoic acid** (**VI**) which separated were collected; yield 11–12.5 g. (38–43%), m. p. 147–149°. This material was used for the next step. A sample for analysis was crystallized to constant melting point from glacial acetic acid, m. p. 149.5–150.5°.

1-*o*-Toluyl-2-naphthoic acid, m. p. 210–211°, was obtained from the first acetic acid mother liquor and purified by repeated recrystallization from the solvent. It forms heavy diamond-shaped prisms resembling those of VI; yield about 1 g. (3%).

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.60; H, 4.86. Found (VI): C, 78.69; H, 5.05. (Isomer): C, 78.17, 78.31; H, 4.83, 5.29.

Methyl 2-*o*-Toluyl-1-naphthoate was obtained in 97% yield as a very viscous, pale yellow oil, b. p. 215–216° (2.5 mm.), by refluxing the acid with methyl alcohol–hydrogen chloride for five hours. An ester similar in appearance and in its behavior in the Grignard reaction was obtained using diazomethane.

Decarboxylation of the Acids.—The reaction proceeded well on a small scale (0.5 g.) using as catalyst a small amount of the blue copper salt of the appropriate acid and heating a mixture of the salt and free acid in a bath at 230–245°. After about ten minutes the product of decarboxylation was distilled at 9 mm. pressure and taken into hexane. The ketones crystallized slowly but well. The acid VI afforded a product identical with Martin's[10] *o*-tolyl-β-naphthyl ketone, m. p. and mixed m. p. 67–68°, while 1-*o*-toluyl-2-naphthoic acid gave *o*-tolyl α-naphthyl ketone, m. p. and mixed m. p. 51.5–52.5°.

Lactone of 2-(α-Hydroxy-*o*,α-dimethylbenzyl)-1-naphthoic Acid, VII.—The condensation of methyl 2-*o*-toluyl-1-naphthoate with slightly more than one equivalent of methylmagnesium iodide, filtered through a plug of glass wool under nitrogen and added inversely, was tried in ether, ether–benzene and ether–xylene at temperatures from 25 to 100° for two to three hours with nearly the same results. After decomposing the reaction mixture with dilute hydrochloric acid the organic layer was washed with water and extracted with potassium carbonate solution. The carbonate extract yielded 15–18% of the original keto acid resulting from the hydrolysis of the ester, and the ether or ether–benzene solution on drying and removing the solvent gave the lactone, which was crystallized from benzene–alcohol or benzene–hexane. The lactone apparently is formed directly in the course of the reaction or during the hydrolysis of the magnesium derivative; hydrolysis of the keto ester also occurs prior to the working up of the reaction mixture. The yields were from 40 to 51%, based on the acid consumed. Methyl zinc chloride gave none of the desired reaction product.

When the free keto acid was used and treated in benzene–ether solution with two equivalents of methylmagnesium iodide, distilling the ether and refluxing four or five hours, 10–40% of the acid was recovered unchanged and the yield of lactone, allowing for the recovery, rose to 70–80%. The most satisfactory results were obtained using methylmagnesium bromide and employing a considerable excess of the reagent (using the ester, an excess of Grignard reagent caused a decrease in the yield). For the preparation of the reagent 0.032 mole of magnesium was covered with ether and methyl bromide was introduced slowly by distillation until the magnesium was very nearly all dissolved. The solution was filtered under nitrogen pressure and added gradually to a benzene–ether solution of 0.01 mole of 2-*o*-toluyl-1-naphthoic acid. A white precipitate of the MgBr-salt separated and changed to a greenish-yellow and then a bright yellow complex. After stirring for three and one-half hours at room temperature, the mixture was refluxed for one-half hour and treated with dilute acid. The potassium carbonate extract contained no appreciable quantity of keto acid, and the lactone was obtained in a good condition in 86% yield.

The lactone dissolves readily in benzene and crystallizes well after the addition of either alcohol or hexane. At first the substance was obtained in a low-melting form which separated as large, flat, elongated, transparent prisms, or as small needles, m. p. 103–104°. In later experiments a second modification appeared more frequently, either alone or together with the low-melting form. This separated as long, square, transparent prismatic rods, m. p. 119–120°. When a solution of the pure low-melting form was seeded with the other material either the high-melting form crystallized directly or a mixture melting between 110 and 117° resulted and gave the pure high-melting form only on further crystallization. On one occasion the low-melting form was obtained as clusters of needles on seeding a solution of the high-melting modification, but usually it was difficult to obtain any but the high-melting form once it had been isolated.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.30; H, 5.60. Found (m. p. 103–104°): C, 83.25; H, 5.62; (m. p. 119–120°): C, 83.43; H, 5.90.

2-(*o*,α-Dimethylbenzyl)-1-naphthoic Acid, VIII.—Using Martin's modification[10] of the Clemmensen method, 0.9 g. of the lactone VII was refluxed with a mixture of 40 g. of amalgamated zinc, 20 cc. of water, 40 cc. of toluene, 10 cc. of glacial acetic acid, and 40 cc. of concentrated hydrochloric acid for twenty-one hours, adding two 30-cc. portions of concentrated acid. The organic material was collected in toluene–ether and the reduction product obtained by extraction with potassium carbonate solution. Unchanged lactone was recovered in a good condition from the toluene–ether. The results were variable, for in one case the pure reduction product was obtained in 80% yield and no lactone was recovered, while more usually 20–26% of starting material was recovered and the yield, allowing for this, was 40–76%. It seems better to use a homogeneous solution. Using 1.5 g. of lactone, 50 g. of amalgamated zinc, 50 cc. of glacial acetic acid and 25 cc. of concentrated hydrochloric acid, and refluxing for eleven hours with the dropwise addition of 150 cc. more acid during this period, the nearly pure reduction product, isolated as above and crystallized from benzene–hexane, amounted to 1.15 g. (76%).

A sample of the acid recrystallized for analysis from benzene–hexane formed clusters of transparent prisms, m. p. 183.5–184°.

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.72; H, 6.25. Found: C, 82.71; H, 6.30.

5,10-Dimethyl-1,2-benzanthracene.—To 10 cc. of concentrated sulfuric acid at 20° 0.8 g. of powdered 2-(*o*,α-dimethylbenzyl)-1-naphthoic acid was added with swirling, and after five minutes the material had all dissolved to an orange solution. After two hours this was poured onto 100 g. of crushed ice, and after standing for two hours at 0° the precipitated, light yellow anthrone was collected and washed with water. As the substance is very sensitive and alterable, the moist anthrone was at once transferred to a flask and a mixture of the substance with 2 g. of zinc dust, 10 g. of sodium hydroxide, and 100 cc. of water was refluxed vigorously for six hours. The yellow, at first oily, material gradually disappeared and gave way to light-colored crystals of the hydrocarbon. The mixture was treated with excess hydrochloric acid to dissolve most of the zinc, and the crude product was collected, dried and crystallized from benzene–alcohol. The yield of colorless material melting at 146–147°, uncorr., was 0.45 g. (64%).

The hydrocarbon forms a picrate which separates from benzene as deep reddish-black flat needles, m. p. 173.7–174.2°. The hydrocarbon regenerated from the purified picrate crystallized from benzene–alcohol or benzene–hexane as colorless plates, m. p. 147–147.5°, having an intense blue fluorescence in ultraviolet light.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.70; H, 6.30. Found: C, 93.72; H, 6.64. Picrate, calcd. for $C_{20}H_{16}\cdot C_6H_3O_7N_3$: C, 64.32; H, 3.95; N, 8.66. Found: C, 64.13; H, 3.74; N, 8.82.

Synthesis of 10-Methyl-1,2-benzanthracene

Reaction of 1,2-Naphthalic Anhydride with Phenylmagnesium Bromide.—The Grignard reaction was carried out as above and the chief reaction product, **2-benzoyl-1-naphthoic acid,** was isolated in 30% yield. The pure substance melted at 141.8–142.8° (Waldmann[8] and v. Braun[20] report the value 139–140°, uncorr.), and gave β-benzoylnaphthalene, m. p. 82–83°, on decarboxylation. The isomeric **1-benzoyl-2-naphthoic acid,** m. p. 223.5–224.5° (Waldmann,[8] 219–220°, uncorr.), seemed to be present to a greater extent than in the case noted above.

Waldmann[8] obtained these two acids by the Friedel and Crafts condensation of 1,2-naphthalic anhydride with benzene, and he reports that the esterification of 2-benzoyl-1-naphthoic acid with methyl alcohol and hydrogen chloride gave an ester, m. p. 153–154°, uncorr. We prepared the substance by this method (m. p. 156–156.5°) and found that after being refluxed for four hours in benzene–ether with one equivalent of methylmagnesium iodide, no addition occurred and after saponification nearly all of the material was recovered as 2-benzoyl-1-naphthoic acid. The compound therefore is regarded as the lactol ether XI. The true **methyl 2-benzoyl-1-naphthoate,** prepared using diazomethane, was found to react normally with the Grignard reagent. The substance forms slender colorless needles from methyl alcohol, or better from hexane, m. p. 72.5–73.5°.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.60; H, 4.86. Found: C, 78.38; H, 5.16.

Lactone of 2-(α-Hydroxy-α-methylbenzyl)-1-naphthoic Acid.—The reaction of the normal ester with one equivalent of methylmagnesium iodide was conducted as above. No acid was recovered and the yield of purified lactone was 56%. On treating the free acid in benzene–ether with three equivalents of methyl bromide and refluxing for three and one-half hours, no appreciable amount of acid was recovered and the lactone was obtained in a very satisfactory condition in 89% yield. Once recrystallized from benzene–alcohol, the substance formed colorless prisms, m. p. 173.8–174.2°.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.18; H, 5.15. Found: C, 83.49; H, 5.34.

2-(α-Methylbenzyl)-1-naphthoic Acid.—On reducing the lactone with amalgamated zinc and acid in the presence of toluene 33% of the lactone was recovered and 90% of the material consumed was obtained as the acid. Using dilute acetic acid the process was simpler and the yield of acid based on the lactone taken was 74%. The acid gives well-formed prisms from benzene–hexane but these contain solvent which is lost only with difficulty. After drying in vacuum at 60° for three hours the product sintered at 118° and melted at 122–124°, and after two crystallizations from glacial acetic acid it finally formed dense prisms melting at 128–129°. This melting point is reached at once when the solvated material is melted and then crystallized from acetic acid.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.76; H, 6.32.

10-Methyl-1,2-benzanthracene was prepared from the above acid exactly as described for the higher homolog, the total yield of pure product, collected partly as such and partly as the picrate, being 66%. The hydrocarbon crystallizes from benzene–hexane as long, flat, very nearly colorless needles, m. p. 140.2–140.8°, bright blue fluorescence in ultraviolet light. Slender needles are formed from benzene–alcohol. The picrate separates from benzene as dark red needles, m. p. 173.5–174°.

Anal. Calcd. for $C_{19}H_{14}$: C, 94.17; H, 5.83. Found: C, 94.08; H, 6.03. Picrate, calcd. for $C_{19}H_{14}\cdot C_6H_3O_7N_3$: C, 63.68; H, 3.64. Found: C, 63.47; H, 3.87.

Other Experiments; 5-Methyl-1,2-benzanthracene

2-(*o*-Toluyl)-1-naphthoic Acid with Ethyl- and with Octadecyl-magnesium Bromide.—The reaction of the ester of the above acid with octadecylmagnesium bromide proceeded very poorly and better results were obtained by treating the free acid in benzene–ether with three equivalents of the reagent. In contrast with the experiences above the complex in this case dissolved completely. The

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[20] v. Braun, Manz and Reinsch, *Ann.*, **468**, 277 (1929).

material from the neutral fraction of the reaction mixture was refluxed for one hour with alcoholic potassium hydroxide, and from the alkaline extract there was obtained on acidification and crystallization (28% yield) a substance identified as the **lactone of 2-(α-hydroxy-*o*-methylbenzyl)-1-naphthoic acid.** The substance forms colorless, pearly plates from benzene–hexane, m. p. 157–157.8°.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.18; H, 5.15. Found: C, 83.23, 83.16; H, 5.27, 5.32.

From the residue unsaponified in the above treatment there was isolated in small amount a substance having the properties of *n*-hexatriacontane, pearly white plates, m. p. 77–78°.

A reducing action also was observed in the reaction of 2-(*o*-toluyl)-1-naphthoic acid (free acid) with ethylmagnesium bromide (3 equivalents), but in this case some of the normal reaction product also was isolated. The neutral fraction from the reaction mixture was first crystallized from a rather dilute solution in benzene–hexane, when crystals of 2-(α-hydroxy-*o*-methylbenzyl)-1-naphthoic acid lactone were deposited in nearly pure condition and in 34% yield. The material in the mother liquor was recovered and crystallized from alcohol, affording fairly pure **2-(α-hydroxy-*o*-methyl-α-ethylbenzyl)-1-naphthoic acid lactone** in 23% yield. On further crystallization from alcohol the substance formed thin hexagonal plates, m. p. 124–125°.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.41; H, 6.00. Found: C, 83.24; H, 6.13.

2-(*o*-Methylbenzyl)-1-naphthoic Acid.—This was obtained in 38% yield by the Clemmensen–Martin reduction of 2-(α-hydroxy-*o*-methylbenzyl)-1-naphthoic acid lactone and also, in very poor yield, by the zinc amalgam acid reduction of 2-*o*-toluyl-1-naphthoic acid in acetic acid solution. Attempted reduction with zinc dust and alkali was unsuccessful. The acid forms clusters of small, thick needles from benzene–hexane, m. p. 144–145°.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.56; H, 6.05.

5-Methyl-1,2-benzanthracene was obtained by cyclization and reduction exactly as described above, the yield of purified product being 78%. Crystallized from benzene–hexane, the hydrocarbon formed fluorescent, colorless plates, m. p. 158.5–159.1°; picrate, m. p. 165.8–166.3°. Cook[12] reports the melting point 157.5–158.5°, uncorr., for the hydrocarbon and 163–163.5°, uncorr., for the picrate.

Anal. Calcd. for $C_{19}H_{14}$: C, 94.17; H, 5.83. Found: C, 93.80; H, 6.20.

Summary

A rather general method is described for the synthesis of substituted 1,2-benzanthracenes, with or without a methyl group at the 10-position, starting with 1,2-naphthalic anhydride (naphthalene-1,2-dicarboxylic anhydride) and an arylmagnesium halide. The methyl group is introduced if desired by the reaction of the free 2-aroyl-1-naphthoic acid with an excess of methylmagnesium bromide. The 5-methyl, 10-methyl and 5,10-dimethyl derivatives of 1,2-benzanthracene have been prepared in this way for comparison with the carcinogenically active 5,10-dimethylene derivative (cholanthrene). Preliminary results of biological tests indicate that 5,10-dimethyl-1,2-benzanthracene has cancer-producing properties and is comparable in potency with methylcholanthrene, cholanthrene and 3,4-benzpyrene.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Synthesis of Phenanthrene and Hydrophenanthrene Derivatives. VII. 5,9-Dimethoxy-1′,3′-diketo-1,2-cyclopentenophenanthrene

BY L. F. FIESER AND E. B. HERSHBERG

In continuation of other work[1,2] it seemed desirable to prepare for bio-assay a methoxylated derivative of the previously described 1′,3′-diketo-1,2-cyclopentenophenanthrene.[2] It was thought that the keto acid I would afford a convenient starting point for the synthesis of such a compound, but, although this acid was obtained in nearly quantitative yield by the condensation of 1,5-dimethoxynaphthalene with succinic anhydride, an unexpected difficulty was encountered in the reduction of the substance with amalgamated zinc and hydrochloric acid, using toluene with or without the addition of acetic acid.[3] Considerable resinification occurred and the desired product of normal reduction (II) was isolated in only 20–25% yield from the distillable material present, although it crystallized well and could be separated readily from more soluble substances. The acid was converted successfully by the sequence of reactions previously described[2] into 5,9-dimethoxy-1′,3′-diketo-1,2-cyclopentenophenanthrene (III), although an unexpected

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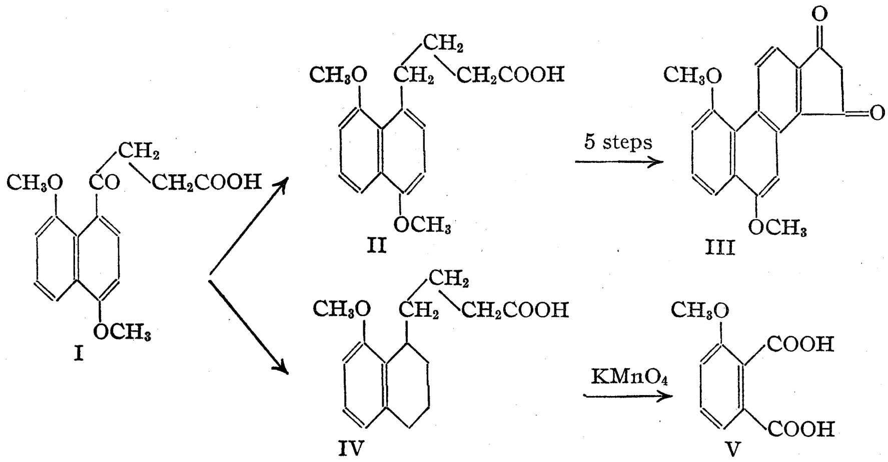
[1] Part IV. Fieser and Hershberg, THIS JOURNAL, **58**, 2314 (1936).

[2] Part VI. Fieser, M. Fieser and Hershberg, *ibid.*, **58**, 2322 (1936).

[3] Martin, *ibid.*, **58**, 1438 (1936).



ether-interchange necessitated the repetition of some of the steps of the process. On boiling 1,5-dimethoxyphenanthrene - 1,2 - dicarboxylic anhydride with ethyl alcoholic hydrogen chloride for conversion to the corresponding diethyl ester, a methyl ⟶ ethyl interchange occurred at one of the two methoxyl groups, probably that located at the more reactive 9-position. This was established by the analyses and by the observation that the diketone obtained differed from the true dimethoxy compound (III) subsequently prepared through the corresponding dimethyl ester.

The Clemmensen reduction of methoxylated keto acids has been observed to proceed rather poorly in certain other cases,[3] but the present reduction appeared exceptional not only because of the very low yield but because the normal reaction product evidently was accompanied by a considerable amount of monomeric material. In the hope of discovering the nature of the side reaction this material was examined carefully and, after some trials, the principal constituent was isolated in a pure, crystalline condition. The substance is acidic, and from the analyses and properties, and from the conversion of the compound by alkaline oxidation into 3-methoxyphthalic acid (V), it can be assigned the structure of γ-(8-methoxytetralyl-1)-butyric acid (IV). While Haberland[4] has reported that the 6-substituted isomer, which he prepared synthetically, is smoothly dehydrogenated by sulfur to the corresponding γ-naphthylbutyric acid, the acid IV on similar treatment gave no crystalline products and the formation of butyric acid was indicated by the odor. Selenium, acting on a crude acid fraction containing IV, gave α-methoxynaphthalene as the only identified product.

The abnormal product of the Clemmensen reduction probably is formed as a result of the primary addition of hydrogen to the conjugated system formed by the carbonyl group and the nuclear double linkages, the elimination of methyl alcohol and the complete saturation of the hydro-aromatic ring occurring at some stage of the process. The mechanism is still obscure. Boiling hydrochloric acid alone slowly attacks the keto acid I with cleavage to 1,5-dimethoxynaphthalene, and consequently it is not likely that the abnormal reduction proceeds through a partially demethylated intermediate. There are no indications that a similar side reaction takes place to an appreciable extent even with similarly constituted compounds. β-*p*-Methoxybenzoylpropionic acid and β-(4-methoxy-1-naphthoyl)-propionic acid give the normal reduction products in 85% and 53% yields,[3] and the by-products are resinous. The reduction of β-(2,6-dimethoxy-1-naphthoyl)-propionic acid was investigated but no by-product comparable with IV was discovered. In view of these observations it is hardly possible to define any general features of structure responsible for the abnormal hydrogenating action noted in this one example of the Clemmensen reduction.

Experimental Part[5]

β-(1,5-Dimethoxy-4-naphthoyl)-propionic Acid.—1,5-Dimethoxynaphthalene was prepared conveniently by methylating the technical dihydroxy compound, distilling the product at 25 mm., and crystallizing the ether from glacial acetic acid. Colorless material melting at 178–180° was obtained in 65–70% yield by weight. A solution of 0.4 mole of the ether and 0.41 mole of succinic anhydride in 400 cc. of tetrachloroethane and 80 cc. of nitrobenzene was cooled and kept at 0 to 5° while adding 0.85 mole of aluminum chloride. After standing at 0° for forty hours, the red-brown solution was poured onto ice and 100 cc. of concentrated hydrochloric acid, the solvent was removed with steam, and the product was precipitated from a sodium carbonate solution after clarification. A pale brown

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[4] Haberland, *Ber.*, **69**, 1380 (1936).

[5] All melting points are corrected. Analyses by Mrs. G. M. Wellwood.

product, m. p. 168–170°, was obtained in 93% yield. Using three equivalents of aluminum chloride instead of two, the yield of material, m. p. 172–175°, was 98%. Crystallized twice from benzene, the acid formed clusters of small, colorless leaflets, m. p. 175–176°.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.64; H, 5.59. Found: C, 66.33; H, 5.30.

The ethyl ester, obtained in 87% yield by the Fischer method, distilled at 200–210° at about 7 microns without decomposition and separated from ether–petroleum ether as lustrous leaflets, m. p. 53–53.5°.

Anal. Calcd. for $C_{18}H_{20}O_5$: C, 68.31; H, 6.39. Found: C, 68.06; H, 5.82.

Clemmensen Reduction.—In a typical experiment 20 g. of β-(1,5-dimethoxy-4-naphthoyl)-propionic acid was suspended in a mixture of 125 g. of amalgamated zinc, 100 cc. of concentrated hydrochloric acid, 50 cc. of water, 75 cc. of toluene and 5 cc. of glacial acetic acid. The keto acid dissolved after refluxing the mixture for about two hours; the boiling was continued for a total of twenty-five hours, during which time 100 cc. more acid was added in portions. The toluene layer was separated after some cooling and the aqueous layer was diluted and extracted with benzene. After washing the hydrocarbon solution with water, 25 cc. of 6 *N* sodium hydroxide and 50 cc. of water were added, together with 0.5 g. of sodium hydrosulfite, and the solvent was removed with steam. For remethylation the alkaline solution was treated with 13 cc. of dimethyl sulfate, and the solution was then acidified. The crude acid which precipitated was dried in vacuum in a distilling flask and distilled at 3 mm. There was obtained at 200–240° 13.5–14.5 g. of a colorless distillate which partially solidified in the receiver, and a considerable amount of resinous material was left as a residue. The distillate was triturated with about 50 cc. of ligroin, which dissolved some of the oil and left a somewhat oily solid. On dissolving this material in 35 cc. of benzene and adding an equal volume of ligroin there was deposited on cooling 3.9–4.8 g. (20–25%) of γ-(1,5-dimethoxy-4-naphthyl)-butyric acid in a nearly pure condition, m. p. 152–154°. Very little of this acid appeared to be left in the ligroin or benzene–ligroin mother liquors while the by-product was isolated from both sources, as described below.

In other experiments the conditions were varied by doubling the time of refluxing, by using as much as 20 cc. of acetic acid, by substituting 50 cc. of methyl alcohol for this solvent, or by omitting a water-miscible solvent, but there was no material change in the total amount of distillable product or in the yield of the easily isolated normal reduction product. The results also were essentially the same when the ethyl ester of the keto acid was employed.

γ-(1,5-Dimethoxy-4-naphthyl)-butyric Acid (II).—Purified by crystallization from benzene, the acid formed small, glistening, colorless blades, m. p. 154–154.5°.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.07; H, 6.57. Found: C, 69.93; H, 6.95.

The methyl ester, obtained in 94% yield, formed large thin plates from methyl alcohol, m. p. 65–65.5°.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.78; H, 7.01. Found: C, 70.72; H, 7.06.

The ethyl ester (90% yield), b. p. 201–203° (1 mm.), crystallized as thin plates, m. p. 47–47.5°.

γ-(8-Methoxytetralyl-1)-butyric Acid (IV).—This by-product of the Clemmensen reduction was first isolated from the benzene mother liquors remaining after the crystallization of the normal product II resulting from 50 g. of the keto acid. The solution was concentrated to a small volume and diluted with ligroin, and on standing 12 g. of crystalline material separated. After two crystallizations from ligroin, in which it is moderately soluble even when pure, the acid was obtained as thick, colorless plates, m. p. 74.5–75.5°.

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.52; H, 8.14. Found: C, 72.56; H, 8.24.

In earlier experiments the mother liquor remaining after triturating the crude distillate with ligroin was evaporated and the residual oil was fractionally distilled. A fraction taken at 183–184° (1 mm.) apparently contained a considerable amount of the above acid along with other substances (found: C, 73.63; H, 8.47), for on standing for several weeks it partially crystallized, and the solid material after purification was identical with the substance described above.

Attempts to dehydrogenate the tetralin derivative with sulfur at temperatures up to 230° were unsuccessful. No crystalline products were isolated and the formation of butyric acid was evident from the odor. Dehydrogenation with selenium was tried only with a liquid fraction of the crude acid, b. p. 203–204° (3 mm.). Considerable butyric acid was formed, and there was isolated after demethylation a small amount of a substance identified as α-naphthol. At a time when the identity was still in doubt, **1-methyl-4-methoxynaphthalene,** b. p. 164.5–165° (21 mm.) (found: C, 83.55; H, 6.88) was prepared for comparison; its picrate forms red needles from alcohol, m. p. 148–149° (found: N, 10.61).

Evidence of the structure of the acid IV was obtained by exhaustive oxidation of the substance in dilute alkaline solution with potassium permanganate (steam-bath). The manganese dioxide was removed by centrifugation and on acidifying the filtrate a clear solution resulted. (When the oxidation is incomplete a gummy precipitate appears.) The solution was extracted with ether in a continuous extractor, and the residue remaining on evaporation of the ether was sublimed in vacuum and then extracted with water in order to remove oxalic acid. On twice crystallizing the residue from ether, elongated prismatic needles softening at 155° and melting at 160–161° were obtained. The substance did not depress the melting point of 3-methoxyphthalic anhydride prepared from 3-nitrophthalic acid.

5,9 - Dimethoxy - 3,4 - dihydrophenanthrene - 1,2 - dicarboxylic Anhydride.—Ethyl γ-(1,5-dimethoxy-4-naphthyl)-butyrate (14.2 g.) was condensed with ethyl oxalate in the presence of potassium ethylate, following the standard procedure,[1] and the crude oxalyl derivative obtained by acidification and extraction was warmed on the steam-bath with 30 cc. of 70% sulfuric acid and then with 300 cc. of 78% acid. After one to two hours the at first oily product of cyclization became completely solid. After cooling it was collected and washed with acid, water and alcohol. The crude product (6.5 g.) gave satisfactory material on one crystallization from 100 cc. of glacial acetic acid; yield 5.3 g. (36%), m. p. 227–230°. Recrystallized from the same solvent, the anhydride formed carmine-colored needles, m. p. 231–232°.

Anal. Calcd. for $C_{18}H_{14}O_5$: C, 69.66; H, 4.55. Found: C, 69.69; H, 4.62.

Incidentally it was noted that the ester condensation proceeded less satisfactorily using the methyl ester of the starting material (II) and ethyl oxalate. Using methyl oxalate the solubility of the potassium methylate addition compound was so slight that no appreciable reaction occurred on adding the ester of II.

5,9 - Dimethoxyphenanthrene - 1,2 - dicarboxylic Anhydride.—A mixture of 500 mg. of the unsaturated red anhydride and 55 mg. of sulfur was heated at 250–300° for three minutes and the product was distilled at 1 mm. and crystallized from glacial acetic acid. It formed cottony clusters of fine yellow needles, m. p. 288–289°, yield 430 mg. (85%). Recrystallized from dioxane the compound melted at 289–290°.

Anal. Calcd. for $C_{18}H_{12}O_5$: C, 70.11; H, 3.93. Found: C, 69.98; H, 4.24.

Dimethyl 5,9 - Dimethoxy - 3,4 - dihydrophenanthrene - 1,-2-dicarboxylate.—The ester was obtained in 72% yield by refluxing the corresponding anhydride with methyl alcohol saturated with hydrogen chloride for two days. It separated from benzene–ligroin as long, greenish-yellow prisms melting at 151–153° and turning red during the process.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.38; H, 5.68. Found: C, 67.41; H, 5.98.

Dimethyl 5,9 - Dimethoxyphenanthrene - 1,2 - dicarboxylate.—The unsaturated ester described immediately above (500 mg.) was dehydrogenated with sulfur (45 mg.) as described for the anhydride; yield 82%. Recrystallized from methyl alcohol, it formed light greenish-yellow prisms, m. p. 133–134°.

Anal. Calcd. for $C_{20}H_{18}O_6$: C, 67.78; H, 5.12. Found: C, 67.52; H, 5.23.

5,9 - Dimethoxy - 1',3' - diketo - 1,2 - cyclopentenophenanthrene (III).—The above ester (1.15 g.) was refluxed with 8 cc. of ethyl acetate and 0.5 g. of sodium for two hours, and then 5 cc. of ethyl acetate and 0.3 g. of sodium were added and the refluxing was continued for four hours longer. A yellow sodium derivative separated during the process, and after adding 50 cc. of dry ether to the cooled mixture this was collected; additional material was recovered from the ethereal filtrate. Decarboxylation to the diketone was effected by boiling the sodium derivative with dilute hydrochloric acid for a few minutes and the product was crystallized from dioxane; yield 0.56 g. (58%). The fully purified material formed deep yellow needles which softened at about 265° and melted at 281–283° with decomposition.

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 74.49; H, 4.61. Found: C, 74.47; H, 4.91.

A Case of Ether-Interchange.—In an early experiment 5,9-dimethoxyphenanthrene-1,2-dicarboxylic anhydride (3.75 g.) was refluxed for twenty-four hours with 150 cc. of ethyl alcohol saturated with hydrogen chloride, in the expectation of obtaining the corresponding diethyl ester. The crude product (4.29 g.) contained a persistent yellow impurity which was removed after six crystallizations from methyl alcohol, and the product was obtained as thick, colorless needles, m. p. 109.5–110°. Analysis indicated that one of the two phenolic ether groups had been transformed from methoxyl to ethoxyl in the course of the esterification and that the substance obtained is **5(9)-methoxy-9(5)-ethoxy-1,2-dicarbethoxyphenanthrene.**

Anal. Calcd. for $C_{23}H_{24}O_6$: C, 69.67; H, 6.11. Found: C, 69.59, 69.71; H, 6.28, 6.02.

This conclusion was confirmed by conversion of the ester into a phenanthrindanedione as above, for the product (yield 81%) differed from the dimethoxy compound (III) already described and had the composition of **5(9)-methoxy - 9(5) - ethoxy - 1',3' - diketo - 1,2 - cyclopentenophenanthrene.** The substance crystallized from dioxane–alcohol as fine, fluffy, yellow needles, m. p. 207–208°.

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 74.98; H, 5.03. Found: C, 74.61; H, 4.83.

β-(2,6-Dimethoxy-1-naphthoyl)-propionic Acid.—Prepared as above by the Friedel and Crafts reaction in 82% yield, this acid crystallized from benzene as colorless needles which became opaque on drying, m. p. 156–156.5°.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.64; H, 5.59. Found: C, 66.40; H, 5.83.

γ - (2,6 - Dimethoxy - 1 - naphthyl) - propionic Acid.—Clemmensen reduction of 34 g. of the above keto acid by Martin's procedure[3] gave, after remethylation and vacuum distillation, 17.5 g. of crude, solid reduction product, the residue being resinous. Crystallization from benzene gave, in the first crop, 11 g. of the normal reduction product in a nearly pure condition, and evaporation of the mother liquor yielded further crops of the same substance. No trace of a by-product comparable with that obtained in the other series was observed. The acid formed needles from benzene, m. p. 122–124°.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.04; H, 6.61. Found: C, 70.25; H, 6.92.

Summary

The diketone mentioned in the title was synthesized by standard methods and in the course of the work an interesting side reaction was observed to occur in the reduction of β-(1,5-dimethoxy-4-naphthoyl)-propionic acid by the Clemmensen method. In the formation of the abnormal product the ketonic group is reduced as usual, but the aromatic ring to which it is attached is hydrogenated in the course of the reaction and a methoxyl group in the para position is eliminated as well.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.
RECEIVED SEPTEMBER 25, 1936

[CONTRIBUTION FROM THE DIVISION OF INSECTICIDE INVESTIGATIONS, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE]

The Solubility of Nicotine Silicotungstate in Solutions of Dilute Hydrochloric Acid

BY JOSEPH R. SPIES

In determining small quantities of nicotine by the silicotungstic acid method,[1] it was necessary to know the solubility of nicotine silicotungstate in dilute hydrochloric acid. No exact quantitative data on the solubility of this substance appear in the literature. Bertrand and Javillier[2] first determined the sensitivity of silicotungstic acid as a reagent for nicotine by noting the maximum dilutions at which turbidity could be obtained when solutions of the two substances containing different concentrations of hydrochloric acid were mixed. The maximum sensitivity was obtained in 1–1000 hydrochloric acid, and it decreased with increasing acid concentration. Chapin[3] later used silicotungstic acid for the precipitation of nicotine as the basis of the widely used gravimetric method for its determination. He found that the loss due to the solubility of nicotine silicotungstate was negligible in the macro method.

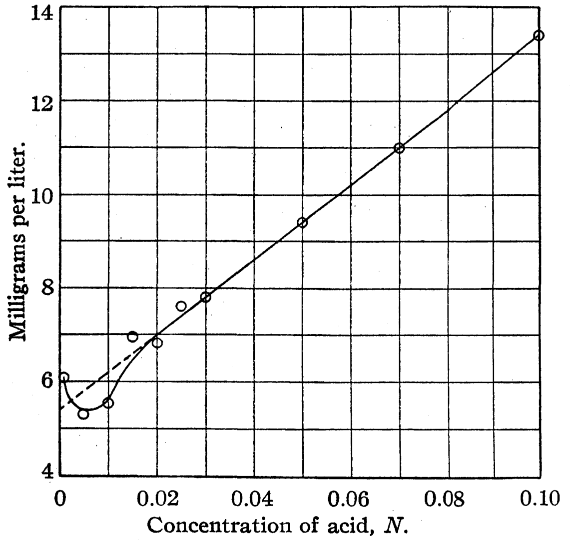

Fig. 1.—Effect of dilute hydrochloric acid on the solubility of nicotine silicotungstate.

The solubility of pure nicotine silicotungstate has been determined at 25 ± 0.02°[4] in distilled water (*p*H 6.5 as determined colorimetrically with brom thymol blue) and in 0.001 to 0.1 *N* hydrochloric acid solutions. The results are summarized in Table I and shown graphically in Fig. 1.

TABLE I

SOLUBILITY OF NICOTINE SILICOTUNGSTATE IN DILUTE SOLUTIONS OF HYDROCHLORIC ACID

Evaporations[a]	Concn. of acid, *N*	Soln. evaporated, ml.	Av. weight of residue, mg.	Av. soly.,[b] mg./liter	Av. deviation from mean ($\Sigma d/N$) mg./liter	Av. deviation from mean ($\Sigma d/N$) %
6	0.10	40	0.543	13.4	0.3	2.2
2	.070	40	.448	11.0	.0	0.0
6	.050	50	.481	9.41	.28	3.0
4	.030	50	.400	7.80	.08	1.0
2	.025	60	.466	7.59	.06	0.8
6	.020	60	.422	6.81	.36	5.3
2	.015	60	.427	6.96	.11	1.6
4	.010	60	.349	5.56	.04	0.7
2	.0050	60	.333	5.30	.00	.0
4	.0010	60	.373	6.08	.08	1.3
8	[c]	30	1.049	38.5	1.6	4.2

[a] Two evaporations were made from each saturated solution, and the average weights given in the fourth column are based on the total number of evaporations. [b] Calculated as $SiO_2 \cdot 12WO_3 \cdot 2H_2O \cdot 2C_{10}H_{14}N_2$. Factor = 1.127. The residue (column 4) was corrected for blank (dissolved glass) at the rate of 0.80 mg. per liter for water and 1.70 mg. per liter for 0.1 *N* acid. Intermediate acid concentrations were corrected proportionately. [c] Distilled water, *p*H of 6.5.

The maximum solubility, 38.5 mg. per liter, was found with water, and the minimum between 0.015 and 0.001 *N* acid. The lowest value obtained was 5.30 mg. per liter in 0.005 *N* acid. The results obtained for from 0.015 to 0.1 *N* acid fall on a straight line, the solubility increasing from 6.96 to 13.4 mg. per liter. It is probable that the break in the curve between 0.015 and 0.001 *N* acid is real and not due to experimental error, since the value obtained at 0.01 *N* is 14.5% lower than it would be if it fell on the straight line passing through the other points. The maxi-

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(1) While the results of the determinations reported in this paper express the "maximum solubility," or the solubility of pure nicotine silicotungstate in solutions of dilute hydrochloric acid, they also accurately represent the actual amount of nicotine lost in analytical determinations involving only nicotine. From analytical data presented by the author (paper accepted for publication in the *Analytical Edition* of *Industrial and Engineering Chemistry*) the excess (up to ten times) silicotungstic acid used apparently does not produce a detectable decrease in solubility of nicotine silicotungstate. The analytical results also indicate that the usual practice of permitting freshly precipitated nicotine silicotungstate to stand overnight (eighteen hours) to crystallize allows sufficient time for even unstirred solutions to attain equilibrium. The solubility values as determined in this paper, therefore, can be used in applying corrections for lost nicotine in analytical procedures where nicotine alone is present.

(2) G. Bertrand and M. Javillier, *Ann. chim. anal. Appl.*, **14**, 165 (1909).

(3) R. M. Chapin, U. S. Dept. Agr. Bur. Animal Ind., *Bull.*, **133**, 22 pp. (1911).

(4) The thermometer used, graduated in 0.1°, was checked against a National Bureau of Standards calibrated thermometer.

mum deviation from the mean found in all the other determinations is 5.3% while the average of the deviations is only 1.8%. No explanation is offered for the occurrence of this minimum solubility. It was more difficult to duplicate saturated solutions in water than when acid was present. This is shown in Table I by the greater deviation from the mean in this case.

At acid concentrations below 0.025 *N* the solid phase settled more slowly when stirring was interrupted. In a preliminary study some colloidal particles passed through the fritted-glass filter used to filter off the saturated solutions. These solutions showed a Tyndall cone when examined with a powerful light beam. At higher acid concentrations this difficulty did not occur, as settling was rapid and clear solutions readily were obtained. In the work reported in this paper a porcelain filterstick with a dense filtering surface was used, and the saturated solutions obtained even at concentrations below 0.025 *N* showed no distinct Tyndall cone.

Solutions saturated at 25° were prepared both by cooling solutions saturated at higher temperature and by stirring nicotine silicotungstate with the solvent at 25°. Where more than one saturated solution was prepared at a given acid concentration, both methods generally were used. The close agreement of the results indicates that true equilibrium was attained.

Experimental

Preparation of Nicotine Silicotungstate.—1.26 g. of nicotine[5] (n^{22}_D 1.5241) was dissolved in 700 ml. of 0.086 *N* hydrochloric acid, and 14.2 g. (slight excess) of silicotungstic acid ($4H_2O \cdot SiO_2 \cdot 12WO_3 \cdot 22H_2O$) in 200 ml. of distilled water was added slowly with stirring. After standing twenty hours with occasional stirring, the precipitate was filtered off and washed with dilute hydrochloric acid on the filter. It was stirred up once with dilute hydrochloric acid, filtered, washed and dried by exposure to air at room temperature. The crystalline character of the precipitate was shown by the familiar scintillating effect produced when the solid was stirred with the dilute acid solution, and was verified by microscopic examination.

Anal. Calcd. for $SiO_2 \cdot 12WO_3 \cdot 2H_2O \cdot 2C_{10}H_{14}N_2 \cdot 5H_2O$: C, 7.29; H, 1.28; N, 1.70; $SiO_2 \cdot 12WO_3$, 86.32. Found: C, 7.29, 7.24; H, 1.28, 1.29; N, 1.75, 1.76;[6] $SiO_2 \cdot 12WO_3$, 86.48, 86.28.

Apparatus.—Pyrex glassware was used throughout. To minimize solution of glass each vessel was leached on the steam-bath with dilute hydrochloric acid for several hours before being used. All apparatus used for measurement of solutions was calibrated.

Preparation of Saturated Solutions.—One-tenth gram of nicotine silicotungstate was agitated with 250 ml. of distilled water on the steam-bath in a 1-liter three-necked Pyrex flask equipped with a glass mechanical stirrer. After about five minutes of warming the flask was placed in the constant-temperature bath at 25 ± 0.02° and the solution stirred until cooled to bath temperature. Sufficient constant-boiling hydrochloric acid was then added to give the desired acid concentration. The alternative procedure was to place the nicotine silicotungstate directly in the hydrochloric acid solution without warming. In either case the solutions were stirred for at least twenty hours, which experiment had shown to be ample for the attainment of equilibrium. A 9-cm. porcelain filterstick was used for withdrawal of the saturated solution so that filtration by suction could be made without removing the flask from the constant-temperature bath. The saturated solutions were stored in glass-stoppered Erlenmeyer flasks in the constant-temperature bath.

Evaporation of Saturated Solutions.—Accurately measured volumes, in 10-ml. portions, were pipetted from the flasks into 15-ml. platinum crucibles that had previously been ignited to constant weight at 650°. To protect the crucibles from dust the evaporations were carried out in an electrically heated (95–105°) glass cylinder of 50 mm. diameter to which two glass wells were sealed to hold the crucibles upright. Air was aspirated through the cylinder to remove the water vapor. To avoid contamination by dust the air was filtered through cotton and a fritted-glass plate, respectively, before it entered the evaporation chamber. With this apparatus 10 ml. of water could be evaporated from a crucible in five hours with no danger of spattering or contamination by dust.

Ignition and Weighing of Residue.—When evaporation of the solution was complete, the crucibles were ignited for fifteen minutes in an electric furnace at 646–652°. This procedure was chosen for the following reasons. It is well known that tungstic oxide is appreciably volatile at the temperature attainable with a Meker burner. Platinum also shows sufficient loss of weight to be detectable on the microchemical balance when ignited for ten minutes at this temperature. In view of these facts, and because of the small amounts of oxides of tungsten and silicon weighed, it was necessary to find a temperature at which small quantities of nicotine silicotungstate could be completely ignited without loss in weight of the residual oxides. Experiments in which weighed quantities of nicotine silicotungstate were ignited in platinum crucibles and weighed under conditions simulating those used in the solubility determinations showed 650° to be a suitable temperature.[7] The nicotine silicotungstate was weighed into the platinum crucibles, which contained residues from previous ignitions. After ignition the crucibles were cooled in air for thirty to forty minutes and then weighed. Table II gives the results of some of these experiments.

The residues were weighed on a Kuhlmann microchemi-

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[5] Purified by the method of Lowry and Lloyd, *J. Chem. Soc.*, 1381 (1929).

[6] The author is indebted to D. F. Houston for the micro Dumas determinations.

[7] C. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 538. The ignition of nicotine silicotungstate is more fully discussed in the paper referred to in footnote 1.

TABLE II

IGNITION OF NICOTINE SILICOTUNGSTATE AT 650°

Time of ignition, min.	Nicotine silicotungstate mg.	Residue, mg.	
		Found	Calcd.
15	2.737	2.366	2.363
15	3.172	2.741	2.738
45	2.107	1.818	1.819
45	2.146	1.869	1.852

cal balance the rider of which was checked against a 10-mg. weight calibrated by the National Bureau of Standards. The tares were adjusted so as to avoid the use of fractional weights. Since weighings were by difference and were sometimes made several days apart, it was necessary to use similar platinum crucibles for tares to eliminate errors due to change in pressure, temperature and humidity. The use of the usual glass lead-shot tares was found to introduce an appreciable error due to these causes. Throughout the experiments the crucibles were handled with platinum-tipped forceps.

The Distilled Water.—Stock distilled water was carefully redistilled into a leached 12-liter flask, with the use of a block-tin condenser. When about half the determinations had been made, blanks were run on the water alone and with 0.1 normal solutions of the hydrochloric acid used. The procedure and apparatus were the same as were used in the preparation of the saturated solutions. On the basis of three runs each, the values of the blanks were 0.80 ± 0.14 mg. per liter for the water and 1.70 ± 0.14 mg. per liter for the acid. The amount of the correction for dissolved glass was applied in proportion to the acid concentration of the solvent.

The author wishes to acknowledge the interest of Nathan L. Drake in this work.

Summary

The solubility of nicotine silicotungstate in water and in 0.001 to 0.1 *N* hydrochloric acid solutions has been determined. The maximum solubility, 38.5 mg. per liter, is found in water and a minimum of 5.30 mg. per liter in 0.005 *N* hydrochloric acid. The solubility increases from 6.96 mg. per liter in 0.015 *N* acid to 13.4 mg. per liter in 0.1 *N* hydrochloric acid.

COLLEGE PARK, MD. RECEIVED SEPTEMBER 5, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Mechanism of Carbohydrate Oxidation. XXIII.[1] A Contribution to the Alkaline Hydrolysis of Oligosaccharides[1a]

BY HARRY GEHMAN, LEONARD C. KREIDER AND WM. LLOYD EVANS

After studying the action of aqueous potassium hydroxide on maltose (4-α-glucosidoglucose) to form lactic acid, Benoy[2] and one of us came to the conclusion that the hexose (reducing) portion of the molecule was first degraded by the alkali to form the following fragments: formaldehyde, glycolaldehyde and 2-glucosidoerythrose. Hydrolysis of the latter was then assumed to occur to produce glucose and erythrose. As it was quite certain from previous work[3] that formaldehyde, glycolaldehyde and erythrose would produce no lactic acid in alkaline solution, it was probable that when maltose was degraded by alkali the entire reducing half of the molecule was lost to lactic acid production. The hexosido-(non-reducing) portion, being released by hydrolysis as glucose, should then produce lactic acid as glucose was known to do. The fact that a solution of maltose (0.25 *M*) yielded approximately half as much lactic acid as was obtained under identical conditions from an equivalent amount of glucose (0.50 *M*) lent considerable weight to this argument.

Later in a similar study of the alkaline degradation of cellobiose (4-β-glucosidoglucose) and lactose (4-galactosidoglucose) Hockett[4] and one of us showed that these disaccharides also yielded only such amounts of lactic acid as would have been expected from their hexosido (non-reducing) portions alone.

The 6-hexosidohexoses, like gentiobiose (6-glucosido-glucose) and melibiose (6-galactosidoglucose), present a different type of behavior, for here the amount of lactic acid produced is considerably greater than that expected from the hexosido portion of the molecule alone. This was explained by pointing out that the reducing portion of these molecules contributed a part of the lactic acid. Simultaneous with the degradation

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[1] Number XXII of this Series, H. W. Arnold and W. L. Evans, THIS JOURNAL, **58**, 1950 (1936).

[1a] Presented before the Organic Section of the American Chemical Society, Pittsburgh Meeting, 1936.

[2] W. L. Evans and M. P. Benoy, *ibid.*, **52**, 294 (1930).

[3] J. U. Nef, *Ann.*, **376**, 40 (1910); J. E. Hutchman, Ph.D. Dissertation, O. S. U., 1927.

[4] W. L. Evans and R. C. Hockett, THIS JOURNAL, **53**, 4384 (1931).

of the reducing half of the molecule, or following it, hydrolysis would liberate the non-reducing half and make it subject to alkaline degradation so it too could make its normal contribution of lactic acid to the total.

This paper offers a mechanism for the alkaline hydrolysis postulated above and presents additional evidence to support and extend the previous theories[2,4] of the action of alkali on oligosaccharides. The use of the recently synthesized glucosidodihydroxyacetone pentaacetate,[5] cellobiosidodihydroxyacetone octaacetate,[5] and gentiobiosidodihydroxyacetone octaacetate[5] was invaluable in the latter phase of this work.

Experimental Part

Carbohydrate Materials.—Glucosidodihydroxyacetone pentaacetate, gentiobiosidodihydroxyacetone octaacetate, and cellobiosidodihydroxyacetone octaacetate were prepared according to directions already published.[5] Dihydroxyacetone monoacetate,[6] cellobiose octaacetate, lactose octaacetate,[7] and glucose pentaacetate, were specimens prepared in the conventional ways and recrystallized until pure. The gentiobiose octaacetate was obtained from The Laboratory Products Co., Cleveland, Ohio.

Analytical Procedure.—The general procedure outlined by Nadeau, Newlin and Evans[8] was followed for the isolation of the lactic acid. The use of acetylated sugars necessitated a normality correction due to the neutralizing action of the acetyl groups and also to the greater expansion of the reaction mixture in these cases. The normalities of alkali reported are corrected values. A nitrogen atmosphere was also used in the reaction flasks instead of an air atmosphere as had formerly been customary. All the work was carried out at a temperature of 50°. The amount of carbohydrate material and volume of alkali used to degrade it are as follows: glucosidodihydroxyacetone pentaacetate, 1.4443 g. (0.25 *M*) in 12.5 cc. KOH; glucose tetraacetate, 1.0878 g. (0.25 *M*) plus dihydroxyacetone monoacetate, 0.4125 g. (0.25 *M*) in 12.5 cc. KOH; glucose pentaacetate, 2.4375 g. (0.50 *M*) in 12.5 cc. KOH; gentiobiose, 1.0687 g. (0.25 *M*) in 25.0 cc. KOH;[4] β-gentiobiose octaacetate, 1.6957 g. (0.20 *M*) in 12.5 cc. KOH; β-gentiobiosidodihydroxyacetone octaacetate 1.5002 g. (0.20 *M*) in 10.0 cc. KOH; β-cellobiose octaacetate, 1.6957 g. (0.20 *M*) in 12.5 cc. KOH; β-cellobiosidodihydroxyacetone octaacetate, 1.8760 g. (0.20 *M*) in 12.5 cc. KOH; gentiobiose octaacetate 1.6957 g. (0.20 *M*) plus dihydroxyacetone monoacetate, 0.3302 g. (0.20 *M*) in 12.5 cc. KOH; β-cellobiose octaacetate, 1.6957 g. (0.20 *M*) plus dihydroxyacetone monoacetate, 0.3302 g. (0.20 *M*) in 12.5 cc. KOH; glucose pentaacetate, 1.56 g. (0.40 *M*) plus dihydroxyacetone monoacetate, 0.3302 g. (0.20 *M*) in 12.5 cc. KOH; glucosidodihydroxyacetone pentaacetate, 0.924 g. (0.20 *M*) plus glucose pentaacetate, 0.78 g. (0.20 *M*) in 10.0 cc. KOH; β-lactose octaacetate 2.197 g. (0.25 *M*) in 12.5 cc. KOH.

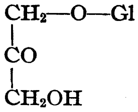
The isolation of non-volatile saccharinic acids other than lactic acid was carried out according to the procedure outlined by Plunkett.[9]

Experimental Results.—The quantitative data obtained in this work are shown in graphical form in Figs. 1 to 6. The lactic acid yields in moles per mole of sugar used are plotted as functions of the corrected alkali normalities.

Theoretical Part

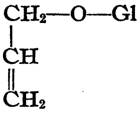
The hydrolysis of glucosides and oligosaccharides usually is achieved with dilute acid and by the aid of enzymes in a neutral solution. Hydrolysis in an alkaline medium has been reported in relatively fewer instances, and hence it is not so well known. The evidence obtained from the action of aqueous alkali on certain disaccharides was of such a nature as to compel Benoy,[2] Hockett[4] and one of us to postulate alkaline hydrolysis during the alkaline degradation of the carbohydrates studied, and results reported here are in complete harmony with this view.

The following comparison of certain of our experimental data is of much interest in connection with the main purposes of this paper. Since glucosidodihydroxyacetone (I) yields lactic acid in alkaline solution, while allyl glucoside (II) does not produce this acid under the same conditions, an explanation for this difference in chemical behavior of these two compounds was sought in some possible change in molecular structure which one of them might undergo in alkaline solutions. If (I) is written in the customary *keto*-form it is evident that the structure of both compounds is the same at the glucosidic link



$$\begin{array}{l} \text{CH}_2\text{—O—Gl} \\ | \\ \text{CO} \\ | \\ \text{CH}_2\text{OH} \end{array}$$

(I)



$$\begin{array}{l} \text{CH}_2\text{—O—Gl} \\ | \\ \text{CH} \\ \| \\ \text{CH}_2 \end{array}$$

(II)

and hence alkaline hydrolysis would be expected in both cases if it were known to occur in either one. From our experimental results it was concluded that glucosidodihydroxyacetone in alkaline solution must possess a different structure at the glucosidic link than does allyl glucoside. If glucosidodihydroxyacetone should undergo enolization in alkaline solution[10] a possible enolic iso-

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[5] Number XX of this Series, L. C. Kreider and W. L. Evans, THIS JOURNAL, **58**, 1661 (1936).

[6] H. O. L. Fischer, E. Baer and L. Feldman, *Ber.*, **63**, 1732 (1930); A. Wohl and C. Neuberg, *ibid.*, **33**, 3095 (1900).

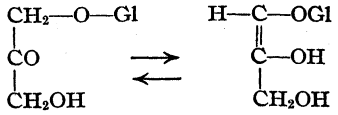
[7] C. S. Hudson and J. M. Johnson, THIS JOURNAL, **37**, 1270 (1915).

[8] G. F. Nadeau, M. R. Newlin and W. L. Evans, *ibid.*, **55**, 4957 (1933).

[9] R. J. Plunkett, Ph.D. Dissertation, The Ohio State University, 1936.

[10] *Cf.* A. Kusin, *Ber.*, **69B**, 1041–1049 (1936).

mer would be 1-triosenediol glucoside, a change which may be shown as follows

(A) 

$$\begin{array}{l} CH_2{-}O{-}Gl \\ | \\ CO \\ | \\ CH_2OH \end{array} \rightleftarrows \begin{array}{l} H{-}C{-}OGl \\ \| \\ C{-}OH \\ | \\ CH_2OH \end{array}$$

It may then be assumed that 1-triosenediol glucoside undergoes hydrolysis as shown by the equation

$$\text{(B)}\quad CH_2OHC(OH){=}CHOGl + HOH \longrightarrow CH_2OHC(OH){=}CHOH + C_6H_{12}O_6$$

Both the triosenediol and glucose thus formed are sources of lactic acid. Since allyl glucoside does not yield lactic acid under our experimental conditions, it is to be concluded that hydrolysis did not take place, *i. e.*, there was no structural opportunity for isomerization to yield an enolic form.

For these reasons the authors examined the literature to ascertain whether certain given types of compounds existed which would undergo alkaline hydrolysis, and on the other hand whether certain other definite types would resist such hydrolysis. The reduction of heated Fehling's solution was accepted as a criterion of hydrolysis in the absence of direct statements, or other experimental evidence that was decisive, such as the production of lactic acid. This statement would of necessity assume that the aglycone was inactive toward the oxidizing solution. Our examination makes it fairly certain that the literature of alkaline hydrolysis is not yet sufficiently understood to justify a conclusive statement concerning the existence of sharply defined classes of compounds that on the one hand undergo alkaline hydrolysis, while another group resists this action. The following facts verify this point of view. (a) Methyl,[11] ethyl,[11] glycol,[11] propyl[12] and benzyl[13] glucosides and trehalose[14] are representatives chosen from a large number of similar compounds that undergo no hydrolysis in aqueous alkali. In our experiments we found that methyl, glycol and allyl glucosides, and trehalose, when treated with aqueous solutions of potassium hydroxide (4.0 *N* and above) for forty-eight hours at 50°, yielded no lactic acid. These results confirm the absence of hydrolysis in these cases. It should be noted that all of these compounds cannot isomerize to an enolic form as given above for glucosidodihydroxyacetone. (b) There are other glycosides that contain a still different type of an aglycone, some of which undergo alkaline hydrolysis while others do not. Helferich and Kühlewein[15] found that the glycosides of theophylline (galactose, glucose and arabinose), chlorotheophylline *d*-glucoside, tetraacetyl-trichloropurine *d*-glucoside, dichloroadenine *d*-glucoside did not reduce Fehling's solution, while the glycosides of theobromine (galactose and glucose), and tetraacetylhydroxycaffeine *d*-glucoside did reduce the same reagent. In those cases where reduction took place, the compound could be isomerized to contain the group $N{=}\underset{|}{C}{-}O{-}Gl$, while in the cases where no reduction occurred the glycosidic portion reacted with the purine compound to form the link N–C, thus excluding the possibility of isomerization after the manner indicated above. Fischer and Helferich[16] found that theobromine glucoside is decomposed by water into its components at ordinary temperature in the course of a few hours. Levene and Sobotka[17] report that tetraacetylhydroxycaffeine was found so unstable that it could not be deacetylated at all without opening the purine linkage. (c) The phenolic glycosides present much interest in this connection. Helferich and Schmitz-Hillebrecht[18] found that the acetylated glucosides of phenol, α- and β-naphthol, methyl arbutin, guaiacol and α- and β-galactosides of phenol and certain other similar glycosides reduce Fehling's solution. On the other hand Helferich and Winkler[19] report that tetraacetyl-phenol-β-*d*-mannoside would not reduce Fehling's solution without previous acid hydrolysis. In the phenolic glycosides we find the group ${=}\underset{|}{C}{-}O{-}Gl$, which was postulated to form in alkaline solutions of compounds possessing the structure which would yield the enolic isomer, and hence were expected to undergo hydrolysis.

More recently Gardner and his collaborators[20] have made a study of hydrolysis of α-hydroxyanthraquinone β,*d*-glucoside and β,*d*-arabinoside,

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[11] E. Fischer, *Ber.*, **26**, 2400 (1893).

[12] E. Fischer and L. Beensch, *ibid.*, **27**, 2478 (1894).

[13] E. Fischer and B. Helferich, *Ann.*, **383**, 68 (1911).

[14] C. S. Hudson, THIS JOURNAL, **38**, 1571 (1916).

[15] B. Helferich and M. von Kühlewein, *Ber.*, **53**, 17 (1920).

[16] E. Fischer and B. Helferich, *ibid.*, **47**, 210 (1914).

[17] P. A. Levene and H. Sobotka, *J. Biol. Chem.*, **65**, 463 (1925).

[18] B. Helferich and E. Schmitz-Hillebrecht, *Ber.*, **66**, 378 (1933).

[19] B. Helferich and S. Winkler, *ibid.*, **66**, 1556 (1933).

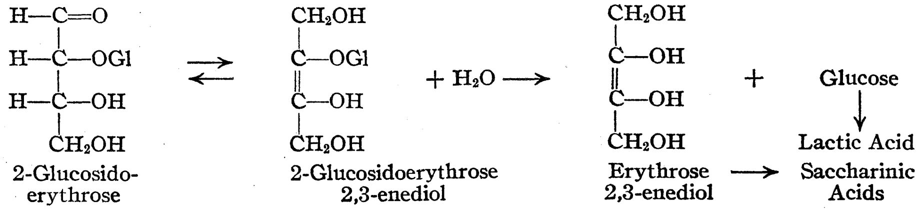
[20] (a) J. H. Gardner, T. F. McDonnell and C. J. W. Weigand, THIS JOURNAL, **57**, 1074 (1935); (b) H. Foster with J. H. Gardner, *ibid.*, **58**, 597 (1936); (c) J. H. Gardner and W. H. Demaree, *ibid.*, **58**, 757 (1936).

1,5- and 1,8-dihydroxyanthraquinone glucoside, and β-hydroxyanthraquinone β,*d*-glucoside in aqueous solutions of potassium hydroxide, borax and hydrochloric acid. These compounds were found to undergo hydrolysis in the three reagents chosen. (d) In striking contrast to the resistance toward alkaline hydrolysis of certain compounds noted in (b) that contain the group N–C at the purine–glycosidic union is the behavior observed by Maurer[21] and Scheidt[21] of certain glycosides of amino acid esters which were found to undergo hydrolysis in alkaline solutions.

It is evident from this brief survey that it is possible for alkaline hydrolysis of *oligosaccharides* to occur in molecules where the biosidic link exists either in the form $\mathrm{Gl{-}O{-}\underset{|}{C}{=}}$, or where the structure can be transformed by the alkaline medium to assume that arrangement.

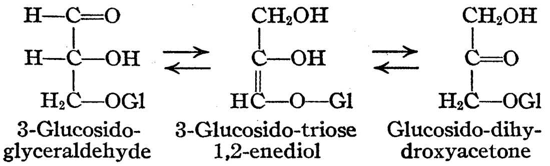
Such a structure could be induced in the fragment 2-glucosidoerythrose, which was postulated as an intermediate in the alkaline degradation of maltose[2] and of cellobiose.[4] The reactions that probably take place are shown in the following

(C)

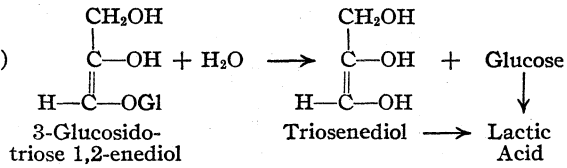


In like manner the various fragments postulated in the degradation of disaccharides of the gentiobiose type[4] could undergo enediolization to form the grouping $\mathrm{Gl{-}O{-}\overset{|}{C}{=}}$ which will then permit hydrolysis in the alkaline medium to liberate the non-reducing portion to the attack of the alkali. For example, if gentiobiose should fragment as postulated[4] to yield glyceraldehyde and 3-glucosidoglyceraldehyde, the latter could undergo the following reactions culminating in an alkaline hydrolysis to form glyceraldehyde and glucose as shown in following reactions

(D)



(E)



The actual isolation of the monosaccharides set free in such an hydrolysis is not possible when working with the stronger alkaline solutions. However, Lobry du Bruyn and Alberda van Ekenstein,[22] using much weaker alkalies, isolated galactose from lactose (4-galactosidoglucose) solutions, but obtained no glucose. This result was a reasonable one because the latter undoubtedly was partially degraded before the alkaline hydrolysis occurred.

Discussion of Experimental Data

Glucosidodihydroxyacetone and Gentiobiose.—From previous studies of the action of alkali on gentiobiose,[4] it was assumed that the reducing half of the molecule was the first to suffer degradation. This action produced fragments of two types: (1) those that form monosaccharides, and (2) those that result in the formation of disaccharides. By the action of alkalies on the monosaccharides so formed, glycol aldehyde yields no lactic acid, the triose gives much lactic acid, and the tetrose no lactic acid. Of the possible disaccharides, 5-glucosidopentose, 3-glucosidotriose and glucosidoglycol aldehyde, the 3-glucosidotriose yields much lactic acid. The newly formed disaccharides could then suffer a similar degradation in the reducing portion of their molecules, or they could undergo alkaline hydrolysis according to the mechanism outlined above. Reactions D and E may be considered the steps in a typical example of such an hydrolysis. The glucose thus liberated could then undergo fragmentation in the presence of alkali with the resulting production of lactic acid.

An experimental study of the amounts of lactic acid produced by the alkaline degradation of the

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[21] (a) Kurt Maurer, *Ber.*, **59B**, 827–829 (1926); (b) K. Maurer and B. Scheidt, *Z. physiol. Chem.*, **206**, 125 (1932); *C. A.*, **26**, 3482 (1932).

[22] Lobry du Bruyn and Alberda van Ekenstein, *Rec. trav. chim.*, **18**, 147 (1899).

individual disaccharide fragments should yield important data regarding the mechanism of the alkaline degradation of gentiobiose itself. One of these compounds, a glucosidotriose, is now available for study in the recently prepared glucosidodihydroxyacetone pentaacetate.[4] In discussing Fig. 1 three cases will be noted.

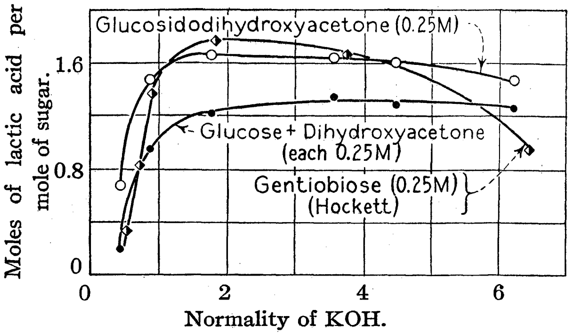

Fig. 1.—A comparison of the lactic acid yields obtained from 0.25 *M* solutions of glucosidodihydroxyacetone with those of a mixture of glucose and dihydroxyacetone, and with those of gentiobiose in the presence of potassium hydroxide at 50°.

(a) This keto sugar should react in alkaline solution in accordance with Reaction D to produce the corresponding aldo sugar, 3-glucosidoglyceric aldehyde,[23] one of the postulated intermediates formed in the alkaline degradation of gentiobiose. If the remaining fragments obtained from the gentiobiose molecule consisted chiefly of formaldehyde and glycol aldehyde, the yields of lactic acid from glucosidodihydroxyacetone at different alkalinities should be approximately the same as those obtained from gentiobiose itself provided the concentration of this glucosidotriosenediol in this very complex mixture were the same in both cases. From Fig. 1 it may be fairly concluded that at alkalinities below 1 *N* gentiobiose molecules have not undergone a sufficient degree of fragmentation to yield a concentration of the glucosidotriosenediol molecules at a given alkalinity equal to that produced by the glucosidodihydroxyacetone used. (b) At favorable alkalinities, it is conceivable for the gentiobiose molecules to undergo fragmentation in the direction of yielding one molecule each of 3-glucosidoglyceric aldehyde and glyceric aldehyde. Since glyceric aldehyde itself is also a source of lactic acid, the total yield of this acid under these conditions may be greater than in the previous case, provided the degree of fragmentation of the gentiobiose molecules is sufficiently great to furnish the required concentration of the enediolic isomers of glyceric aldehyde and of the glucosidoglyceric aldehyde necessary for this purpose. This explanation would account for the greater yields of lactic acid from gentiobiose between 1.2 and 4 *N* (Fig. 1) than those from glucosidodihydroxyacetone in the same alkaline range. (c) If at the highest alkalinities the fragmentation of gentiobiose molecule yields a tetrose and glucosidoglycol aldehyde the yields of lactic acid should tend toward that obtained from the glucose molecule (a hydrolytic product) under the same conditions. It will be shown later that in addition to the effect of such a postulated fission on the yields of lactic acid produced in these cases, the formation of saccharinic acids exercises a marked influence in this connection.

The assumption that glucosidoglyceric aldehyde is a possible intermediate in the alkaline degradation of gentiobiose seems justified by the discussion set forth above concerning the experimental facts presented in Fig. 1. Unfortunately, the other disaccharide fragments have not yet been synthesized in a pure form, so that they too could be tested for lactic acid production. However, by making use of the accumulated experience of previous workers,[2,4,24] we can predict with a fair degree of assurance that the glucosidobioses will yield about the same amount of lactic acid as their constituent glucose portions alone would produce and that glucosidotetroses and glucosidopentoses would probably yield somewhat more lactic acid than their constituent glucose portions.

Glucosidodihydroxyacetone and Cellobiosidodihydroxyacetone.—Benoy,[2] Hockett,[4] and Evans postulated that in the alkaline degradation of 4-glucosidoglucoses, such as maltose and cellobiose, the reducing section of the molecule would decompose into fragments which were not sources of lactic acid, while the hexosido portion of the disaccharide molecule was the only available source of this acid. The recent syntheses[5] of glucosidodihydroxyacetone pentaacetate and cellobiosidodihydroxyacetone octaacetate has made it possible to test this assumption in a very simple manner.

If glucosidodihydroxyacetone pentaacetate undergoes alkaline hydrolysis in the manner indicated in Reactions D and E, two lactic acid producing compounds, namely, dihydroxyacetone

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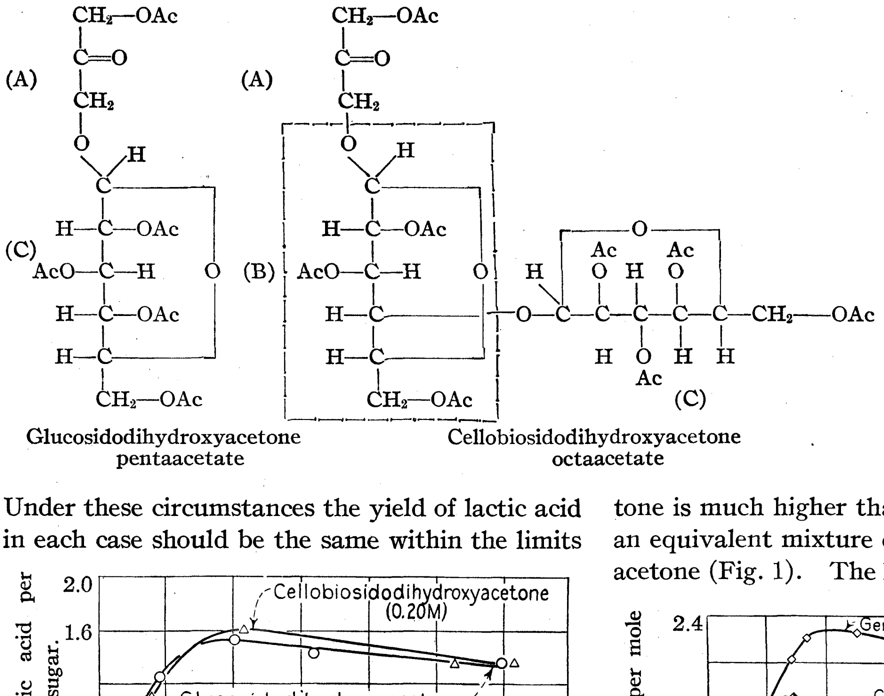
[23] L. C. Kreider and W. L. Evans, THIS JOURNAL, **57**, 229 (1935).

[24] W. L. Evans, *Chem. Rev.*, **6**, 281 (1929).

and glucose, would be formed in the reaction mixture. If cellobiosidodihydroxyacetone octaacetate were subjected to the same treatment under the same experimental conditions, dihydroxyacetone and glucose derived from the hexosido section of the molecule would be present in the reaction mixture in addition to the non-lactic acid producing fragments into which the hexose section of the molecule was decomposed. Thus it is seen that both systems would contain the same common lactic acid sources. A comparison of the structural formulas of these two carbohydrates will make this point more clear. The monosaccharide sections designated A and C produce lactic acid when degraded by alkali, while section B produces no lactic acid under the same conditions.[4]



Glucosidodihydroxyacetone pentaacetate

Cellobiosidodihydroxyacetone octaacetate

Under these circumstances the yield of lactic acid in each case should be the same within the limits of experimental error. This is shown to be the case in Fig. 2.

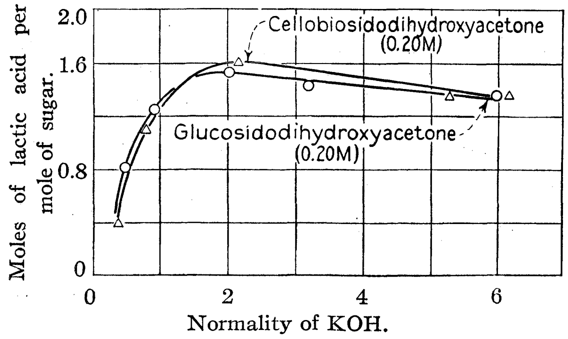


Fig. 2.—A comparison of the lactic acid yields obtained from 0.20 M solutions of glucosidodihydroxyacetone with those of cellobiosidodihydroxyacetone in the presence of potassium hydroxide at 50°.

Cellobiosidodihydroxyacetone and Gentiobiosidodihydroxyacetone.—In Fig. 3 we note that gentiobiose (0.20 M) produces between 0.5 and 0.6 mole more lactic acid at the maximum than does cellobiose (0.20 M). Since a comparable difference exists between the gentiobiosidodihydroxyacetone and the cellobiosidodihydroxyacetone it is evident that whatever may be the mechanism of the fragmentation of these molecules its effects on the parent disaccharides are analogous. The degradation proceeds so that the cellobiosidic portion reacts as cellobiose and the gentiobiosidic portion reacts as gentiobiose. This is evidence that the mechanism of break at the oxygen link connecting the dihydroxyacetone is such that the non-reducing portions of the residual disaccharides are not disturbed until after their hydrolysis has taken place, and that all alkaline degradations originate at the reducing regions only.

Relative Yields of Lactic Acid from Oligosaccharides and their Hydrolytic Fractions.—The lactic acid yields from these oligosaccharides can be shown to differ markedly from those of their possible hydrolytic fractions. The yield of lactic acid from glucosidodihydroxyacetone is much higher than the yield obtained from an equivalent mixture of glucose plus dihydroxyacetone (Fig. 1). The lactic acid produced by the

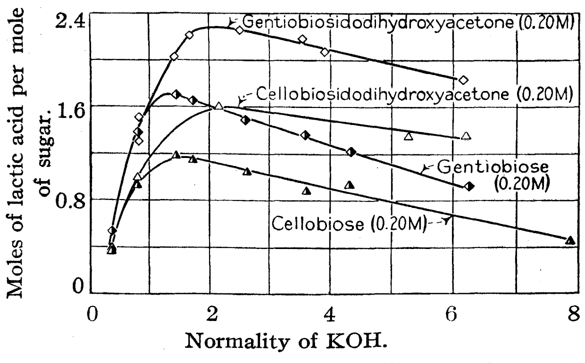


Fig. 3.—A comparison of the lactic acid yields obtained from 0.20 M solutions of gentiobiosidodihydroxyacetone with those of gentiobiose, and cellobiosidodihydroxyacetone with those of cellobiose in the presence of potassium hydroxide at 50°.

alkaline degradation of cellobiosidodihydroxyacetone differs greatly from the possible hydrolytic products that might be formed (Fig. 4). In the same way there is an absence of any correlation between the lactic acid yields obtained from gentiobiosidodihydroxyacetone and from any of its possible hydrolytic products is shown in Fig. 5. These facts can best be interpreted as evidence that, in general, oligosaccharides do not hydrolyze immediately and entirely when they are placed in alkali, but rather that hydrolysis is a relatively slow process and is probably preceded by a partial alkaline degradation of the reducing end of the molecule. It should also be pointed out that the possible hydrolytic fractions and their degradation products tend to undergo rearrangements in alkaline solutions to form their respective saccharinic acids, thus proportionally reducing the yields of lactic acid, which itself may be considered the saccharinic acid of the trioses.

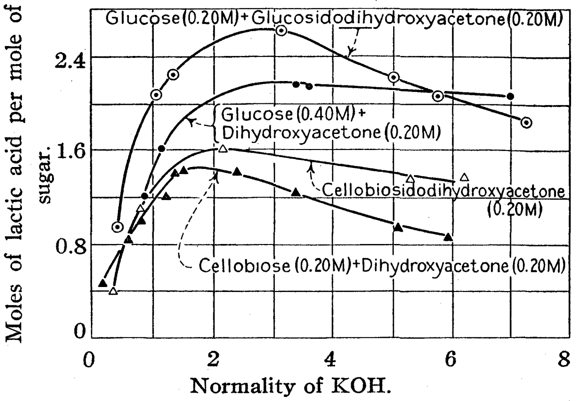


Fig. 4.—A comparison of the lactic acid yields obtained from 0.20 *M* solutions of cellobiosidodihydroxyacetone in the presence of potassium hydroxide at 50° with mixtures of its theoretically possible saccharidic components.

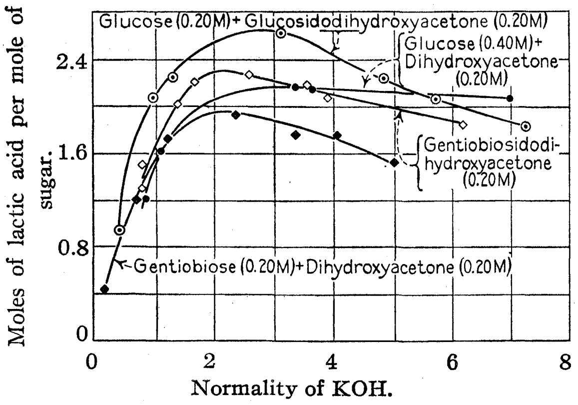


Fig. 5.—A comparison of the lactic acid yields obtained from 0.20 *M* solutions of gentiobiosidodihydroxyacetone in the presence of potassium hydroxide at 50° with mixtures of its theoretically possible saccharidic components.

The yields of lactic acid obtained from glucosido-dihydroxyacetone, cellobiosidodihydroxyacetone, and gentiobiosidodihydroxyacetone are in general greater than those obtained from mixtures simulating the products obtained in the first step in the alkaline hydrolysis of these oligosaccharides, *i. e.*, glucose and dihydroxyacetone, cellobiose and dihydroxyacetone, and gentiobiose and dihydroxyacetone, respectively (Figs. 1, 4 and 5). In the case of mixtures representing other possible hydrolytic reactions, the yields of lactic acid tend to be higher than those obtained from the oligosaccharide itself.

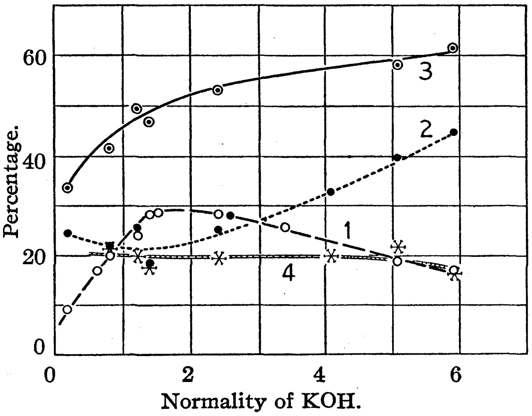


Fig. 6.—A comparison of the lactic acid and saccharinic yields obtained from a mixture of cellobiose octaacetate (0.20 *M*) and dihydroxyacetone monoacetate (0.20 *M*) in the presence of potassium hydroxide at 50°: 1, percentage of the sugars returned as lactic acid; 2, percentage of the sugars returned as saccharinic acids other than lactic acid; 3, total saccharinic acids recovered; 4, zinc oxide content of the salts obtained in 2.

The much slower release of the carbohydrate material of the parent oligosaccharide into the alkali sensitive hydrolytic portions makes possible a more efficient formation of lactic acid. This result is in agreement with an earlier observation of Shaffer and Friedemann[25] concerning the effect of the concentration of sugar molecules on the yields of lactic acid.

Lactose (4-Galactosidoglucose).—The use of an improved technique enabled us to obtain well crystallized zinc lactate in small amounts from

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(25) P. A. Shaffer and T. E. Friedemann, *J. Biol. Chem.*, **86**, 345 (1930).

the alkaline degradation of this sugar. Lactose being a disaccharide linked in the same fashion as cellobiose, it was expected that its lactic acid yields plotted on a molar basis should closely approximate those of galactose just as those of cellobiose[4] and maltose[2] approximate those of glucose. This was found to be true.

Non-volatile Saccharinic Acids Other than Lactic Acid.—The materials extracted at this stage were found to be distinctly salt forming in nature with the zinc oxide content of these salts varying widely according to the carbohydrate source. As stated above it is reasonable to assume that the formation of these other saccharinic acids occurs at the expense of lactic acid formation so that a reciprocal relationship with the latter would be established. This condition was not always realized experimentally, but Fig. 6 shows the results from the cellobiose octaacetate and dihydroxyacetone monoacetate mixture. The acids involved here are undoubtedly of varying carbon content.

The zinc oxide content of the acids obtained in the case mentioned above remains constant at about 20% (approximately that required for a 6-carbon saccharinic acid). However, in some cases the cellobiosidodihydroxyacetone, for example, these salts showed a regular rise from about 10% zinc oxide content at the lower alkalinities to that required for the C_6 acids. Undoubtedly the lower zinc oxide indicates the formation of glycosidic saccharinic acids, the lactic acid yields always being low in these cases. The method used here for their isolation was not such as to permit their identification, a feature of the work that should be investigated further. It was not possible to account for 100% of the sugar because of its removal by decolorizing agents of tars which probably consist of polymeric acetol, formaldehyde, and condensed forms of other carbonyl compounds. The formation of acetic and formic acids in the alkali reactions is well known.

Summary

1. Following the interpretation of Benoy,[2] Hockett and Evans[4] for the alkaline degradation of reducing disaccharides, a mechanism has been proposed for the alkaline hydrolysis of the theoretically possible intermediates that may form. These intermediates are assumed to form glucosidic enediols that in turn are hydrolyzed to glucose and an enediol which in the case of triosenediol is converted to lactic acid, and in that of tetrosenediol is converted to the corresponding saccharinic acids. The glucose released in the hydrolysis is also a source of lactic acid.

2. A comparative study of the lactic acid yields obtained from gentiobiose and glucosidodihydroxyacetone justifies the assumption that the corresponding glucosidoaldotriose, 3-glucosidoglyceric aldehyde, is a fragmentation product of gentiobiose in alkaline solution.

3. A comparative study of the lactic acid yields obtained from alkaline solutions of glucosidodihydroxyacetone and cellobiosidodihydroxyacetone confirms[2,4] the view that the hexosido section of the 4-hexosidohexoses is the source of the lactic acid and not the hexose section.

4. A comparative study of the yields of lactic acid obtained from gentiobiosidodihydroxyacetone and gentiobiose, and also those from cellobiosidodihydroxyacetone and cellobiose confirms the general view expressed in 3.

5. The yields of lactic acid obtained from mixtures of the possible hydrolytic products of the oligosaccharides investigated are greater than those from the parent carbohydrate in each case except in those instances involving the release of dihydroxyacetone as the first step in these alkaline hydrolyses. This may be ascribed either to a slow degradation of the oligosaccharides, or to the concurrent rearrangements taking place with the resulting formation of saccharinic acids, or both.

6. A study of alkaline solutions of varying normalities which contained a mixture of cellobiose octaacetate and dihydroxyacetone monoacetate shows that there is a definite relation between the yields of lactic acid obtained and those of the saccharinic acids.

COLUMBUS, OHIO RECEIVED AUGUST 5, 1936

[CONTRIBUTION FROM GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 557]

Stereochemical Relationships of the Isomeric 2,3-Butanediols and Related Compounds; Evidence of Walden Inversion

BY CHESTER E. WILSON AND HOWARD J. LUCAS

This investigation has been undertaken for the purpose of synthesizing *cis*- and *trans*-2-butene in a pure state and of studying the Walden inversion. Incidentally, the work has constituted an independent confirmation of the observation that the butene produced in the dehydration of 1-butanol in the presence of sulfuric acid is approximately 68% *trans*-2-butene and 32% *cis*-2-butene.[1] The reliability of this result has been questioned,[2] on the basis that the dibromide method of analysis[3] is faulty.[4] This confirmation rests upon the observation that *cis*-2-butene is converted through the chlorohydrin to *cis*-2,3-epoxybutane and that the crude epoxybutane mixture obtained from the crude butene mixture is approximately 65% *trans*-2,3-epoxybutane and 35% *cis*-2,3-epoxybutane, with little or no 1,2-epoxybutane.

The Method of Synthesis.—This is outlined below: 1-butanol $\xrightarrow{-H_2O}$ 2-butenes $\xrightarrow{HOCl}$ 3-chloro-2-butanols $\xrightarrow{-HCl}$ 2,3-epoxybutanes $\xrightarrow{distn.}$ *cis* (or *trans*)-2,3-epoxybutane $\xrightarrow{H_3O^+}$ *dl* (or *meso*)-2,3-butanediol $\xrightarrow{Ac_2O}$ *dl* (or *meso*)-2,3-butanediol diacetate $\xrightarrow{HBr}$ *meso* (or *dl*)-2,3-dibromobutane $\xrightarrow{Zn}$ *trans* (or *cis*)-2-butene. The butene mixture from the decomposition of 1-butanol was converted into a mixture of chlorohydrins and this into a mixture of epoxybutanes by hot potassium hydroxide solution. Fractionally distilling the oxides is more satisfactory than distilling the butenes because the former are liquids, whereas the latter are gases, and because the difference in boiling points of the isomeric 2,3-epoxybutanes is 6°, whereas it is 2.7° for the isomeric 2-butenes. Each oxide, contaminated with a small amount of its stereoisomer, was hydrated to a 2,3-butanediol, which could be purified from the small amount of its diastereomer by crystallization. Conversion of the glycol to its diacetate afforded another opportunity for purification, especially in the case of the lower melting (liquid) glycol, for its diacetate is a solid. Each pure diacetate was converted into a pure 2,3-dibromobutane by saturated, aqueous hydrobromic acid. The dibromides are known to yield the isomeric 2-butenes.[5]

A necessary condition of obtaining pure compounds at the different steps is the avoidance of racemization, that is, there must be, at each asymmetric carbon atom, either zero or 100% Walden inversion. Fortunately, under the conditions employed, this condition held. No attempt was made to modify conditions so as to bring about racemization.

Possibility of Walden Inversions.—An odd number of Walden inversions are involved, starting with a pure 2-butene and passing, through the changes outlined above, to a pure 2-butene, since *cis*-2-butene is obtained from *trans*-2-butene. Because of the symmetrical structure of the compounds involved, it should be possible to determine whether only one Walden inversion takes place during the following changes:

Epoxybutane → butanediol
Butanediol → butanediol diacetate
Butanediol diacetate → dibromobutane
Dibromobutane → 2-butene

In order to establish the possibility of Walden inversions, the compounds involved (except the 2-butene) must be prepared with optical activity. An epoxybutane and a diol have been obtained with optical activity, although not in the pure form. The hydration of the epoxybutanes to the butanediols takes place through a Walden inversion, which is 100% in each case.[6] Although

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[1] Young and Lucas, THIS JOURNAL, **52**, 1964 (1930). A similar conclusion has been drawn independently by H. B. Hass, who has separated the isomeric 2,3-epoxybutanes and has converted each to a glycol (private communication).

[2] Komarewsky, Johnstone and Yoder, *ibid.*, **56**, 2705 (1934); Pines, *ibid.*, **55**, 3892 (1933).

[3] Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930).

[4] See also Young and Winstein, *ibid.*, **58**, 102 (1936).

[5] The purity of the dibromides was regarded as proof that pure butenes would result, for it has been shown already, Ref. 1, that a butene and its dibromide are interconvertible. Since this work was started, Kistiakowsky, *et al.*, *ibid.*, **57**, 879 (1935), have obtained these hydrocarbons in a high state of purity.

[6] Walden inversions have been observed in the hydration of epoxy compounds to glycols: Kuhn and Ebel, *Ber.*, **58B**, 919 (1925); Van Loon, Thesis, Delft, 1918; Böeseken, *Rec. trav. chim.*, **47**, 683 (1928).

the hydration of the oxide is the only step for which there is a definite proof of Walden inversion in this work, it is probable that a total of five single inversions are involved in passing from *cis*-2-butene to *trans*-2-butene, as outlined in Fig. 1, in which the stereochemical relationships of the different compounds are shown. Similar stereochemical relationships are outlined in Fig. 2 for the conversion of *trans*-2-butene to *cis*-2-butene. In this case the second compound, the chlorohydrin, has not yet been obtained pure. A Walden inversion is indicated by the letters W. I. In the case of the *dl*-compounds, the configuration of but one of the two possible antipodes is shown.

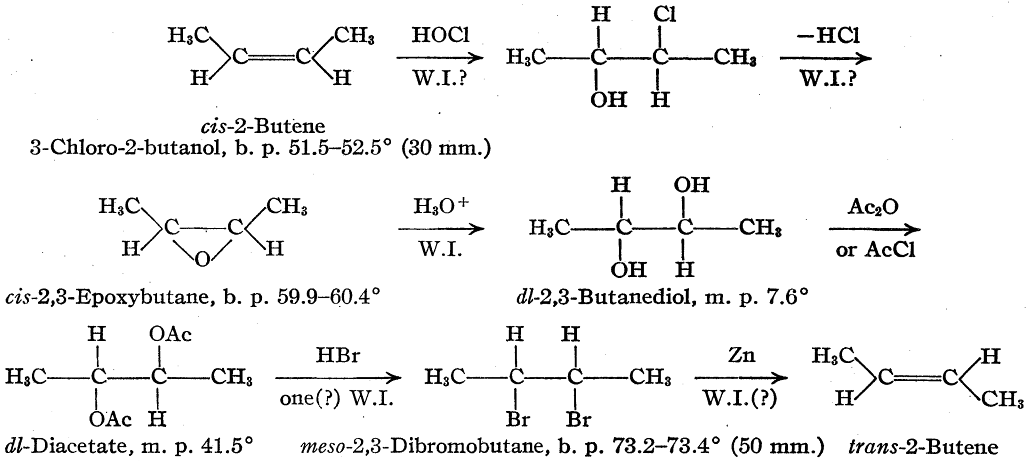

Fig. 1.—*trans*-2-Butene from *cis*-2-Butene.

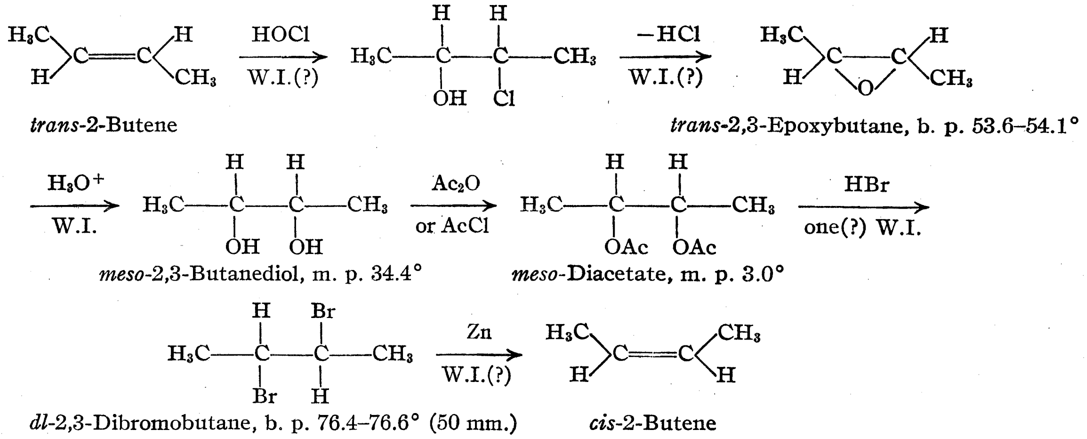

Fig. 2.—*cis*-2-Butene from *trans*-2-Butene.

Although no evidence is available as yet to show that a Walden inversion is involved in the conversion of the butenes to the chlorohydrins, and of these to the oxides, it is reasonable to postulate an inversion at the first step, in conformity with the general rule of *trans* addition to the double bond.[7] If this is true, then an inversion is involved at the second step, that is, during the closing of the oxide ring. At the third step, *i. e.*, the opening of the oxide ring through hydration, a Walden inversion is definitely proved, by establishing the configuration of the oxides and glycols.

Configurations of the Isomeric 2,3-Epoxybutanes.—These were established by obtaining one (the lower boiling isomer) with optical activity, although not as a pure isomer. For this purpose the oxide was converted by the usual steps to a corresponding *dl*-3-dimethylamino-2-butanol, *dl*-α,β-dimethylcholine iodide and *dl*-α,β-dimethylcholine. The latter was partially resolved with tartaric acid. Distillation of the active base with aqueous sodium hydroxide gave trimethylamine and an *optically active* butene

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[7] Michael, *J. prakt. Chem.*, **52**, 344 (1893); Chavanne, *Rev. gen. sci.*, **35**, 229 (1924).

oxide.[8] It was shown further that each *dl*-α,β-dimethylcholine gave the pure oxide from which it had been prepared. Therefore the original lower boiling oxide, b. p. 54°, as well as the recovered active oxide, must have the *trans* configuration, and the higher boiling, b. p. 60°, must have the *cis* configuration.

Configurations of the Isomeric 2,3-Butanediols.—These have been established by three independent observations, as follows: (a) when the optically active oxide is hydrated, the inactivity of the resulting glycol, which is the higher melting isomer, shows that it is the internally compensated form; (b) when the lower melting glycol is partially esterified by *d*-camphor sulfonic acid, the optical activity developed in the unesterified glycol shows that this is the *dl*-glycol; (c) when the higher boiling, *cis*-oxide undergoes hydration in the presence of either *d*-camphor sulfonic acid or *d*-tartaric acid, the optical activity possessed by the resulting, lower melting glycol shows that it is the *dl*-glycol. These results confirm those of Böeseken and Cohen,[9] who resolved the acid sulfate of the liquid glycol by means of brucine. An independent confirmation of their results seemed desirable because of the possibility that a Walden inversion may have taken place in their work, and also because it is sometimes assumed that the solid glycol is the *dl*-isomer since it is produced by bacterial fermentation, and possesses some optical activity.[9,10]

A Walden Inversion.—The hydration of the optically active, *viz.*, the *trans* oxide, to the inactive, *viz.*, the *meso* glycol, proves that a complete Walden inversion, *i. e.*, a *trans* opening of the oxide ring, takes place. If there were no inversion, *i. e.*, if there were *cis* opening of the ring, the resulting glycol should possess optical activity, since an optically active glycol would be present. The optical activity could disappear only by conversion to the *meso* form through racemization at one carbon atom or to its antipode through racemization at both asymmetric carbon atoms. Racemization, even at one carbon atom, was never observed during the hydration of the inactive oxides, for a pure *dl*- or *meso*-glycol was obtained.

Other Possible Inversions.—Inspection of Figs. 1 and 2 shows that either zero or an even number of inversions are involved between the glycols and the final butenes. It is hardly likely that an inversion accompanies the formation of the diacetate, since the C–O bonds are not altered. It is probable that an inversion accompanies the conversion of each butene to its dibromide, and *vice versa*,[1] in line with similar changes[7]. If this is the case, then only one Walden inversion is involved in the formation of the dibromides from the diacetates. This would constitute an unusual and unexpected type of Walden inversion.[11] It is planned to investigate this possibility by attempting to prepare an optically active diacetate and dibromide.

It seems probable, therefore, that five Walden inversions in all are associated with the changes shown in each of Figs. 1 and 2. Of these, the first two are not susceptible of direct proof by the stereochemical method, whereas the last three are. A Walden inversion has been shown to accompany the third step; the fourth and fifth steps require further study.

This research has been aided by a grant from Dr. George Piness, of Los Angeles, whose financial aid is gratefully acknowledged. For the advice and assistance of his colleague, Dr. Gordon A. Alles, the authors desire to express their appreciation and thanks.

Experimental

Preparation of 2-Butene.—The 2-butene,[1] obtained by heating a mixture of 444 g. (6.0 moles) of 1-butanol,[12] 400 ml. of water, and 600 ml. of concd. sulfuric acid, and purified by passing through a sodium hydroxide solution, sulfuric acid, 50–55% by wt., and a drying tower, is condensed, at −15 to −20°, in previously weighed ampoules; yield 130–180 g. (38–48%).

Preparation of 3-Chloro-2-butene.—In a 2-liter three-necked flask provided with a mercury-sealed stirrer, a delivery tube and a reflux condenser cooled by carbon dioxide and alcohol,[13] is placed 400–500 g. of a mixture of water and ice, and 295 g. of H. T. H.[14] (1.34 moles of calcium hypochlorite). The flask is cooled by a freezing bath at −10 to −15° and 150 g. (2.68 moles) of liquid butene is poured into the flask through the delivery tube from the weighed

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[8] See Rabe and Halbensleben, *Ber.*, **43**, 2622 (1910); Read and Campbell, *J. Chem. Soc.*, 2377 (1930).

[9] Böeseken and Cohen, *Rec. trav. chim.*, **47**, 839 (1928).

[10] Harden and Walpole, *Proc. Roy. Soc.* (London), **77B**, 399 (1906). The optical activity is due to contamination by an active form.

[11] A similar change in configuration has been observed in the case of the 4,5-octanediols and corresponding dibromooctanes by Young, Jasaitis and Levanas, who will publish their results soon.

[12] 2-Butanol was not used because it might possibly be contaminated by 2-methyl-2-butanol.

[13] The condenser is made of two large concentric glass tubes in the shape of a Dewar flask, except that there are two small tubes leading into the annular space, *viz.*, a vertical tube at the bottom, up which the warm gas rises and a horizontal tube near the top, out of which the uncondensed gas passes. A mixture of solid carbon dioxide and alcohol is placed in the inner tube.

[14] H. T. H., 65% available chlorine, manufactured by the Mathieson Alkali Works, is a mixture of calcium hypochlorite and sodium chloride.

ampoule. The tube is then replaced by a dropping funnel and 175 ml. (2.9 moles) of glacial acetic acid is slowly run in during vigorous agitation and good cooling. The time is two to three hours, unless one does not object to excessive refluxing.

Nitric acid is added to break the emulsion, the chlorohydrin is separated and the aqueous phase is extracted with three 100-ml. portions of isopropyl ether. After adding a small amount of water to the combined chlorohydrin–ether extracts, the contained acid is neutralized by the addition of potassium carbonate, in small portions. A part of the dissolved water is removed by the addition of calcium chloride and the mixture is then fractionally distilled under reduced pressure. After dichlorobutane, b. p. 50–60° at 80 mm., 30–40° at 30 mm., has been removed, the mixture of the two *dl*-chlorohydrins distils at 50–60° under a pressure of 30 mm.;[15] yield, 160 g. (55%).

Some attempt was made to separate the mixture of chlorohydrins by fractional distillation, but when it was found that the oxides could be separated more easily, the purification of the chlorohydrins was abandoned. Later, when a good supply of *cis*-2-butene was available, its chlorohydrin was prepared and the properties determined as follows: b. p. 51.5–52.5° (30 mm.); d^{20}_4 1.0626; $n^{20}\text{D}$ 1.4403.

Preparation of 2,3-Epoxybutane.—In a 2-liter three-necked flask provided with a mercury-sealed stirrer, a bent tube leading to a condenser, a dropping funnel, and a thermometer extending nearly to the bottom of the flask, 1000 g. (16–17 moles) of technical potassium hydroxide flakes (or pellets) is dissolved in 500 ml. of water, with stirring. With the solution at a temperature of 90°, 400 g. (3.72 moles) of 3-chloro-2-butanol is slowly added during vigorous agitation, over a period of about two hours. A slow current of air drawn through the apparatus at the end will carry over some additional oxide. The liquid is dried by anhydrous potassium carbonate (calcium chloride must not be used, as it forms an addition product with the higher boiling oxide), filtered and distilled. The 50–60° fraction is collected;[16] yield 235 g. (87–90%).

The Isomeric 2,3-Epoxybutanes.—A quantity of 1700 g. of the mixed epoxybutanes was subjected to three fractional distillations through a 2-meter column filled with glass rings and under total reflux, using a high reflux ratio, and making cuts at 0.5° intervals. Bromobenzene was added to the last fraction, as a still base. The distillation curves are shown in Fig. 3. The over-all recovery at the end of the third distillation was 90%. No 1,2-epoxybutane could be isolated. The physical properties of the isomeric oxides are given in Table I.

TABLE I

PROPERTIES OF THE ISOMERIC 2,3-EPOXYBUTANES

	trans	*cis*
B. p., ° C., 747 mm.	53.6–54.1	59.9–60.4
Sp. gr., 20/20	0.8053	0.8272
Refractive index, $n^{20}\text{D}$	1.3736	1.3826
Molar refraction, *M*D	20.45	20.34
M. p., ° C.	−85 (?)	−80 (?)
Weight recovered, g.	661	280
Estimated purity, %	96	90

The specific gravities were determined with a 10-ml. pycnometer; the refractive indices with an Abbé refractometer; and the melting points, which are approximate only, with a pentane thermometer immersed in a small test-tube of the material cooled with liquid air in a Dewar flask. The tube was raised or lowered until crystals surrounded the lower half of the thermometer bulb, and the reading was taken after it had remained constant over a period of time while there was no appreciable melting or freezing. The purity of each oxide was estimated from the melting point of the crude glycol obtained when the oxide was hydrated.

Later, after the pure chlorohydrin had been prepared from pure *cis*-2-butene, pure *cis*-2,3-epoxybutane was prepared in 75% yield. Because of the relatively small amount, *viz.*, 10.7 g., the yield was low and the constants were not as satisfactory as those in Table I; b. p. 58.4–61.3°; $n^{20}\text{D}$ 1.3822.

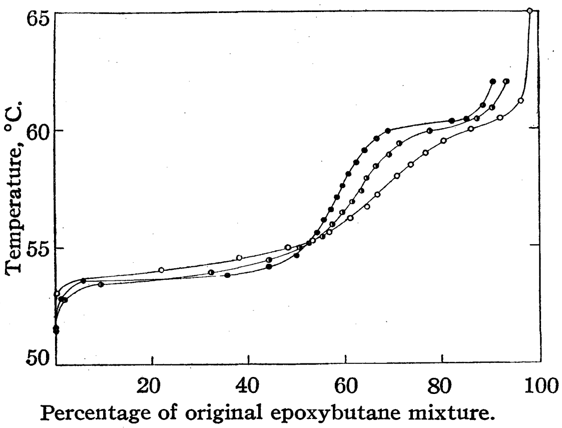

Fig. 3.—Fractionation of epoxybutanes: -○-○-○-, first distillation; -◐-◐-◐-, second distillation; -●-●-●-, third distillation.

Optically Active 2,3-Epoxybutane

Preparation of *dl*-3-Dimethylamino-2-butanols.—In a pressure bottle are placed 30 g. (0.417 mole) of crude 2,3-epoxybutane (*cis* and *trans* mixture) and 75 ml. of approximately 30% (6.1 normal) aqueous dimethylamine solution (0.457 mole). The bottle is placed in a water-bath which is slowly brought to boiling and kept at this temperature for about one hour. After cooling, several batches are united, nearly saturated with potassium carbonate and extracted three times with ether. The ether extracts, after drying with powdered potassium hydroxide, are fractionated under a pressure of 30 mm. through a 2-meter column with total reflux, yielding 33% of product distilling at 53.7–54.7°, 47% at 72.0–72.3°, total recovery, including intermediate fractions, 86%. At 743 mm. the two main fractions distilled at 141.0–142.0° and 152.5–153.5°, respectively.[17] These dimethylamino alcohols were also prepared from the pure oxides, but since these amino alcohols are more easily purified than the oxides, it is preferable to proceed as described above.

Since the *cis* oxide yielded the lower boiling and the *trans*

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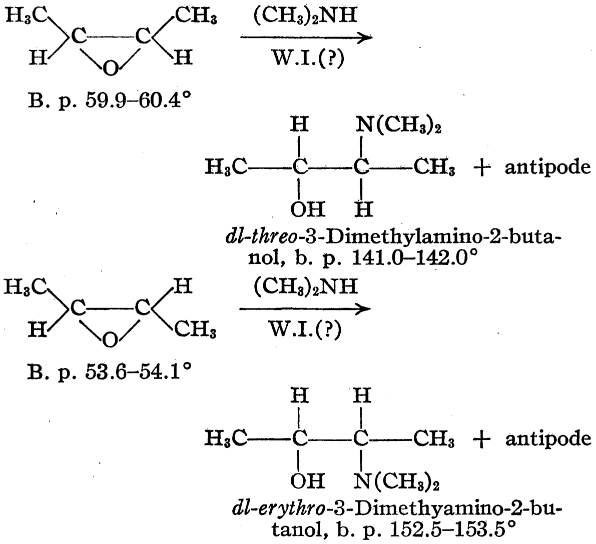
[15] Fourneau and Puyal, *Bull. soc. chim.*, **31**, 424 (1922), reported 138–140° as the boiling point of the chlorohydrin.

[16] Fourneau and Puyal[15] report 56° as the boiling point.

[17] Forneau and Puyal[15] report the boiling point of 3-dimethylamino-2-butanol as 53° under 18 mm., and 145° under ordinary pressure.

oxide the higher boiling dimethylamino alcohol, it is possible to assign a provisional configuration to each of these *dl*-amino alcohols, assuming that a Walden inversion takes place here, as it does when the oxides are hydrated. In conformity with the nomenclature adopted for the α,β-dihydroxybutyric acids[18] the amino alcohol corresponding to the *dl* glycol is called the *threo* and the one corresponding to the *meso* glycol is called the *erythro* amino alcohol (Fig. 4).



dl-threo-3-Dimethylamino-2-butanol, b. p. 141.0–142.0°

dl-erythro-3-Dimethyamino-2-butanol, b. p. 152.5–153.5°

Fig. 4.—Configurations of the *dl*-3-dimethylamino-2-butanols.

Preparation of *dl*-α,β-Dimethylcholine Iodides.—A solution of 29.5 g. (0.252 mole) of a pure *dl*-3-dimethylamino-2-butanol in 150 ml. of absolute ether is added to a similar solution of 36 g. (0.254 mole) of methyl iodide. A cloudiness develops at once. The higher boiling alcohol reacts much more rapidly than the lower boiling isomer and it is necessary to cool the solution of the former. After standing for several days at room temperature the solid is filtered off and dried. Yields are 93 and 84%, respectively. Iodine,[19] found, 48.8%; calculated for $C_7H_{18}ONI$, 49.0%.

Regeneration of 2,3-Epoxybutanes from *dl*-α,β-Dimethylcholine Iodides.—An aqueous solution of the choline, obtained by adding 9 g. (an excess) of silver oxide to 20 g. of a pure iodide in 20 ml. of water and filtering out the silver iodide, is distilled through a well-cooled condenser. On saturating the aqueous distillate with potassium carbonate, a lighter phase of trimethylamine and epoxybutane separates. This is dried with solid potassium carbonate and fractionally distilled. The yield of oxide is 2.4 g. (43%). The iodide prepared from the lower boiling dimethylamino alcohol yielded an oxide, b. p. 56.0–58.3°, the glycol from which melted at about 4°, while the one from the higher boiling alcohol yielded an oxide, b. p. 51.3–53.8°, whose glycol melted at 28°. This shows that the original oxide was regenerated in each case.

Resolution of *dl-erythro*-α,β-Dimethylcholine.—To 128 g. (0.497 mole) of dimethylcholine iodide prepared from *dl-erythro*-3-dimethylamino-2-butanol dissolved in 350 ml. of absolute alcohol is added an excess of silver oxide which has been washed with alcohol. The mixture is agitated until the solution fails to give a precipitate with silver nitrate in dilute nitric acid and the solid is filtered out. To the solution is added 76.5 g. (0.510 mole) of *d*, tartaric acid. The resulting bitartrate, at first an oil, is recrystallized many times from absolute alcohol. The specific rotation of the first fraction was $[\alpha]_{Hg}$ +17.9°, and of the final fraction, +19.1°, after nine crystallizations. Although this final product was probably contaminated with some of its stereoisomer, it was used for preparing an oxide having optical activity.

Anal. Calcd. for $C_{10}H_{21}O_7N$: N, 5.24. Found:[19] N, 5.11.

Optically Active 2,3-Epoxybutane.—The pyrolysis of cholines, by the method of Rabe and Halbensleben and of Read and Campbell,[8] was applied to the α,β-dimethylcholine obtained from the tartrate of higher rotation, without, however, isolating the choline. To a solution of 14 g. (0.05 mole) of α,β-dimethylcholine bitartrate, $[\alpha]_{Hg}$ +18.8°, from the lower boiling oxide, in water, made neutral to phenolphthalein with dilute sodium hydroxide, was added an aqueous solution of 19 g. (0.112 mole) of silver nitrate. After filtering off the silver tartrate, the specific rotation, $[\alpha]_{Hg}$, of dimethylcholine nitrate, was +3.0°. The volume was reduced to 15 ml. by evaporation under reduced pressure, 5 g. of sodium hydroxide was added and the solution was distilled at atmospheric pressure. The aqueous distillate, 12–14 ml., was diluted to 18 ml. Its observed rotation, α, was −1.40° in a 2-dm. tube. Assuming a 50% yield of oxide, as in other experiments, the specific rotation $[\alpha]_{Hg}$ of the oxide is approximately −7°. The distillate obtained by the same procedure from unresolved *dl-erythro*-α,β-dimethylcholine *d*-tartrate had zero rotation. The active oxide was not isolated, but was hydrated to a glycol.

The 2,3-Butanediols and the 2,3-Dibromobutanes

Preparation of the Inactive 2,3-Butanediols.—The 2,3-epoxybutanes hydrate readily to the corresponding glycols, in the presence of a strong acid. The best acid to use is perchloric acid[20] and the weight ratio of water to oxide should not be much below 3, otherwise undesirable by-products, probably ethers, result. To a mixture of 300 ml. of water and 90 g. (1.25 mole) of 2,3-epoxybutane is added 6 drops of 60% perchloric acid and the mixture is cooled under the tap from time to time so that the stopper will not be forced from the flask. After five or ten minutes the undissolved oxide goes into solution. The solution is neutralized at the end of an hour and then fractionally distilled at reduced pressure, the pressure being decreased gradually so that the temperature of the liquid does not rise above 100°. The water fractions are used for hydrating subsequent batches of the same oxide; yield 101–107 g. (90–95%).

The glycols are purified by crystallization from dry isopropyl ether.[21] The *meso* glycol, m. p. 34.4°, is but mode-

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[18] Braun, THIS JOURNAL, **51**, 228 (1929).

[19] Analysis by D. Pressman.

[20] Brönsted, Kilpatrick and Kilpatrick, *ibid.*, **51**, 428 (1929).

[21] Drying is easily accomplished by distillation through an efficient fractionating column and discarding the fraction distilling below 67°.

rately soluble and a good recovery is obtained when the solution is cooled from about 27 to 0°. Four crystallizations give a very pure product. The *dl*-glycol, m. p. 7.6°, is very soluble and the solution must be cooled to temperatures approaching that of solid carbon dioxide. Five or six crystallizations are necessary.

Properties of the 2,3-Butanediols.—Some physical properties of the inactive glycols and derivatives are shown in Table II. The melting point of each crude glycol shows that the purity of the *meso* isomer was about 96%, and of the *dl* isomer about 90% (from Fig. 5), assuming that no water was present. Since water was present, the purity was actually higher than indicated by the above figures.

TABLE II

PROPERTIES OF THE INACTIVE 2,3-BUTANEDIOLS

Glycol, configuration	*meso*	*dl*
Oxide from which obtained	*trans*	*cis*
Glycol, b. p., ° C., 742 mm.	181.7	176.7
Glycol, b. p., ° C., 16 mm.	89	86
Glycol, m. p., ° C.	34.4	7.6
Glycol, m. p., ° C., crude	31.8	3.0
Diacetate, m. p., ° C.	2.5–3.0	41.0–41.5
Diacetate, b. p., ° C., 5.5 mm.	66	70
Dibenzoate, m. p., ° C.	75.5–76.2	53.0–54.0
Di-*p*-bromobenzoate,[a] m. p., ° C.	139.0–139.8	205–209

[a] Analysis[19] of the di-*p*-bromobenzoates for bromine by the Carius method gave: *meso* ester, 36.5%; *dl*-ester, 34.2%; calculated for $C_{18}H_{16}O_4Br_2$, 35.1%.

The esters were prepared by the use of a large excess of the corresponding acid chloride in the presence of either pyridine or dimethylaniline. The yields were above 100% on the basis of monoesters. The liquid diacetate was crystallized from isopropyl ether by cooling with solid carbon dioxide. The lower melting dibenzoate cannot be obtained crystalline unless the glycol is quite pure. It is surprising that the higher melting glycol yields a lower melting diacetate and di-*p*-bromobenzoate, but a higher melting dibenzoate.

For larger scale preparation of the diacetates, the following procedure gave good results: to a mixture of 117 g. (1.15 moles) of acetic anhydride and 45 g. (0.50 mole) of the glycol is added a drop of concd. sulfuric acid. It is necessary to cool the flask after a short time. After standing a day the mixture is fractionally distilled under reduced pressure. When this is 5.5 mm., the *meso* diacetate distils at about 66° and the *dl* at about 70°; yield 78–83 g. (90–95%). A given glycol yields the same diacetate, whether prepared with acetyl chloride in the presence of a tertiary amine or with acetic anhydride, as above. The *dl*-diacetate is easily purified by crystallization from petroleum ether. It is more convenient to purify this diacetate than to attempt to purify the corresponding glycol. Harden and Walpole[10] give 181–183° as the boiling point, and 28° as the melting point of their glycol, obtained by bacterial fermentation. Böeseken and Cohen[9] report a boiling point of 177–180° and a melting point of 25° for a similar product. Ciamician and Silber[22] report that one dibenzoate melts at 77° and that the other is a liquid.

Melting Point Curve.—The effect of mixing each inactive glycol with a small amount of the other is shown in Fig. 5. The readings were obtained by slowly warming, in a stoppered test-tube provided with a calibrated thermometer, a partially solidified mixture of the two glycols. The glycols are very hygroscopic and must be protected from the moisture of the air. When water is added, the curve obtained with the *meso* glycol, on a molal basis, is almost identical with the one shown.

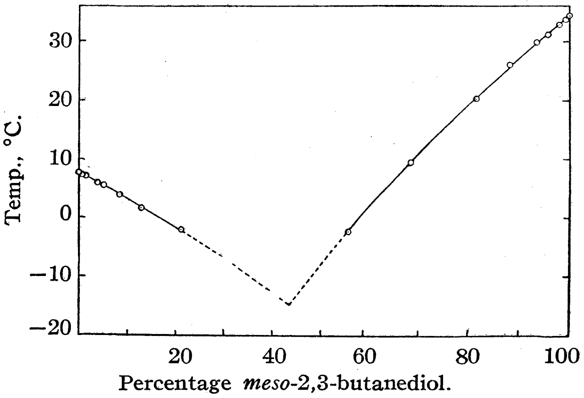

Fig. 5.—Melting point curve of the inactive 2,3-butanediols.

Configurations of the 2,3-Butanediols; Hydration of the Active Oxide.—The aqueous distillate obtained from the decomposition of the partially resolved dimethylcholine (page 2400) contained trimethylamine and an optically active 2,3-epoxybutane. It was carefully acidified with 60% perchloric acid and the solution was allowed to stand for a day. The solution was cooled, freed from trimethylammonium perchlorate by filtration, and was then found to have zero rotation. The resulting solid glycol was therefore the internally compensated form. If it were not, then it should possess optical activity. **Partial Resolution of the Liquid Glycol.** A mixture of 11.1 g. (0.123 mole) of the liquid glycol and 13.8 g. (0.059 mole) of *d*-camphorsulfonic acid was placed in a small flask in an oven at 65°, and left there for three weeks. The unreacted glycol was then distilled out of the mixture under a pressure of 3 mm. The 2.9 g. of recovered glycol was dissolved in 18 ml. of water; the solution had an observed rotation of +0.13 ± 0.02°. When the solid glycol was similarly treated, the product had zero rotation. **Asymmetric Hydration of *cis*-2,3-Epoxybutane (Higher Boiling).** When 10 g. (0.139 mole) of the *cis* oxide was added to a solution of 5 g. of *d*-camphorsulfonic acid in 25 ml. of water, heat developed at once. The observed rotation of the resulting glycol, 9.5 g. (0.105 mole) in a 1-dm. tube, was +0.06°, and of 11 g. of glycol, from another experiment, was +0.13° in a 2-dm. tube. The glycol was a liquid. The *trans* oxide, under the same treatment, yielded a solid glycol of zero rotation. Likewise, when the *cis* oxide was hydrated in the presence of *d*-tartaric acid, and the tartrate ion was removed as insoluble silver tartrate before distillation, the observed rotation of the resulting liquid glycol was −0.05°; the solid glycol from the *trans* oxide had zero rotation.

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(22) Ciamician and Silber, *Ber.*, **44**, 1280 (1911).

Preparation of the Isomeric 2,3-Dibromobutanes.—When attempts were made to prepare these from the glycols by the usual methods, *i. e.*, concentrated hydrobromic acid, concentrated hydrobromic acid and zinc bromide, phosphorus tribromide or phosphorus pentabromide, the mixtures became dark colored and only very small yields of the dibromides were obtained. Moreover, the products were mixtures. A pinacol rearrangement was responsible for the low yields. This was established by isolating methyl ethyl ketone from the reaction mixture. The dibromides can be prepared in good yield by the action of hydrobromic acid upon the diacetates.

Saturated aqueous hydrobromic acid is prepared by saturating the constant boiling acid with dry hydrogen bromide (from tetralin and bromine). In 200 ml. of this solution is dissolved 52 g. (0.3 mole) of a diacetate and the mixture is allowed to stand at room temperature for three or four days. In a short time the solution becomes cloudy and after some time a layer of dibromobutane rises to the top. This is separated, washed with water, aqueous sodium carbonate and water and then dried with calcium chloride; yield of crude dibromide, 61 g., 94%. When fractionated through a 40-cm. Weston column[23] with total reflux, about 50 g. distils within a range of 0.2°.

Properties of the Dibromides.—The properties of the dibromides, shown in Table III, are practically identical with the properties of the dibromobutanes obtained by a wholly different synthetic method.[24] The configurations of the butenes, assumed in a previous paper, are now known to be the correct ones, for they have been settled by Brockway and Cross[25] through electron diffraction studies.

TABLE III

PROPERTIES OF THE INACTIVE 2,3-DIBROMOBUTANES

Dibromide configuration	*dl*	*meso*
Diacetate from which obtained	*meso*	*dl*
Dibromide, b. p., ° C., 50 mm.	73.2–73.4	76.4–76.6
Dibromide, sp. gr., d^{20}_4	1.7783	1.7922
Dibromide, n^{25}D	1.5098	1.5120
Dibromide, k^a	0.0541	0.0285

[a] Specific reaction rate constant with KI; see ref. 3; the authors are indebted to Mr. Saul Winstein for these values.

The dibromobutanes shown in Table III are reassigned the configurations previously given them. These configurations still appear to be the correct ones, in the absence of new evidence, on the usual assumption that one Walden inversion takes place when bromine adds to a pure 2-butene.[1,17]

Summary

trans-2-Butene has been obtained from *cis*-2-butene through a series of changes, as follows: *cis*-2-butene ⟶ 3-chloro-2-butanol ⟶ *cis*-2,3-epoxybutane ⟶ *dl*-2,3-butanediol ⟶ *dl*-butanediol diacetate ⟶ *meso*-2,3-dibromobutane ⟶ *trans*-2-butene. Through a similar series of changes, *cis*-2-butene has been obtained from *trans*-2-butene.

The lower boiling 2,3-epoxybutane has been shown to have the *trans*, and the higher boiling to have the *cis* configuration. The liquid 2,3-butanediol has the *dl* and the solid the *meso* configuration.

It has been shown that a Walden inversion is involved in the formation of the *dl*-glycol from the *cis* oxide and of the *meso* glycol from the *trans* oxide. It is believed that five inversions are involved when either of the 2-butenes is converted into its stereoisomer, as outlined above.

The inactive 2,3-butanediols undergo a pinacol rearrangement in contact with concentrated hydrobromic acid.

The butene mixture resulting from the decomposition of 1-butanol by hot sulfuric acid (60 by volume) is approximately 35% *cis*-2-butene and 65% *trans*-2-butene.

PASADENA, CALIF. RECEIVED AUGUST 10, 1936

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(23) Weston, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 177 (1931).

(24) Young, Dillon and Lucas, THIS JOURNAL, **51**, 2528 (1929). Their butenes boiled (when corrected to 760 mm.) at the same temperatures as the butenes prepared by Kistiakowsky, *et al.*[5]

(25) Brockway and Cross, *ibid.*, **58**, 2407 (1936). The melting points, by Kistiakowsky, *et al.*, ref. 5, lead to the same conclusion.

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 566]

The Structure of the Pentaborane B_5H_9

BY S. H. BAUER AND LINUS PAULING

The hydrides of boron are especially interesting to the chemist because of the failure of the usual valence theory to account for their observed formulas and properties. Despite the large amount of experimental[1] and theoretical[2] work which has been done in this field in recent years, little progress has been made in assigning structural formulas to these substances, and it seems probable that in order for this to be done with confidence it will be necessary to obtain information about the structure of the molecules by the application of physical methods. Electron diffraction and x-ray methods have been applied in a few cases: the boron–boron distance in B_2H_6 has been evaluated as 1.8–1.9 Å. from x-ray powder photographs,[3] the structure of $B_3N_3H_6$ has been shown to be similar to that of benzene by an electron-diffraction study,[4] and the unit of structure and space-group symmetry of $B_{10}H_{14}$ have been determined.[5] We have now investigated the pentaborane B_5H_9 by the electron diffraction method, and have found a model which accounts satisfactorily for our photographs and which can be accepted with considerable confidence as representing correctly the atomic arrangement in molecules of this substance.

Preparation of the Photographs.—We were provided with 18 cc. (S. T. P.) of B_5H_9 gas through the generosity of Dr. Anton B. Burg of the University of Chicago. The substance (with melting point $-46.9°$ and vapor pressure 65 mm. at $0°$) had been prepared from diborane by the method of Schlesinger and Burg[6] and purified by repeated fractional condensation. The amount of boron trichloride and foreign boron hydrides present is believed to have been very small.

Eleven useful photographs, of varying density, were prepared with the electron diffraction apparatus designed and recently described[7] by Brockway, using the standard technique of handling the borane.[8] The gas was kept at liquid-air temperature in a bulb connected with the nozzle of the apparatus through a stopcock and was warmed to room temperature only long enough for each exposure to be made, in order to minimize the chance of decomposition and reaction with stopcock grease. The film distance was 10.43 cm. and the electronic wave lengths used about 0.06 Å.

Description and Interpretation of the Photographs.—The photographs show five rings, with the qualitative character sketched in Fig. 1. The first ring appears as a small maximum followed by a barely perceptible minimum, the second ring looking like a shelf. The third ring is sharp and strong, with well-pronounced minima on each side. The fourth ring appears broad, and the fifth sharp. Values of s ($= (4\pi \sin \theta/2)/\lambda$) for the apparent maxima and minima are given in Table I; these are averages of closely-agreeing measurements made on eleven photographs by two experienced observers (Brockway and Pauling). Estimated apparent intensities (I) of the rings are also given in the table.

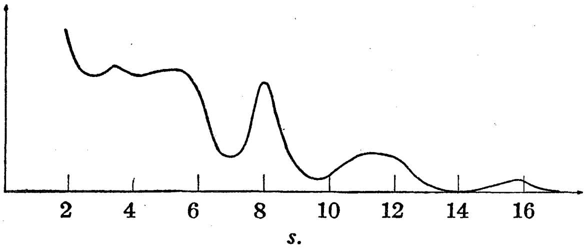

Fig. 1.—Curve representing the visual appearance of electron diffraction photographs of B_5H_9.

TABLE I

Max.	Min.	I	s, obsd.	s, calcd. for model R	B–B, Å.
1		1	3.36	4.18	(2.21)
2		3	5.34	5.59	(1.86)
	3		6.80	6.75	1.767
3		5	8.00	7.94	1.766
	4		9.67	9.40	1.730
4		3	11.49	11.40	1.766
5		1	15.61	15.54	1.771
				Average	1.760

The five-term radial distribution function[9] cal-

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[1] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1932; Stock and collaborators, *Z. anorg. allgem. Chem.*, **225**, 221–270 (1935); H. I. Schlesinger and collaborators, THIS JOURNAL, **58**, 407 (1936), and earlier papers.

[2] See R. S. Mulliken, *J. Chem. Phys.*, **3**, 635 (1935), and references quoted by him.

[3] H. Mark and E. Pohland, *Z. Krist.*, **62**, 103 (1925).

[4] A. Stock and R. Wierl, *Z. anorg. allgem. Chem.*, **203**, 228 (1931).

[5] H. Möller, *Z. Krist.*, **76**, 500 (1931).

[6] I. Schlesinger and A. B. Burg, THIS JOURNAL, **53**, 4321 (1931).

[7] L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

[8] See A. B. Burg, THIS JOURNAL, **56**, 499 (1934), and references quoted therein.

[9] L. Pauling and L. O. Brockway, *ibid.*, **57**, 2684 (1935).

culated for these *s* and *I* values is shown in Fig. 2. The peaks at 1.17 and 1.73 Å. can be accepted as representing bonded B–H and B–B interactions, respectively, and that at 2.52 Å. as representing in the main the interaction of boron atoms separated by another boron atom in a chain or ring, the ratio 2.52/1.73 corresponding to a B–B–B bond angle of 93°. The outer peaks are not reliable, and the curve provides no further evidence for choice among various ring and chain models.

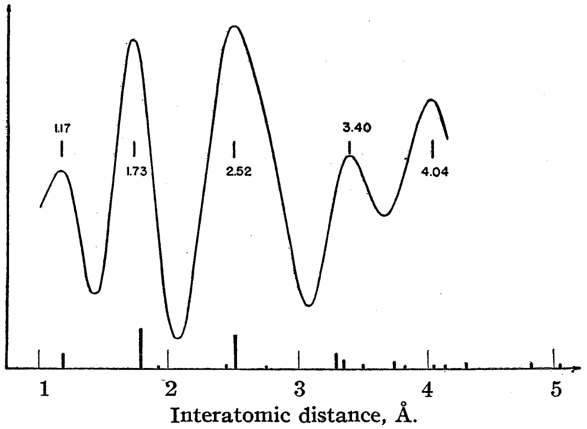
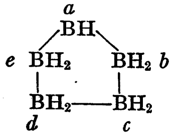


Fig. 2.—Radial distribution curve for B_5H_9. The small rectangles below represent interatomic distances for the final model R.

Intensity curves were calculated for eighteen models, described below. In all of these models except B the B–H distances were taken as 1.18 Å., the sum of the single-bonded radii,[10] this value being supported by the radial distribution value 1.17 Å. Bonded B–B distances were assumed in the neighborhood of 1.78 Å. (the sum of single-bond radii), 1.73 Å. (as given by the radial distribution curve), or 1.60 Å. (sum of double-bond radii). The hydrogen atoms were located at tetrahedron corners for boron atoms forming four bonds and at coplanar triangular corners for boron atoms forming three bonds. The B–B–B bond angles were taken as 109°28′ for boron atoms forming four bonds and 120° for those forming three bonds except where otherwise noted.

A–D, Models of type



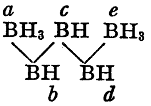
A. All angles 108°; all B–B bond distances 1.78 Å.

B. Same as A, except all B–H distances 1.25 Å.

C. Angles *c* and *d* 107°, *b* and *e* 105°, *a* 116°; B–B distances *ab* and *ae* 1.66 Å., others 1.78 Å.

D. Angles *c* and *d* 106°, *b* and *e* 104°, *a* 120°; B–B distances *ab* and *ae* 1.60 Å., others 1.78 Å.

E–G, Models of type

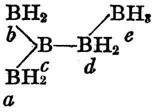


E. All B–B–B angles tetrahedral; B–B distances 1.78 Å.

F. Angles at *c* 120°, others tetrahedral; B–B distances *bc* and *cd* 1.66 Å., others 1.78 Å.

G. Same as F, but with *bc* and *cd* 1.60 Å.

H–J, Models of type

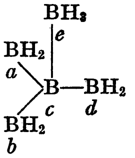


H. B–B–B angles at *c* 120°, others tetrahedral; B–B distances *ca*, *cb*, and *cd* 1.60 Å., *de* 1.78 Å.

I. All B–B–B angles tetrahedral; all B–B distances 1.78 Å.; boron atom *e* oriented to minimize distances *ae* and *be*.

J. Same as I, but with maximum values of *ae* and *be*.

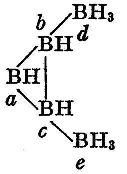
K.



Boron atoms *abcd* coplanar, with 120° angles at *c*, and bond *ce* perpendicular to plane; B–B distances *ac*, *be* and *cd* 1.60 Å., *ce* 1.78 Å.

L. Same as K but with all angles at *c* tetrahedral and all B–B distances 1.78 Å.

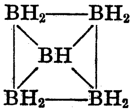
M.



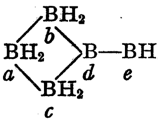
Angles tetrahedral except for distortion to 60° in triangle; B–B distances 1.78 Å.; atoms *d* and *e* both above plane of triangle.

N. Same as M except *d* above and *e* below plane of triangle.

O. Square pyramid, with BH above plane of BH_2's. All B–B distances 1.78 Å.



P–R. Models



Angles in coplanar square 90°; HBH angles tetrahedral; all B–B distances 1.78 Å.

P. Boron atom *e* above plane of square, with angle *ade* 90°.

Q. Same as P but with *ade* 135°.

R. All boron atoms coplanar.

In calculating the intensity curves, shown in Figs. 3, 4 and 5, all terms in the expression[11] $I = \Sigma_{ij}Z_iZ_j(\sin l_{ij}s)/l_{ij}s$ were used except those corresponding to two hydrogen atoms separated by three or more boron atoms. Only one orientation of each BH_3 group was considered, the effect of rotation being negligible.

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(10) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

(11) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

All models A to N are eliminated by comparison of their curves (Figs. 3 and 4) with the photographs (Fig. 1), there being not even rough qualitative agreement in any case. The discrepancies are so striking as to show that not only these models but also others obtained from them by small changes in distances and angles or by rearrangement of hydrogen atoms are unsatisfactory.[12]

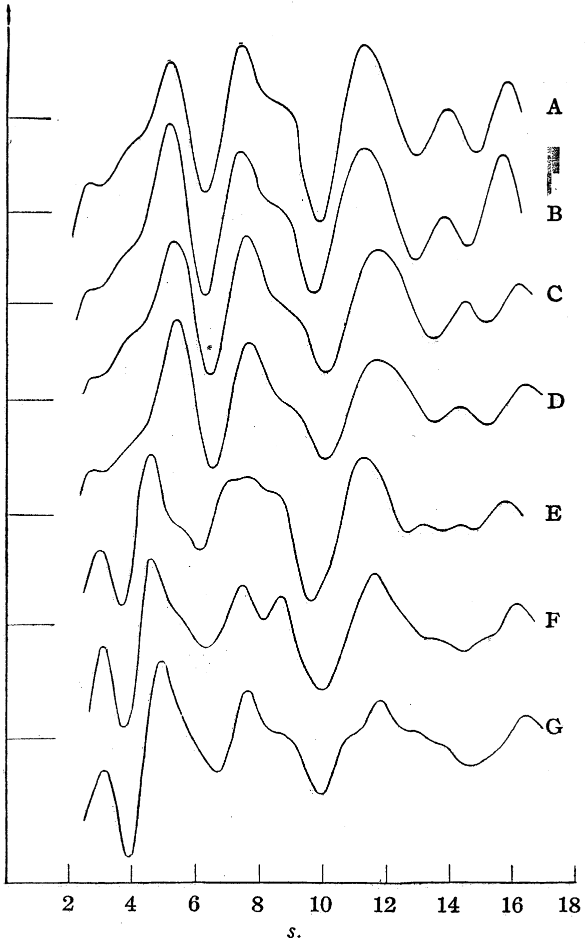

Fig. 3.—Calculated intensity curves for models A to G, with vertical scale twice that in Figs. 4 and 5.

On the other hand, each of the models involving a four-membered square boron ring (Fig. 5) shows rough agreement with the photographs, especially in regard to the strong and sharp third ring. Whereas models O, P and Q are not completely satisfactory, however, the agreement shown by model R is extremely good, the visual appearance of the photographs being well reproduced for all five rings. (The absence on the photographs of a small peak shown at about s = 14 on the curve for R may be attributed to the weakness of the photographs in this region, the much larger peak at s = 16 appearing only faintly.) We accordingly accept model R as representing the structure of the B_5H_9 molecule. The quantitative comparison of $s_{\text{obsd.}}$ and $s_{\text{calcd.}}$ values shown in Table I leads to the value 1.76 Å. for the B–B distances, with an estimated probable error of ±0.02 Å.

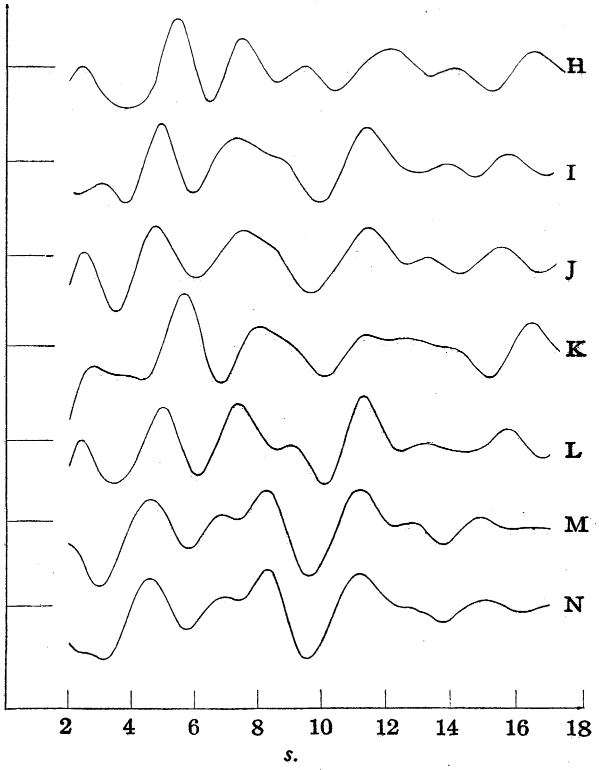

Fig. 4.—Calculated intensity curves for models H to N.

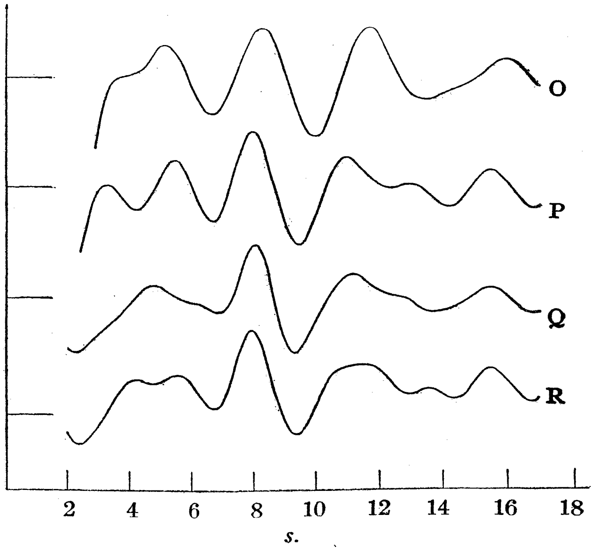

Fig. 5.—Calculated intensity curves for models O to R

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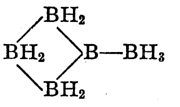
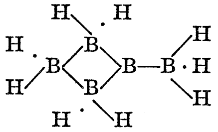
(12) Models A to G were also eliminated by application of the analytic method [S. H. Bauer, *ibid.*, **4**, 406 (1936)].

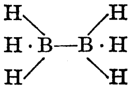
Discussion of the Structure.—We have shown that the various ring and chain models which suggested themselves to us for test are unsatisfactory except for those involving a four-membered ring of boron atoms, and that of these the model in which the fifth boron atom is coplanar with the ring is definitely superior to the others. In this structure



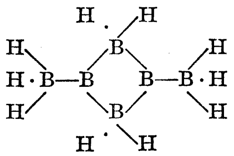
we have not tested the assumed distribution of the hydrogen atoms among the boron atoms; that shown seems to us to be the only reasonable one. The value 1.76 ± 0.02 Å. found for the boron–boron bond distances may be an average of several which differ slightly from one another. For the B–H bond distance the comparison of Table I leads to 1.17 Å., which is, however, determined to a large extent by the assumed model. The radial distribution curve also leads to the value 1.17 Å. We have not endeavored to test the possibility of distortion of the four-membered ring from a square. From experience with other substances we would estimate from the agreement shown by model R that the angles are equal to within about 10° and the B–B distances are equal to within about 5%.

At present discussion of the electronic structure of the boron hydrides is still speculative. We might point out that the structure

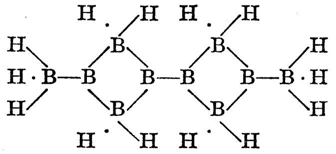


for B_5H_9, involving electron-pair bonds between boron atoms and electron-pair or one-electron bonds between boron and hydrogen atoms,[13] with no more than one one-electron bond per boron atom, is closely similar to the structure  suggested for B_2H_6 by Sidgwick[14] and Pauling,[15] and that these structures are supported by the observed interatomic distances, which correspond to single bonds.

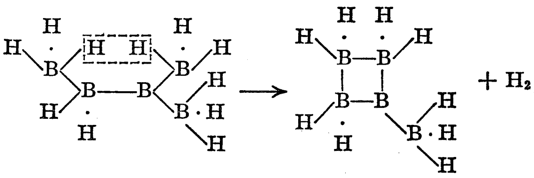
Starting with the basic assumption that a four-membered ring of boron atoms such as is found in B_5H_9 brings about a stability of the hydride as contrasted with a straight or forked chain arrangement which introduces in the other boranes a characteristic lack of stability, we tentatively suggest the related structures



(or the corresponding 1,2-structure) and



for B_6H_{10} and $B_{10}H_{14}$, respectively. Of the entire class of hydrides these show the closest analogies to B_5H_9 in most chemical properties. These structures are compatible in the main with the chemical behavior of the substances. Besides the factor of stability we may mention that the number of molecules of ammonia these boranes add is reported to be equal to the number of one-electron bonds present in the above structures. Further, the reported synthesis of B_5H_9 from B_5H_{11} is reasonably accounted for in the following way



and a similar reaction can be written for the formation of B_6H_{10} from B_6H_{12}. The facts that B_5H_{11} is produced under very similar but milder conditions than is B_5H_9[16] and that under the less stringent circumstances the higher hydride is always present along with the lower one lend strong support to the above equation.

We wish to thank Dr. Anton B. Burg for giving us the pentaborane and for a number of interesting communications, and Dr. L. O. Brockway for the use of the electron diffraction apparatus and for his aid during the investigation.

Summary

From the study of electron diffraction photographs of B_5H_9 it is concluded that the substance

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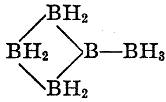
[13] There is, of course, resonance between the B:H and B·H bonds, making the hydrogen atoms equivalent. In these formulas we have used a line to represent an electron-pair bond and a dot to represent a one-electron bond.

[14] N. V. Sidgwick, "The Electronic Theory of Valency," London, 1929, p. 103.

[15] L. Pauling, This Journal, **53**, 3225 (1931).

[16] A. Stock and W. Mathing, *Ber.*, **69**, 1456 (1936).

has the structure  the fifth boron atom being coplanar with the square four-membered ring. The values found for interatomic distances are B–B = 1.76 ± 0.02 Å. and B–H = 1.17 ± 0.04 Å.

PASADENA, CALIF.

RECEIVED SEPTEMBER 8, 1936

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 567]

The Molecular Structures of the 2-Butenes and the 2,3-Epoxybutanes

BY L. O. BROCKWAY AND PAUL C. CROSS

During an investigation of the reactions of the 2-butenes and some of their derivatives conducted in this Laboratory by Professor Howard J. Lucas[1,2] and his collaborators it was necessary to distinguish between the *cis* and *trans* forms of the 2-butenes and also of the 2,3-epoxybutanes. At the request of Professor Lucas these substances have been investigated by the electron diffraction method of determining the molecular structure of gas molecules. The experimental procedure has been described in detail.[3]

2-Butenes.—The two isomers of 2-butene have boiling points of 3.0 and 0.3°, respectively, at 745 mm. The compounds were photographed at a camera distance of 10.43 cm. with electrons having a wave length of about 0.06 Å. The photographs from each of the compounds show four maxima and in general are very similar in appearance. Two distinguishing features were observed, however. Photographs from the lower boiling butene show a pronounced inner maximum (preceding the first measured maximum at $s = 5.67$ in Fig. 1) which does not appear on the other photographs. The fourth minimum in the photographs of this compound is broad and flat in comparison with the sharp, distinct fourth minimum in the photographs of the higher boiling compound.

Calculations of the theoretical diffraction curves were made with the aid of the formula, $I = \Sigma_i\Sigma_j Z_iZ_j \frac{\sin sr_{ij}}{sr_{ij}}$, in which r_{ij} is the distance between the *i*th and *j*th atoms; the summations extend over all of the atoms in the molecule. The curves for 2-butene in Fig. 1 are based on models in which the four carbon atoms are coplanar with a distance of 1.38 Å. between the two center atoms and 1.54 Å. for the bond distances connecting the outer atoms. The C–H distances are 1.06 Å. The angle between adjacent carbon–carbon bonds is 125° and the H_3C–C–H bond 110°. In the *cis* model the two methyl groups lie on the same side of the line joining the center atoms and on opposite sides in the *trans* model. All of the interatomic interactions were included in the calculation with the exception of those with small coefficients corresponding to the H–H separations.

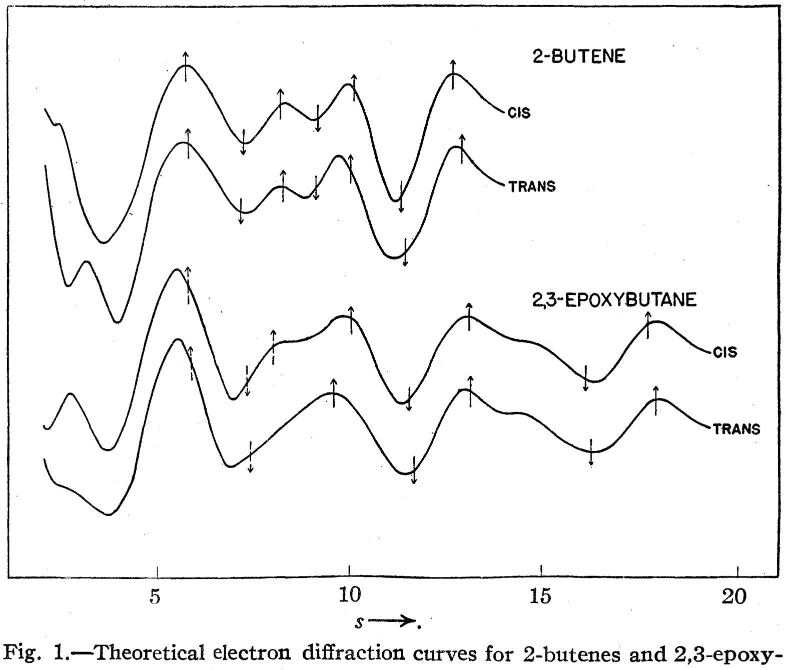


Fig. 1.—Theoretical electron diffraction curves for 2-butenes and 2,3-epoxybutanes. The arrows mark the positions of the observed maxima and minima.

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[1] W. G. Young, R. T. Dillon and H. J. Lucas, THIS JOURNAL, **51**, 2528 (1929).

[2] C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2396 (1936).

[3] L. O. Brockway, *Rev. Modern Phys.*, **8**, 239 (1936).

The curves are very much alike because most of the interatomic distances are the same in the *cis* and the *trans* models. Comparison of the coefficients of the terms in the scattering formulas shows that 80% of the total scattering is represented by terms which are identical for the two models. For this reason there are only small differences by which the *cis* and *trans* compounds can be distinguished. One such difference is the maximum at $x = 3.13$ which occurs only in the *trans* curve. Accordingly we conclude that the lower boiling compound has the *trans* configuration. The comparison of the fourth minima for the two compounds supports this assignment. As mentioned above the photographs of the lower boiling compound have a fourth minimum which is less sharp and distinct than the corresponding minimum from the higher boiling compound. The difference between the theoretical curves at this point is not marked but the *trans* curve definitely has the broader fourth minimum. The compound boiling at 0.3° (745 mm.) is, therefore, the *trans* isomer and the compound boiling at 3.0° (745 mm.) is the *cis* isomer.

G. B. Kistiakowsky and co-workers[4] have made the same assignment of the molecular configurations of the 2-butenes on the basis of their heats of hydrogenation. The compound whose heat of hydrogenation is nearly the same as that of cyclohexene was chosen as the *cis* isomer. These authors report *cis*-2-butene, b. p. 3.73° (759.8 mm.), f. p. −139.3°; and *trans*-2-butene, b. p. 0.96° (760 mm.), f. p. −105.8°.

The determination of the size of the molecule is given in Table I. The observed s values are defined by $4\pi(\sin\theta/2)/\lambda$, in which θ is the observed angle of scattering for the successive maxima and minima and λ is the effective wave length of the bombarding electrons. The calculated s values depend on the interatomic distances assumed in the molecular model described above. The general agreement between the observed points and the maxima and minima on the theoretical curves indicates that the model is probably the correct one. The final column in Table I shows the measured values of the carbon–carbon single bond distance for all of the observed points. The average value in the *cis* modification is 1.54 ± 0.03 Å., and the double bond distance is accordingly 1.38 ± 0.03 Å. The final values for the *trans* modification are 1.56 and 1.40 Å., respectively, but an extra uncertainty in the accelerating potential during the exposures allows a somewhat larger error than in the results from the *cis* compound; the deviations from the accepted value, 1.54 Å., for the single carbon–carbon bond is not significant.

TABLE I

2-BUTENES

Cis b. p. = 3.0° (746 mm.)

Max.	Min.	s, obsd.	s, calcd.[a]	C–C, Å.
1		5.67	5.72	1.527
	2	7.22	7.33	1.517
2		8.16	8.32	1.511
	3	9.13	9.06	1.556
3		10.08	9.93	1.565
	4	11.30	11.15	1.560
4		12.62	12.70	1.531
			Average	1.538
			Av. dev.	0.019

[a] See text for description of model.

Final result: C—C = 1.54 ± 0.03 Å.; C═C = 1.38 ± 0.03 Å.

Trans b. p. = 0.3° (744 mm.)

Max.	Min.	s, obsd.	s, calcd.[a]	C–C, Å.
1		5.77	5.67	1.566
	2	7.18	7.29	1.516
2		8.27	8.23	1.547
	3	9.11	8.83	1.588
3		10.02	9.72	1.588
	4	11.42	11.16	1.578
4		12.89	12.75	1.556
			Average	1.563
			Av. dev.	0.019

[a] See text for description of model.

Final result: C—C = 1.56 ± 0.04 Å.; C═C = 1.40 ± 0.04 Å.

2,3-Epoxybutanes.—The photographs of the 2,3-epoxybutanes show an extra maximum beyond those observed for the butenes. The second and third maxima of the butene photographs are only partly resolved in one of the epoxybutanes and not at all resolved in the other. Photographs of the two modifications are very similar but they are distinguishable by the partial resolution of the second maximum and the appearance of a marked inner maximum (preceding the first measured maximum at $s = 5.80$) in the photographs of the lower boiling modification.

The molecular models for which theoretical curves were drawn consist of a chain of four carbon atoms separated by distances of 1.54 Å. and with angles of 109°28′. An oxygen atom is connected to the two center atoms by bonds 1.43 Å. in length. The two center carbon atoms also

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(4) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, THIS JOURNAL, **57**, 879 (1935).

have a hydrogen atom attached to each at 1.06 Å. and angles of 109°28′ and the end carbon atoms each hold three hydrogen atoms. The CCO plane bisects the H–C–CH_3 angles on each of the center carbons and the two models differ in having the methyl groups on the same or opposite sides of the CCO planes. Terms for all interactions were included in the calculation with the exception of the H–H terms.

TABLE II

2,3-EPOXYBUTANES

Cis b. p. = 54° (747 mm.)

Max.	Min.	*s*, obsd,	*s*, calcd.[a]	C–C, Å.
1		5.80	5.52	(1.467)
	2	7.37	7.04	(1.471)
2a		8.02	8.42	(1.617)
2b		10.06	9.86	1.508
	3	11.54	11.35	1.516
3		13.10	13.08	1.538
	4	16.09	16.33	1.563
4		17.68	17.91	1.560
			Average	1.537
			Av. dev.	0.020

[a] See text for description of model.

Final result: C—C = 1.54 ± 0.03 Å.; C—O = 1.43 ± 0.03 Å.

Trans b. p. = 60° (747 mm.)

Max.	Min.	*s*, obsd.	*s*, calcd.[a]	C–C, Å.
1		5.89	5.55	(1.451)
	2	7.46	6.98	(1.442)
2		9.59	9.58	1.538
	3	11.69	11.47	1.513
3		13.16	13.05	1.526
	4	16.25	16.32	1.547
4		17.89	18.07	1.556
			Average	1.536
			Av. dev.	0.013

[a] See text for description of model.

Final result: C—C = 1.54 ± 0.03 Å.; C—O = 1.43 ± 0.03 Å.

The curve in Fig. 1 corresponding to the *cis* modification shows the inner maximum (at *s* equals about 3.0) and the slightly resolved second maximum. Accordingly, the correct assignment of the isomers of 2,3-epoxybutane is the following: *cis*—b. p. 54° (747 mm.); *trans*—b. p. 60° (747 mm.). In the work reported in reference 2 the same identification of these isomers was made by a study of the optical activity of the glycols obtained on hydrolysis of the epoxybutanes.

The results of the quantitative comparison of the photographs and the curves are contained in Table II. The observed distances from the first two points are much smaller than the average from the remaining points because of the contrast effect of the dense central image on the measurement of heavy photographs taken at short distances. The averages for each compound lead to the values: C—C = 1.54 ± 0.03 Å. and C—O = 1.43 ± 0.03 Å.

Summary

The direct determination of the molecular structures by electron diffraction of the vapors has led to the following identification of the isomeric forms and molecular sizes of *cis* and *trans* 2-butene and *cis* and *trans*-2,3-epoxybutane:

	B. p., °C.	Mm.	C–C, Å.	C=C, Å.
		2-Butene		
Cis	3.0	746	1.54 ± 0.03	1.38 ± 0.03
Trans	0.3	744	1.56 ± .04	1.40 ± .04
		2,3-Epoxybutane		
				C–O, Å,
Cis	54	747	1.54 ± .03	1.43 ± .03
Trans	60	747	1.54 ± .03	1.43 ± .03

PASADENA, CALIF. RECEIVED SEPTEMBER 15, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF MERCK & CO., INC.]

A New Method for the Preparation of Aldehydo Sugar Acetates

BY ELMER W. COOK AND RANDOLPH T. MAJOR

Aldehydo sugar acetates have been prepared by acetylation of the aldehydo mercaptals[1] followed by removal of the thio-acetal groups and also by acetylation of the aldehydo semicarbazones or oximes[2] with the subsequent removal of the semicarbazone or oxime groups.

A new method based upon Rosenmund's[3] method for the reduction of acyl chlorides to aldehydes by means of hydrogen in the presence of palladiumized barium sulfate has been found. The acetyl derivatives of the sugar acid chloride may be reduced almost quantitatively to aldehydo sugar acetates.

Experimental

Aldehydo-*d*-glucose Pentaacetate.—Pentaacetyl-*d*-gluconyl chloride[4] (5 g.) in 25 cc. of anhydrous xylene (dried over sodium) was heated under reflux in the presence of 2 g. of 5% palladiumized barium sulfate. Hydrogen was passed in at such a rate that the catalyst was kept in a lively suspension. The reduction was complete within one and one-half hours as shown by the absence of ammonium chloride fumes when a rod moistened with ammonium hydroxide was held in the escaping gases. Complete reduction may also be determined by passing the exit gases through water and testing for chloride ion. After reduction the hot xylene solution was filtered. Upon cooling aldehydo-glucose pentaacetate[5] crystallized. It was recrystallized from xylene; yield was nearly quantitative; m. p. 117–118°; $[\alpha]^{20}_{\mathrm{D}}$ $-3°$ (dry chloroform, *c*, 2); $[\alpha]^{20}_{\mathrm{D}}$ $+10°$ (in methanol, 5 min., *c*, 2) changing slowly in the dextro direction.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.21; H, 5.68. Found: C, 49.52, 49.34; H, 5.85, 5.60.

Summary

Aldehydo-*d*-glucose pentaacetate has been prepared by the reduction of pentaacetyl-*d*-gluconyl chloride.

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[1] Wolfrom, THIS JOURNAL, **51**, 2188 (1929).

[2] Wolfrom, Georges and Soltzberg, *ibid.*, **56**, 1794 (1934).

[3] Rosenmund, *Ber.*, **51**, 585 (1917).

[4] Major and Cook, THIS JOURNAL, **58**, 2474 (1936).

[5] Wolfrom, *ibid.*, **51**, 2191 (1929).

RAHWAY, N. J. RECEIVED SEPTEMBER 25, 1936

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Temperature–Concentration Equilibria in the Systems Chloroform–Chlorine and Chloroform–Bromine. The Chloroform Chlorinates[1]

BY J. ALLEN WHEAT, II, AND A. W. BROWNE

In view of the well-known fact that chlorine occupies a higher position than bromine in the activity series of electronegative elements and radicals[2] arranged in the descending order of electronegativity, it has seemed reasonable to suppose that dissolved chlorine should be removed from chloroform more readily than dissolved bromine on treatment with metallic sodium. Quite the opposite is true.

As the result of an extended series of experiments in which chloroform solutions containing free bromine and chlorine in molar ratios (Br_2:Cl_2) ranging from about 0.25 to 2.50 were subjected at room temperature to the action of metallic sodium in excess, it was found that a considerable amount of free chlorine remained in solution in every case after complete removal of the bromine had been effected.

This entirely unanticipated result might conceivably be attributable either (1) to chemical action of the chlorine upon the chloroform and lack of similar action on the part of the bromine, or (2) to formation of one or more coördination compounds between molecular chlorine and chloroform and either (a) non-formation of similar bromine compounds, or (b) formation of relatively less stable bromine compounds. The first explanation is clearly invalidated by the presence of "free" (though possibly coördinated) chlorine in the residual solutions, as already noted, and by

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by Joseph Allen Wheat, II, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Birckenbach and Kellermann, *Ber.*, **58**, 786, 2377 (1925).

the absence of hydrogen chloride and carbon tetrachloride from these solutions, as well as from controls to which no sodium was added.

In order to test the validity of the second explanation an investigation of the temperature–concentration equilibria in the binary systems chloroform–chlorine and chloroform–bromine has been undertaken. The results of this investigation are presented herewith.

Experimental Procedure.—Freezing points in the systems under investigation were determined in the conventional manner with the aid of a calibrated pentane thermometer, and with liquid air or solid carbon dioxide as refrigerant. The mixtures of chloroform and chlorine were quantitatively synthesized either (1) by introducing successive measured volumes of chlorine gas into a known amount of chloroform, or (2) by adding successive measured volumes of chloroform to a known amount of liquid chlorine. The composition of the system was accurately determined at the end of each series of temperature measurements, by treatment with potassium iodide in excess, and titration of the liberated iodine against standard sodium thiosulfate. The absence of hydrogen chloride and carbon tetrachloride from the solutions justifies the conclusion that no *chloridation*[3] of the chloroform has taken place under the conditions prevailing in the experiments.

TABLE I

TEMPERATURE–CONCENTRATION OR SOLUBILITY DATA OF THE SYSTEM $CHCl_3$–Cl_2

Temp., °C.	Concn., mole. % Cl_2	Curve (Fig. 1)
− 63.5	0.0	A. (Solid $CHCl_3$, liq., vapor)
− 64.8	3.8	AB. (Solid $CHCl_3$, satd. soln., vapor)
− 67.5	7.5	
− 70.5	11.0	
− 74.0	14.3	
− 77.5	17.5	
− 81.0	20.3	
− 84.0	23.2	
(− 90.0)	25.0	B. (Eutectic: solid $CHCl_3$, solid $(CHCl_3)_2 \cdot Cl_2$, satd. soln., vapor)
− 88.5	25.3	BCD. (Solid $(CHCl_3)_2 \cdot Cl_2$, satd. soln., vapor)
− 84.5	25.8	
− 82.0	28.6	
− 81.0	30.6	
− 79.5	32.7	
− 80.5	32.9	
− 82.0	34.9	
− 84.5	37.9	
− 87.5	40.0	
− 91.0	42.7	
− 94.0	44.3	
− 97.5	45.5	
−102.0	47.5	D. (Eutectic: solid $(CHCl_3)_2 \cdot Cl_2$, solid $CHCl_3 \cdot Cl_2$, satd. soln., vapor)
−100.0	48.0	DEF. (Solid $CHCl_3 \cdot Cl_2$, satd. soln., vapor)
− 98.0	48.6	
− 97.0	49.0	
− 99.0	51.8	
−101.5	54.1	
−105.0	56.6	
−107.5	58.5	
−111.0	60.5	
−112.0	61.6	
−114.5	63.0	
−117.0	64.0	
(−118.0)	64.7	F. (Eutectic: solid $CHCl_3 \cdot Cl_2$, solid $CHCl_3 \cdot 2Cl_2$, satd. soln., vapor)
−116.0	65.3	FGH. (Solid $CHCl_3 \cdot 2Cl_2$, satd. soln., vapor)
−113.0	66.4	
−115.5	68.0	
−118.5	68.9	
(−121.0)	69.3	H. (Eutectic: solid $CHCl_3 \cdot 2Cl_2$, solid $CHCl_3 \cdot 3Cl_2$, satd. soln., vapor)
−118.0	70.8	HIJ. (Solid $CHCl_3 \cdot 3Cl_2$, satd. soln., vapor)
−116.0	72.9	
−116.0	76.0	
−118.5	78.0	
−121.0	79.0	
(−123.0)	79.1	J. (Eutectic: solid $CHCl_3 \cdot 3Cl_2$, solid Cl_2, satd. soln., vapor)
−121.7	81.0	JK. (Solid Cl_2, satd. soln., vapor)
−118.0	84.2	
−114.5	87.8	
−108.4	93.5	
−104.5	97.8	
−102.0	100.0	K. (Solid Cl_2, liquid, vapor)

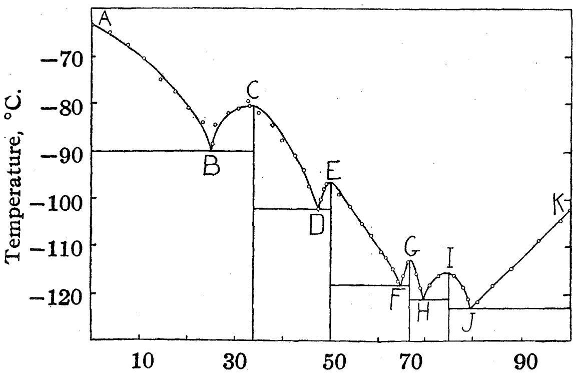

Fig. 1.—Freezing point *vs.* composition in system of $CHCl_3$–Cl_2.

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[3] Since the term chlorination seems appropriate as a means of designating the process by which solvates ("chlorinates") are formed in liquid chlorine solutions, it is suggested that *chloridation* be used for the process of chloride formation.

The mixtures of chloroform and bromine were prepared in each case by bringing together accurately measured volumes of the two liquid components.

Results Obtained.—Temperature–concentration data of the system chloroform–chlorine are presented in Table I and are plotted in Fig. 1.

Temperature–concentration data of the system chloroform–bromine are presented in Table II and are plotted in Fig. 2.

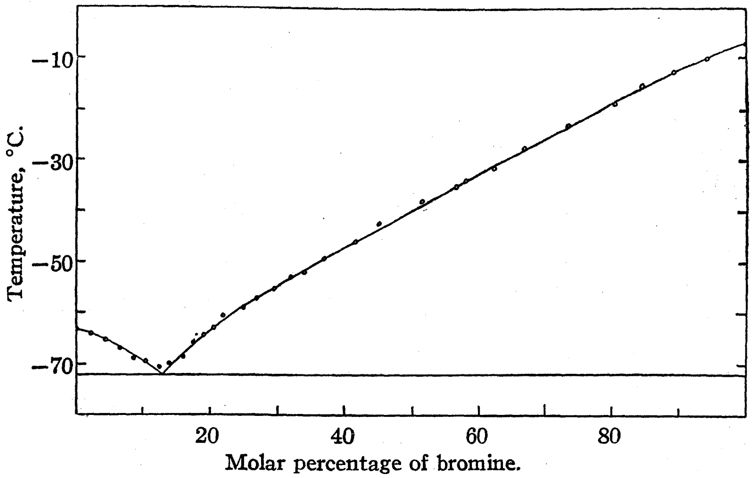


Fig. 2.—Temperature–concentration curves of system chloroform–bromine.

Table II

Temperature–Concentration or Solubility Data of the System $CHCl_3$–Br_2

Temp., °C.	Concn., mol. % Br_2	Temp., °C.	Concn., mol. % Br_2
−63.5	0.0	−53.0	32.0
−64.0	2.1	−52.0	34.0
−65.5	4.5	−49.5	37.1
−67.0	6.5	−46.0	41.5
−69.0	8.5	−42.5	45.1
−69.5	10.6	−38.0	51.5
−70.5	12.4	−35.0	56.4
−70.0	14.0	−34.0	58.0
−68.5	15.9	−31.5	62.2
−66.0	17.5	−27.5	67.5
−64.5	18.9	−23.0	73.4
−63.0	20.5	−18.5	80.6
−61.0	22.0	−15.0	84.6
−59.5	24.8	−12.5	89.4
−57.5	27.3	−10.0	94.4
−55.5	29.7	− 7.0	100.0

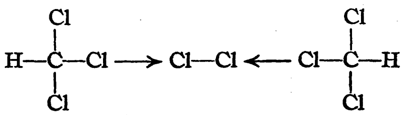
Discussion of Results.—It is obvious from the foregoing that bromine forms no solvates with chloroform, while chlorine forms four solvates, with congruent melting points, as follows:

(1) chloroform hemichlorinate, $(CHCl_3)_2 \cdot Cl_2$, −80.0°
(2) chloroform monochlorinate, $CHCl_3 \cdot Cl_2$, −96.5°
(3) chloroform dichlorinate, $CHCl_3 \cdot 2Cl_2$, −112.5°
(4) chloroform trichlorinate, $CHCl_3 \cdot 3Cl_2$, −115.0°

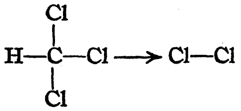
While no evidence whatsoever concerning the structure of these compounds is furnished by the current investigation, the authors venture to make the following tentative statement. It seems rather improbable that the chlorine molecules should be attached to the chloroform by other than coördinate links.

That the chlorine does not coördinate through the hydrogen of the chloroform is attested (1) by the paucity of evidence, up to the present time, that coördination through hydrogen attached to carbon is likely to occur;[4] (2) by the failure of the authors to obtain a chloroform tetrachlorinate; and (3) by the existence of a carbon tetrachloride tetrachlorinate.[5]

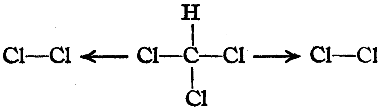
On the assumption that coördination takes place through the chlorine of the chloroform it is conceivable that this chlorine might serve either (1) as the acceptor, or (2) as the donor. For reasons that may be reserved for later discussion it seems that the latter alternative is preferable. The following tentative formulas are therefore suggested as the best present means of indicating the structure of the four chlorinates of chloroform



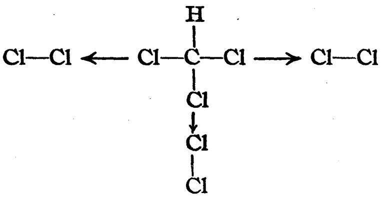
$$\mathrm{H{-}\underset{Cl}{\overset{Cl}{C}}{-}Cl \longrightarrow Cl{-}Cl \longleftarrow Cl{-}\underset{Cl}{\overset{Cl}{C}}{-}H}$$



$$\mathrm{H{-}\underset{Cl}{\overset{Cl}{C}}{-}Cl \longrightarrow Cl{-}Cl}$$



$$\mathrm{Cl{-}Cl \longleftarrow Cl{-}\underset{Cl}{\overset{H}{C}}{-}Cl \longrightarrow Cl{-}Cl}$$



$$\mathrm{Cl{-}Cl \longleftarrow Cl{-}\underset{\begin{array}{c}Cl\\ \downarrow\\ Cl\\ |\\ Cl\end{array}}{\overset{H}{C}}{-}Cl \longrightarrow Cl{-}Cl}$$

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[4] See N. V. Sidgwick, "The Electronic Theory of Valency," Oxford University Press, Oxford, England, 1927, p. 117.

[5] It has been established by a series of preliminary experiments performed in this Laboratory that carbon tetrachloride forms a tetrachlorinate, $CCl_4 \cdot 4Cl_2$, which shows a congruent melting point at −113°. Investigation of this system, and of various binary systems containing inorganic and organic halides is now in progress in this Laboratory, and results will be communicated in later articles.

Summary

The formation of four chlorinates of chloroform has been demonstrated during an investigation of the temperature–concentration relations of the system chloroform–chlorine:

(1) *chloroform hemichlorinate,* $(CHCl_3)_2\cdot Cl_2$ (m. p. −80.0°)
(2) *chloroform monochlorinate,* $CHCl_3\cdot Cl_2$ (m. p. −96.5°)
(3) *chloroform dichlorinate,* $CHCl_3\cdot 2Cl_2$ (m. p. −112.5°)
(4) *chloroform trichlorinate,* $CHCl_3\cdot 3Cl_2$ (m. p. −115°)

The five eutectic points are located, respectively, at −90, −102, −118, −121 and −123°.

On the assumption that one or more atoms of chlorine in the chloroform may act as donor to the free chlorine, tentative structural formulas for the chlorinates have been suggested.

Bromine forms no coördination compounds with chloroform. The eutectic point of the system chloroform–bromine is located at −72°.

ITHACA, N. Y. RECEIVED JUNE 22, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Temperature Dependence of the Energy of Activation in the Rearrangement of N-Chloroacetanilide

BY JOHN O. PERCIVAL AND VICTOR K. LA MER

Introduction

Until recently it has been an almost universal assumption to consider the energy of activation, defined as $E_{\text{act}} = RT^2(\text{d} \ln k/\text{d}T)$, as independent of the temperature. In 1933 La Mer[1,2] showed that Tolman's statistical development[3] demanded in general that E_{act} must be a function of temperature. He pointed out the importance of considering not only the energy but also the entropy and consequently the free energy of activation as concepts important for the interpretation of reaction velocity. A similar treatment involving a more explicit use of statistical formulas,[4,5] or the concept of an energy surface[6] for the calculation of the properties of the state and the reactivity of the intermediate complex for gaseous reactions[7] has proved useful in the hands of the authors cited.[8]

The reluctance in many quarters toward accepting E_{act} as a function of temperature arises from the fact that the precision obtainable in the study of the kinetics of gaseous reactions is rarely sufficient to establish small variations. On the other hand, the situation is quite different for reactions in solution.

A reinvestigation of the depolymerization of diacetone alcohol in the presence of dilute sodium hydroxide has established that $\text{d}E_{\text{act}}/\text{d}T$ not only may be surprisingly large, but that E_{act} reaches a maximum at about 35°.[9]

Since further information regarding the behavior of the E_{act} for different types of reaction is of importance for the elucidation of chemical kinetics, we have studied the rearrangement of N-chloroacetanilide to C-chloroacetanilide in 0.2 molal hydrochloric acid, a reaction which requires simultaneous catalysis by H^+ and Cl^- ions. Harned and Seltz[10] found that E_{act} increases with temperature, but their E_{act} values do not agree with those which we calculate from Rivett's[11] earlier work, as shown in Fig. 1. The length of the arrows indicates the probable experimental error.

A preliminary study disclosed disturbing factors which had not been considered previously: *e. g.* (a) the possibility of interfering side reactions which might invalidate conclusions regarding E_{act}; (b) the unreliability of certified thermometers as temperature standards. We will present evidence that side reactions are insignificant, and will submit more precise values for E_{act} over a carefully selected set of temperatures, using an improved analytical technique.

Mechanism

The mechanism of the conversion has received

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[1] V. K. La Mer, *J. Chem. Phys.*, **1**, 289 (1933).

[2] V. K. La Mer, THIS JOURNAL, **55**, 1739 (1933).

[3] R. C. Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, pp. 259–269.

[4] W. H. Rodebush, *J. Chem. Phys.*, **1**, 440 (1933).

[5] O. K. Rice and H. Gershinowitz, *ibid.*, **2**, 853 (1934).

[6] H. Eyring and N. Polanyi, *Z. physik. Chem.*, **12B**, 279 (1931).

[7] H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

[8] Wynne-Jones and Eyring, *ibid.*, **3**, 492 (1935).

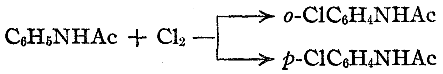
[9] V. K. La Mer and M. L. Miller, THIS JOURNAL, **57**, 2674 (1935).

[10] H. S. Harned and H. Seltz, *ibid.*, **44**, 1475 (1922).

[11] A. C. D. Rivett, *Z. physik. Chem.*, **82**, 201 (1913).

attention in Orton's laboratory.[12–16] In acetic acid solution, the reaction proceeds in two stages, the first of which is the rate determining step

(A) $C_6H_5NClAc + HCl \rightleftharpoons C_6H_5NHAc + Cl_2$

(B) 

$$C_6H_5NHAc + Cl_2 \rightarrow \begin{cases} o\text{-}ClC_6H_4NHAc \\ p\text{-}ClC_6H_4NHAc \end{cases}$$

N-Chlorinated anilides oxidize iodide ion to iodine while C-chlorinated anilides do not. The reaction is followed by titrating the iodine liberated with sodium thiosulfate when a sample is run into potassium iodide solution. Although direct proof is lacking, considerable circumstantial evidence exists to indicate that the above mechanism applies to aqueous solutions also.[14,16,17]

Blanksma[18] using 20% acetic acid as solvent and Rivett[11] using aqueous solutions found the rate of disappearance of the N-chloroacetanilide to be first order and proportional to the square of the hydrochloric acid concentration. Harned and Seltz[10] show for aqueous solutions that the observed rate is proportional to the activity of the hydrochloric acid

$$k = k_{\text{obsd.}}/a_{\text{HCl}} \qquad (1)$$

where $a_{\text{HCl}} = a_{\text{H}^+} \cdot a_{\text{Cl}^-} = a^2_{\pm}(\text{HCl}) = m^2f^2_{\pm}$ (a is thermodynamic activity, f is activity coefficient, m is molality).

Soper and Pryde[19] state that the observed rate is proportional not only to the activity of hydrochloric acid but also to the activity coefficient of the N-chloroacetanilide

$$k = k_{\text{obsd.}}/a_{\text{HCl}}f_{:\text{NCl}} \qquad (2)$$

and that the following interfering side reactions occur for which corrections should be made

(C) $C_6H_5NClAc + OH^- \rightleftharpoons C_6H_5NHAc + OCl^-$

(D) $ClC_6H_4NHAc + Cl_2 \longrightarrow ClC_6H_4NClAc + HCl$[20]

Pryde and Soper[19] conclude that (C) causes a 6% rate decrease in one tenth molar acid by a study of the rate of disappearance of N-chloroacetanilide in the presence of sulfuric, nitric, and chloric acids using phenol to remove hypochlorite. Soper[16] and Pryde and Soper[26] find the rate of hydrolysis in neutral solutions to be very small. We measured the hydrolysis at each temperature. It is only 0.1% of the rate of (A) in 0.2 molal hydrochloric acid.

It does not seem reasonable to suppose that the 6% decomposition of N-chloroacetanilide in acid solution was due to reaction (C), which is the reverse of the preparative reaction. Reaction (C) is analogous to (E)

(E) $Cl_2 + OH^- \rightleftharpoons Cl^- + ClO^- + H^+$

One would expect hydrogen ion to reverse both (C) and (E). Jakowkin[27] found this to be true for (E). Accordingly the effect they observe can be explained by (F) proposed by Rivett[11] where X is any acid anion

(F) $C_6H_5NClAc + HX \longrightarrow C_6H_4NXAc + HCl$

followed by reaction (A) *et cetera*. Belton reports[28] instability of N-chloroacetanilide in sulfuric acid solutions even with no phenol present. Chattaway and Orton[29] have detected the formation of hydrochloric acid in solutions of N-chloroacetanilide in other acids. Soper[16] states that (D) causes a decrease in k of about 9% for 0.2 molal hydrochloric acid. If reaction (D) occurs, since its rate is a function of the concentration of the ortho and para chloroacetanilides, which increase with time by (B), the contribution of the N-chlorochloroacetanilide to the titer will become progressively greater causing k to drift downward.

However, since no time drift in k has been reported to date, nor detected in the present investigation after a careful search, we conclude that Soper's postulated side reaction (D) cannot occur to any perceptible extent.

Equation (2) of Soper and Pryde received experimental support from data making these two extensive corrections. Belton,[30] using NaCl–HCl mixtures and making no corrections, obtains data more satisfactorily explained by equation (1) than (2). For the present investigation, the reaction rates were obtained at constant activity of hydrochloric acid by equation (1).

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(12) K. J. P. Orton, *Proc. Roy. Soc.*, **71**, 156 (1902).

(13) K. J. P. Orton and W. J. Jones, *J. Chem. Soc.*, **95**, 1456 (1909).

(14) F. S. Kipping, K. J. P. Orton, S. Ruhemann, A. Lapworth and W. J. Jones, Brit. Ass. Adv. Sci. Reports, 1910, p. 85.

(15) F. S. Kipping, K. J. P. Orton, S. Ruhemann, J. T. Hewitt and W. H. Grey, *Chem. News*, **108**, 155 (1913).

(16) F. G. Soper, *J. Phys. Chem.*, **31**, 1192 (1927).

(17) K. J. P. Orton and W. J. Jones, *J. Chem. Soc.*, **P25**, 233 (1909).

(18) M. J. J. Blanksma, *Proc. Akad. Sci. Amsterdam*, **5**, 178, 359 (1902); *Rec. trav. chim.*, **22**, 290 (1903); *ibid.*, **21**, 366 (1902).

(19) F. G. Soper and D. R. Pryde, *J. Chem. Soc.*, 2761 (1927).

(20) (B) and (D) have been studied in the following references: 13, 14, 16, 21, 22, 23, 24, 25; and (C) in 15, 16, 19; the rate of (B) is found (16) to be about one hundred times that of (D).

(21) K. J. P. Orton and H. King, *J. Chem. Soc.*, **99**, 1369 (1911).

(22) K. J. P. Orton and A. E. Bradfield, *ibid.*, 986 (1927).

(23) K. J. P. Orton, F. G. Soper and G. Williams, *ibid.*, 998 (1928).

(24) G. Williams, *ibid.*, 37 (1930).

(25) D. R. Pryde and F. G. Soper, *ibid.*, 1510 (1931).

(26) D. R. Pryde and F. G. Soper, *ibid.*, 1514 (1931).

(27) A. A. Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

(28) J. W. Belton, *Proc. Leeds Phil. Lit. Soc.*, **2**, 178 (1931).

(29) F. D. Chattaway and K. J. P. Orton, *Proc. Chem. Soc.*, **18**, 200 (1902).

(30) J. W. Belton, *J. Chem. Soc.*, **116** (1930).

The above considerations show that the rate of disappearance of N-chloroacetanilide catalyzed by hydrochloric acid may be followed through its reaction with iodide ion without interfering side reactions and is suitable for a temperature coefficient study.

Precision Analysis

The important variables are: temperature (T), time (t), analyses for the concentration of the reacting compound (A, $A - x$), thermodynamic activity of the hydrochloric acid. The relation of these variables to E is shown in equations (1), (3) and (4)

$$E = \frac{RT_1T_2 \ln (k_2)/(k_1)}{T_2 - T_1} \tag{3}$$

$$k_{\text{obsd.}} = \frac{1}{t} \ln \frac{(A)}{(A - x)} \tag{4}$$

The influence of errors in determination of the variables on E was investigated by partial differentiation of these equations. The experimental procedure was then adjusted so that the combined effect of all calculable errors would be less than the effect of the uncertainty in the activity of hydrochloric acid given in the literature. Table I shows the effect of significant errors on k and E.

TABLE I

CALCULATED PROBABLE ERRORS

$e_k() = \left(\frac{(10^2)}{k}\right)\left(\frac{\delta_k}{\delta()}\right) \Delta()$	
	%
$e_k(m)$	± 0.06
$e_k(f)$	± .12
$e_k(A)$	± .05
$e_k(A - x)$	± .05
$e_k(T)$	± .06
$e_k(t)$	± .01
$\Delta k = \sqrt{\Sigma(e_{k()})^2}$	±16
$e_E() = \frac{(10^2)}{E}\left(\frac{\delta_E}{\delta()}\right) \Delta()$	
$e_E(T)$	± .06
$e_E(k)$	± .38
$\Delta E = \sqrt{\Sigma(e_{E()})^2}$	± .42
$\frac{\Delta E}{100} E$	±84.0 cal.

Experimental

The saturated solution of the compound was prepared by agitation *at the temperature of the run*[31]; a calculated amount was taken such that when mixed with the constant boiling hydrochloric acid, weighed out in a sealed thin glass capsule, would give a solution 0.2 m in hydrochloric acid. The reaction was terminated by pipetting samples into potassium iodide in the larger compartment of a special 125-cc. glass-stoppered Erlenmeyer flask[34] and by immediate mixing with a sodium hydroxide–sodium acetate solution contained in a side arm compartment. The final concentration of iodide was 4%[35]; the sodium hydroxide–sodium acetate was calculated to leave the solution at a pH of 5.75 ± 0.20.[36] This was verified by e. m. f. measurements using a glass electrode.

The liberated iodine was titrated with sodium thiosulfate from a weight buret using a starch indicator *within fifteen minutes* after taking the sample. The weight *in vacuo* of thiosulfate per gram of sample was substituted directly in equation (4). The precipitate formed during the reaction—of which no mention occurs in the literature—is excluded from the sample by drawing it through a sintered glass filter funnel. The extent of hydrolysis was determined by a second analysis of the saturated solution at the end of the experiment.

Preparation of the *N*-Chloroacetanilide.—The A solution was prepared according to directions of Barnes and Porter[37]; the remainder of the procedure was modified as follows. B solution, 9.6 g. of sodium hydroxide and 3.2 g. of sodium carbonate are dissolved in 150 cc. of solution. C solution, 1.9 g. potassium iodide in 37 cc. water; add 0.1 cc. of concentrated sulfuric acid immediately before addition of sample; add 2 cc. of 0.5% starch solution at the end-point. Chlorine is passed into B solution at 5° until 1 cc. added to C solution requires between 1.6/M and 1.8/M cc. of M molar thiosulfate. Add (220/Mn) cc. (n is the number of cc. of thiosulfate used) of solution B to solution A at 5°. Preserve the compound in a darkened vacuum desiccator over phosphorus pentoxide. If solution B is made from sodium carbonate only, the chlorine causes vigorous evolution of carbon dioxide which interferes with sampling.

Any method of recrystallizing involving heat treatment gave colored products with excessive melting point changes of from −10 to +70° due to decomposition. Addition of excess water at room temperature to an absolute alcohol solution was found to be the only satisfactory method of purification. The crystals were always white needles of reproducible m. p., 89.5°.

Temperature.—The temperature variation of the thermostats was ±0.005° or less. Baudin thermometer No. 18537 was used as a standard of temperature. The method of calibration leaves no doubt regarding the self-consistency of the scale.

The pipets were constructed from eight and twenty-four mm. Pyrex with no constriction of the tip to reduce errors of timing and heat losses in the fast runs. The main body was removed 4 to 5 cm. from the line of stems and was suspended in the thermostat before use long enough to reach temperature equilibrium. The pipets delivered 26 ± 2 cc. in less than two seconds, the exact value being determined by weight.

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[31] The solution is customarily prepared by boiling several hours in water.[10,11] Porter and Wilbur,[32] and Bradfield[33] show that complete decomposition occurs within one-half to two hours at 100°.

[32] C. W. Porter and P. Wilbur, THIS JOURNAL, **49**, 2145 (1927).

[33] A. E. Bradfield, *J. Chem. Soc.*, 351 (1928).

[34] V. K. La Mer and M. E. Kamner, THIS JOURNAL, **57**, 2664 (1935); Fig. 1.

[35] R. M. Chapin, *J. Chem. Soc.*, **41**, 351 (1919).

[36] I. M. Kolthoff, I. H. Menzel and N. H. Furman, "Volumetric Analysis," John Wiley and Sons, New York, 1929, Vol. II, p. 354.

[37] C. D. Barnes and C. W. Porter, THIS JOURNAL, **52**, 1721 (1930).

Buffer.—A buffer is required for the following reasons. (a) Oxidation of iodide ion to iodine by dissolved oxygen will occur in the solution before the end-point is reached, unless the hydrochloric acid catalyst is neutralized. (b) Thiosulfate titrations[36] of dilute iodine require a definite acidity for quantitative results. (c) Hydrogen ion is needed for the reaction between the N-chloroacetanilide and iodide

$$C_6H_5NClAc + 2I^- + H^+ \longrightarrow C_6H_5NHAc + Cl^- + I_2$$

If N-chloroacetanilide is run into neutral potassium iodide, the *p*H rises to 10.75 and the reaction stops with only 60% of the compound reduced. Subsequent addition of acid will not yield the theoretical amount of iodine. (d) The fast running pipets used do not deliver reproducible quantities of solution (within ±2 cc.). The sodium acetate–sodium hydroxide mixture meets these requirements.

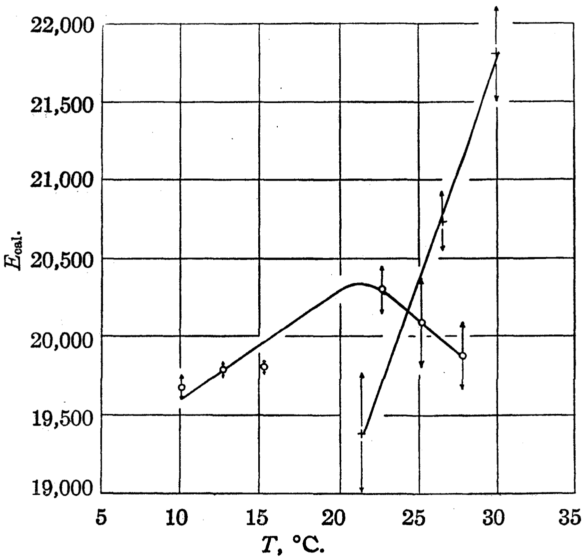

Fig. 1.—Energy of activation–temperature: +, Harned and Seltz; ○, Rivett.

Analysis.—The starch–iodine end-points are observed by holding the flask on a line with the eye and a lamp behind translucent glass in an otherwise light-tight box; the room is darkened. As the reaction progresses, the solution becomes slightly yellow so that successive end-points cannot be compared to obtain reproducibility. The solution is over-titrated with one drop of thiosulfate; a few cc. are placed in the side-arm and iodine added in 0.003-g. portions to the main body until the first perceptible difference in shade is observed between the two portions. This end-point is highly reproducible; when reaction products are present, it is red-yellow. A normality change of 1 × 10^{-6} is readily detected. The a. d. of four iodine–thiosulfate titrations was one-half this quantity. *Light.*—No difference was found on comparing runs in clear and blackened flasks. *Reagents.*—Eimer and Amend Technical Purity grade sodium thiosulfate was twice recrystallized between 60 and 5°. Approximately 0.02 *M* solutions were made in carbon dioxide-free water[38] which were kept free of carbon dioxide with soda-lime tubes. No decomposition of these solutions could be detected during the period of any run. Iodine was distilled from potassium iodide and copper sulfate[35] and sublimed three times. Potato starch ground for five hundred hours in a ball mill readily forms a suspension in water at room temperature. The blank for 2 cc. of a 0.5% solution is 2.1 × 10^{-7} equivalent of iodine. The constant boiling hydrochloric acid was prepared by the standard methods.[39,40]

TABLE II

k, *E*, *B* AT CONSTANT ACTIVITY HCl

T, °C.	k_{av}	Δk ± (%)	E_{act}	ΔE ± (%)	*B*	ΔB ± (%)
0.305	0.008550	0.79				
6.333			19170	1.36	13.23	1.5
12.362	.03792	.39				
12.645			19790	0.68	13.73	0.72
18.673			20440	.86	14.21	.91
18.925			20090	.49	13.96	.50
24.954			20590	.51	14.33	.56
24.984	.1742	.42				
31.264			20750	1.09	14.45	1.10
37.545	.7178	.52				

Calculation of Results

Values of *k*, E_{act} and *B* at constant activity of hydrochloric acid are shown in Table II with their experimental error. The errors represent the deviation between duplicate runs. *k* and *E* were calculated from (4), (1) and (3); *B* from (5).

$$B = \log k + (E_{act}/2.3\ RT) \qquad (5)$$

The activity coefficients were calculated to within ±0.0005 by the equation of Harned and Ehlers.[41] E_{act} and *B* are plotted against temperature in Figs. 2 and 3, respectively. The data of Rivett were recalculated to a molal basis. The E_{act} from Rivett, and Harned and Seltz were calculated using the activity coefficients of Harned and Ehlers[41] and are plotted in Fig. 1. The error in Rivett's data was calculated from the a. d. of a single run at each temperature. Harned and Seltz do not indicate whether they made duplicate runs, merely stating that "the maximum variation in a series was ±1%." This figure was used to calculate their ΔE. Our *k* values and those of Harned and Seltz agree at 25° to 3% when the latter are multiplied by 2.303. Time is in minutes.

Discussion

The increase of *E* from 19,170 to 20,750 cal. for the temperature range 6.333 to 31.264° corresponds to a mean molar heat capacity of activa-

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[38] F. O. Rice, M. Kilpatrick and W. Lemkin, THIS JOURNAL, **45**, 1361 (1923).

[39] C. W. Foulk and M. Hollingsworth, *ibid.*, **45**, 1220 (1923).

[40] W. D. Bonner and A. C. Titus, *ibid.*, **52**, 633 (1930).

[41] H. S. Harned and R. W. Ehlers, *ibid.*, **55**, 2179 (1933).

tion of 63 cal./deg. Figure 1 compared with Fig. 2 shows our data to give the most precise values of E. The change with temperature is unquestionably greater than experimental error, and cannot be due to side reactions nor to inconsistencies in the temperature scale used.

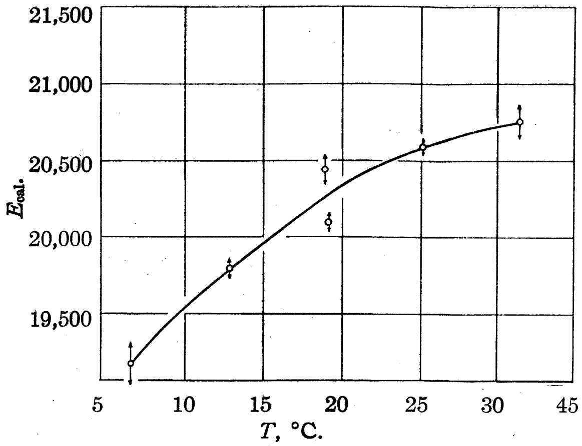

Fig. 2.—Energy of activation-temperature.

By integrating $\partial \ln k/\partial T = E_{act}/RT^2$ under the general assumption that $E_{act} = f(T)$, La Mer obtained

$$\ln k = \text{frequency constant} + (S_{act}/R) - (E_{act}/RT) \quad (6)$$

where S_{act} is the entropy of activation. When E_{act} is considered independent of temperature, S_{act}/R vanishes, since it is equal to

$$\frac{1}{R}\int_0^T \left(\frac{\partial E_{act}}{\partial T}\right) dT/T$$

He evaluated the constant of integration by assuming a collisional mechanism for the reaction, in which case the frequency term = ln $Z°$. Comparison of eq. (5) with eq. (6) shows that for this mechanism

$$B = \log Z° + S_{act}/2.3R \quad (7)$$

The experimental value of B, equal to 13.23 at 6.33°, compares favorably with the value of log $Z°$ equal to 13.10, assuming σ equal to 5A°. However at 31.26° B has increased 1.22 units. whereas log $Z°$, which varies as $T^{1/2}$ has increased but 0.02 unit. This constitutes further experimental proof of the existence of an appreciable entropy of activation. The simple collision theory of reaction kinetics obviously is quite inadequate.

Eyring has proposed a statistical theory which avoids the collisional mechanism for evaluating the frequency constant in eq (6). His theory yields

$$B = \log \kappa kT/h + S_{act}/2.3R \quad (8)$$

Here kT/h is a universal frequency which varies as T; κ is a transmission coefficient representing the probability that the activated complex will not be reflected back after passing the energy barrier. Calculations of κ are not available except for extremely simple reactions.

The entropy of activation in (7) differs from that in (8) in that the collisional mechanism for the process $A + B \rightleftarrows X$ apportions the entropy contribution associated with the ordinary translational degrees of freedom of A, B and X to $Z°$, whereas in eq. (8) these contributions are included under S_{act}.

It is of interest to note the striking similarity between the form of the curve, E_{act} *versus* T (Fig. 2), and that for the depolymerization of diacetone alcohol.[9] Our reaction involves a neutral molecule and two oppositely charged ions, while the latter reaction concerns a neutral molecule and one negative ion.

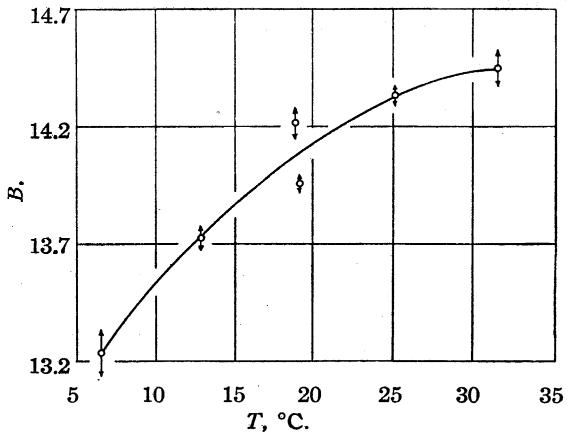

Fig. 3.—B-Temperature.

Summary and Conclusions

1. The rate of conversion of N-chloroacetanilide in the presence of aqueous 0.2 molal hydrochloric acid has been measured at 0, 12.5, 25, 37.5°. The temperature dependence of the energy of activation has been calculated for a constant activity of hydrochloric acid.

2. The analytical procedure has been refined so that the velocity constants can be reproduced to 0.5%.

3. The complete absence of time drifts of the velocity constant shows that the secondary N-chlorinations postulated recently by Soper do not exist.

4. The E_{act} rises steadily from 19,170 cal.

for the interval 0–12.5° to 20,750 cal. for 25–37.5°, corresponding to a mean heat capacity of activation of 63 cal./deg.

5. The form of the curve E *versus* T for this reaction is similar to that for the depolymerization of diacetone alcohol by hydroxyl ion.

6. The action constant B—which is equal to the entropy of activation plus a frequency term—varies from 13.2 at 6.33° to 14.45 at 31.3°. The magnitude and temperature dependence of B furnish additional evidence of the inadequacy of the collision theory, and of the existence of an appreciable entropy of activation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Orthobaric Densities of Substances as a Function of Reduced Temperatures

BY HAROLD A. FALES AND CLARA S. SHAPIRO

In the present investigation it is our purpose to make a comparative study of the equilibrium between the liquid and vapor phases of different elements and chemical compounds over the entire range of coexistence of the two phases from the melting point to the critical temperature with particular reference to the relationship between the orthobaric densities and the "reduced" temperatures.

Cailletet and Mathias studied the densities of the liquid and gaseous phases and discovered in 1886[1] that the arithmetical mean of their sum is a function of centigrade temperature. Likewise, they found that the "reduced" mean density can be expressed as a function of "reduced" temperature; this relationship is discussed in detail by Van Laar.[2] Recently two interesting papers have appeared along the lines of our subject. One is by C. H. Meyers[3] in which orthobaric volumes are connected with "reduced" pressures and absolute temperatures. This author shows for twenty-three substances that provided the vapor pressure–temperature relation for the saturated fluid, the critical pressure, and approximate values for liquid densities are known, the specific volume of the saturated vapor can be calculated, except near the critical temperature, with the determination of one empirical constant in the equation

$$\log_{10}\left(1-\frac{pv}{RT}\right)\left(1-\frac{pv'}{RT}\right) = A\log_{10}\frac{p}{2.718p_c} \qquad (1)$$

where p = saturation pressure, p_c = critical pressure, v and v' = specific volumes of liquid and vapor respectively, R = gas constant, T = absolute temperature and A = empirical constant which varies slightly from 0.72 for noble gases to 0.61 for methanol, with an average value of 0.69 for twenty-three substances. The above relationship is very accurate up to one-fourth to one-half the critical pressure, which corresponds to 0.8 to 0.9 the absolute critical temperature.

The second paper is by J. Horiuchi[4] and deals with the expression $\ln v_g/v_l$. Assuming that Maxwell's distribution law and van der Waals' equation apply to the equilibrium liquid $\rightleftharpoons$ saturated vapor, and introducing a certain correction Horiuchi develops an equation which expresses $\ln v_g/v_l$ in terms of two variables: the volumes themselves and the absolute temperatures, namely

$$\ln v_g/v_l = \frac{A}{RT}\left(\frac{1}{v_l - E} - \frac{1}{v_g - E}\right) \qquad (2)$$

where A and E are constants characteristic for each substance. This equation holds well for a large number (60) of organic and inorganic liquids up to 0.8–0.9 of the critical temperature. It deviates considerably in the case of methyl alcohol and does not hold at all for water; according to Horiuchi this discrepancy is due to the strong association of these liquids. As to constants A and E they differ in numerical value for different substances. For normal organic liquids $A = 32.3\ T_{cr}^2/P_{cr}$ and $E = 0.17\ V_{cr}$, so that a "reduced" equation is obtained for these liquids[4]

$$\ln\frac{\phi_g}{\phi_l} = \frac{1.47}{R\tau}\left(\frac{1}{\phi_l - 0.17} - \frac{1}{\phi_g - 0.17}\right) \qquad (3)$$

where τ, ϕ_g, ϕ_l are the reduced temperatures and reduced volumes, respectively.

The expression $\ln v_g/v_l$ has previously received considerable attention in the literature, mostly in

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(1) Cailletet and Mathias, *Compt. rend.*, **102**, 1202 (1886); **104**, 1563 (1887); Mathias, *ibid.*, **200**, 1643 (1935); **200**, 1902 (1935).

(2) Van Laar, "Zustandgleichung," ed. 1924, pp. 74, 342–350.

(3) C. H. Meyers, *Bur. Standards J. Research*, **11**, 691 (1933).

(4) J. Horiuchi, *Bull. Chem. Soc. Japan*, **1**, 189 (1926); and **2**, 213 (1927). *Sci. Papers, Inst. Phys. Chem. Research, Tokyo*, **15**, 89 (1931).

the effort to connect it with the latent heat of evaporation. Of the numerous though only partially successful attempts in this direction the most interesting is perhaps the equation of Crompton[5]

$$\ln\frac{v_g}{v_l} = \frac{Ml_{ev}}{2RT} \tag{4}$$

where M is the molecular weight, l_{ev} the latent heat of evaporation, R the gas constant, and T the absolute temperature.

This equation is approximately true for many organic liquids, giving particularly good agreement in the neighborhood of the critical point, but it shows considerable deviation for alcohols, acetic acid, ammonia, water and other liquids commonly called "associated" although the deviations become small as the critical point is approached.

Considering the relationships which Horiuchi and Crompton have sought to develop one might infer that liquids fall into two types, commonly known as associated and non-associated, since equations (2) and (4) give agreement with observed values in a certain number of cases but not in others. On the other hand, no such division into classes follows from the equation of Meyers because it applies equally well to twenty-three diverse substances including alcohols, ammonia and water.

The question may now be asked: is there some inherent peculiarity in the function $\ln v_g/v_l$ which necessitates that liquids be divided into two classes? We will attempt to show in this paper that it is possible to use the function $\ln v_g/v_l$ in conjunction with "reduced" temperature and obtain a relationship which is equally applicable to substances of the utmost chemical diversity and that on the basis of this there is no support to the contention that liquids are divisible into two classes.

We have selected thirty substances which represent every type of element, inorganic substance and organic compound for which measurements of orthobaric densities are available.

These substances arranged in the ascending order of the volume ratio are:

1 Helium
2 Hydrogen
3 Neon
4 Argon
5 Oxygen
6 Carbon monoxide
7 Nitrogen
8 Ethylene
9 Ethane
10 Hydrogen chloride
11 Nitrous oxide
12 Acetylene
13 Methyl ether
14 Carbon tetrachloride
15 Benzene
16 *i*-Pentane
17 *n*-Pentane
18 Monofluorobenzene
19 Sulfur dioxide
20 Ammonia
21 Methyl formate
22 Ethyl ether
23 *n*-Hexane
24 Acetic acid
25 Ethyl propionate
26 Sulfur trioxide
27 Water
28 Methyl alcohol
29 Ethyl alcohol
30 Nitrogen tetroxide

In studying the ratio of the volumes we have employed the natural log of the ratio v_g/v_l instead of the ratio itself, since the variation of the latter with temperature is far too fast. We have also employed the reduced temperature instead of the absolute temperature in order to have a common scale of comparison. It is obvious that at the critical point the ratio becomes unity and its natural log becomes zero for all substances; therefore in plotting the $\ln v_g/v_l$ against the reduced temperature $\tau = T/T_{cr}$ for different substances we obtain a series of curves all having a common origin at the point $\tau = 1.000$. Comparing these curves we find that they all belong to one and the same family as illustrated by the eight representative curves a,. . .h, in Fig. 1.

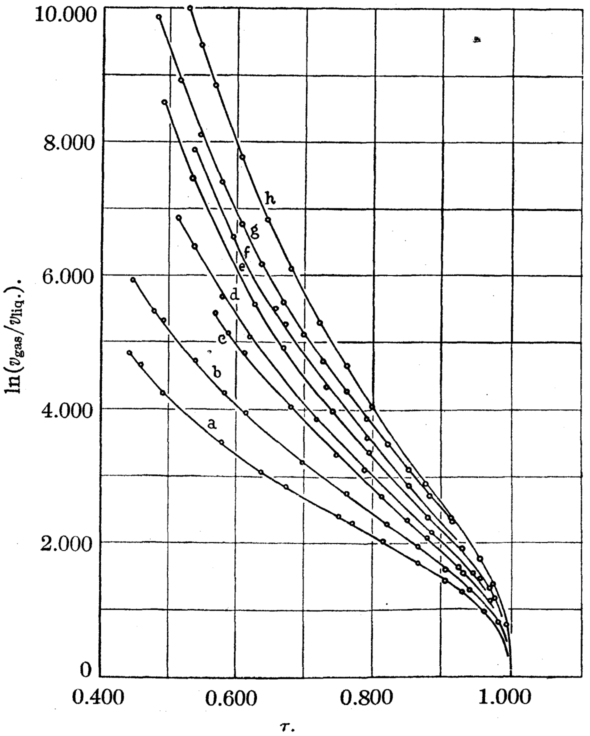

Fig. 1.—$\ln(v_{gas}/v_{liq.}) = k[(1-\tau^2)^m/\tau^n]$: a, helium; b, hydrogen; c, neon; d, nitrogen; e, carbon tetrachloride; f, *n*-hexane; g, water; h, ethyl alcohol.

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[5] Crompton, *Proc. Chem. Soc. London*, **17**, 61 (1901).

The domain bounded by the curves a and h includes all the curves for the thirty typical substances, while the more restricted domain bounded by c and g includes a majority of the curves. The eight representative curves a, . . .h portray the behavior of the following substances:

a—Helium
b—Hydrogen
c—Neon
d—Nitrogen
e—Carbon tetrachloride
f—*n*-Hexane
g—Water
h—Ethyl alcohol

Analytical Expression of the Curves.—We find that all these curves can be represented by the equation

$$\ln \frac{v_g}{v_l} = k \frac{(1 - \tau^2)^m}{\tau^n} \qquad (5)$$

where v_g and v_l are the orthobaric volumes; $\tau = T/T_{cr}$ is the reduced temperature and k, m and n are constants characteristic for a given liquid.

If we use "reduced" volumes instead of orthobaric volumes we get the same functional relationship, namely

$$\ln \frac{\phi_g}{\phi_l} = \ln \frac{\dfrac{v_{gas}}{v_{cr}}}{\dfrac{v_{liq.}}{v_{cr}}} = k \frac{(1 - \tau^2)^m}{\tau^n} \qquad (6)$$

where ϕ_g and ϕ_l are the "reduced" volumes.

Equation (5), as well as (6), is applicable to all substances tried and in most cases represents the data within the experimental accuracy as will be seen from the ensuing Tables I to III. It embraces substances of utmost diversity in physical and chemical properties. Thus the critical temperature ranges from 5.19°K. for helium to 674.2°K. for water; the number of atoms from 1 for helium to 20 for hexane; and the molecular weight from 2 for hydrogen to 153 for carbon tetrachloride.

This equation holds equally well for associated and non-associated liquids. It will be seen from the tables that the typical associated substances—acetic acid, water, ethyl alcohol, ammonia—show just as good an agreement between calculated and experimental curves, as do the representatives of normal liquids—benzene, carbon tetrachloride or hexane.

In Table I we give an example of our calculations in detail for water represented in Fig. 1 by curve g. In this table the three reference points used for calculating k, m and n are marked with an asterisk; at these points the deviation is, of course, always zero. Also in this table are given the de-

TABLE I

Water, Curve (g) Fig. 1. $k = 4.122$, $m = 0.3770$, $n = 1.338$

Gas volumes in parentheses have been extrapolated by the Bureau of Standards. The corresponding observed ln values are also in parentheses.

t, °C.	τ	v_{gas} obsd., cc./g.	$v_{liq.}$ obsd., cc./g.	$\ln \frac{v_g}{v_l}$ obsd.	$\ln \frac{v_g}{v_l}$ calcd.	Differences Actual[a]	Differences Percentage[b]
0	0.4220	(206430)	1.000	(12.24)	12.15	−0.09	−0.7%
+ 20	.4529	(57872)	1.002	(10.97)	10.92	− .05	− .4
+ 40	.4838	(19550)	1.008	(9.873)	9.871	− .002	− .0
+ 60	.5147*	7678.8	1.017	8.930*	8.930*	.000	−0*
+ 80	.5456	3409.4	1.029	8.106	8.118	+ .012	+0.1
+100	.5765	1673.3	1.0434	7.380	7.399	+ .019	+ .3
+120	.6074	891.79	1.0603	6.735	6.755	+ .020	+ .3
+140	.6383	508.61	1.0798	6.155	6.172	+ .017	+ .3
+160	.6692	306.78	1.1021	5.629	5.641	+ .012	+ .2
+180	.7001	193.80	1.1275	5.147	5.153	+ .006	+ .1
+200	.7310*	127.16	1.1565	4.700*	4.700*	.000	0*
+220	.7619	86.060	1.1900	4.281	4.276	− .005	−0.1
+240	.7928	59.674	1.2291	3.883	3.872	− .011	− .3
+260	.8237	42.145	1.2755	3.498	3.484	− .014	− .4
+280	.8546	30.124	1.3321	3.119	3.104	− .015	− .5
+300	.8855	21.634	1.4036	2.736	2.722	− .014	− .5
+320	.9164	15.454	1.4992	2.333	2.323	− .010	− .4
+340	.9473	10.776	1.6409	1.882	1.879	− .003	− .2
+350	.9628*	8.798	1.7468	1.617*	1.617*	.000	0*
+360	.9782	6.941	1.9070	1.292	1.298	+ .006	+0.5
+374.11	1.0000	3.1975	3.1975	0	0		...

[a] Values are the differences, $\ln_{obsd.} - \ln_{calcd.}$. [b] Values are the percentage differences, $\dfrac{\Delta \ln v_g/v_l}{\ln v_g/v_l} \times 100$.

* Asterisks signify the reference points used for calculating k, m and n.

viations between calculated and observed values of $\ln v_g/v_l$. They are expressed as actual differences in the natural log, and also as percentage differences. By percentage difference we mean the proportional error in the logarithm of the ratio of the volumes × 100, namely, $\Delta \ln v_g/v_l / \ln v_g/v_l \times 100$.

If it is desired to find the percentage difference in the ratio of the volumes themselves, multiply the differences $\ln_{\text{obsd.}} - \ln_{\text{calcd.}}$ in column 7 of Table I by 100. This follows from the property of natural logarithms that for two nearly equal numbers the difference between their natural logarithms is sensibly equal to the proportional difference of the numbers themselves, thus

$$\ln (x + \Delta x) - \ln x = \ln x + \ln \left(1 + \frac{\Delta x}{x}\right) - \ln x =$$
$$\ln \left(1 + \frac{\Delta x}{x}\right) = \frac{\Delta x}{x} - \frac{1}{2}\left(\frac{\Delta x}{x}\right)^2 + \ldots \doteq \frac{\Delta x}{x}$$

In Table II we give the differences between observed and calculated values of $\ln v_g/v_l$ for the remaining seven substances of Fig. 1 represented by curves (a) helium, (b) hydrogen, (c) neon, (d) nitrogen, (e) carbon tetrachloride, (f) *n*-hexane, (h) ethyl alcohol, and one additional substance, acetic acid, the curve for which is closely adjacent to that for water (g). The differences $\ln_{\text{obsd.}} - \ln_{\text{calcd.}}$ were obtained from an enlarged graph giving the differences as ordinates against τ as abscissa and then selecting for each substance the values of the differences corresponding to τ = 0.400, τ = 0.450, *et cetera*. The average difference in each case was obtained by integrating the area under a curve and dividing this area by the appropriate length of the abscissa.

TABLE II

ACTUAL DIFFERENCES: $\ln v_g/v_l$ obsd. − $\ln v_g/v_l$ calcd.

Substance:	(a) Helium	(b) Hydrogen	(c) Neon	(d) Nitrogen	(e) Carbon tetrachloride	(f) *n*-Hexane	(g) Acetic acid[a]	(h) Ethyl alcohol
Constants: k	2.659	3.166	3.134	3.203	3.724	3.837	3.960	4.266
m	0.4003	0.430	0.3735	0.351	0.3896	0.386	0.388	0.388
n	.8215	.900	1.247	1.315	1.290	1.376	1.396	1.558
τ = 0.400	...	+0.003	...	...	...	...	...	...
.450	−0.066	.000	...	...	...	...	...	...
.500	.000	+ .002	...	+0.045	...	...	+0.016	...
.550	+ .016	+ .008	...	− .005	...	...	+ .003	0.000
.600	+ .035	+ .018	+0.012	− .011	...	...	− .004	− .026
.650	+ .051	+ .035	− .008	− .004	0.001	0.000	− .015	− .013
.700	+ .020	+ .035	− .020	− .023	+ .008	+ .006	− .002	− .008
.750	.000	+ .005	− .030	− .030	+ .010	+ .003	− .001	− .004
.800	− .005	+ .010	− .004	+ .001	+ .001	+ .002	+ .006	+ .002
.850	− .002	+ .012	+ .014	+ .004	+ .006	+ .012	+ .006	− .003
.900	+ .005	+ .040	+ .029	.000	+ .002	+ .010	+ .005	− .002
.950	− .002	+ .010	+ .015	− .020	+ .001	+ .003	+ .002	+ .013
1.000	.000	.000	.000	.000	.000	.000	.000	.000
Av. diff.	.023	.014	.019	.012	.005	.006	.006	.010

[a] The curve for acetic acid is closely adjacent to that for water.

If it is desired to find the percentage difference in the ratio of the volumes themselves, multiply the differences $\ln_{\text{obsd.}} - \ln_{\text{calcd.}}$ by 100.

Table III gives a summary of the results obtained for all 30 substances. For each substance its calculated curve was constructed from only three known density data, and the differences between observed and calculated values were obtained for the whole experimental range exactly as illustrated in Table I, but for lack of space the results are given only in very condensed form.

The liquids are arranged in the ascending order of the curves in the coördinate system. In each case are given: the critical temperature, the molecular weight, the number of atoms, the value of $\ln v_g/v_l$ at τ = 0.600, the values of the constants *k*, *m*, *n*, the average difference $\ln_{\text{obsd.}} - \ln_{\text{calcd.}}$, and the average percentage difference. These two sets of values were obtained by the use of graphs in a manner entirely analogous to that described in the preceding paragraph for Table II. For the sake of comparison estimated deviations are also given in the last column. These estimates are based upon the assumption that the effects of errors in v_g and T_{cr} upon $\ln v_g/v_l$ are additive as explained subsequently in the text.

Evaluation of the Constants *k*, *m* and *n*.—In evaluating the constants *k*, *m* and *n* it has been our purpose to find a method applicable to any known substance for which only three density measurements have been made (at three different temperatures). With this view in mind, we have used only three known data for densities and corresponding temperatures in calculating the constants *k*, *m* and *n* of each substance given in Table III.

In selecting the three reference points we have been guided by the following considerations: (1) to use a uniform procedure for all substances, so as to obtain comparable results; (2) to use only those density values as reference data which have been actually observed, or calculated from a trustworthy equation of state; (3) to have the first reference point always between the melting and the boiling point, *i. e.*, at $\tau = 0.5$ to 0.65; to have the third point always in the abrupt region of the curve, namely, the third point should always lie between $\tau = 0.96$ and 0.97 but not any closer to unity. This is an important precaution to observe, since in the region between $\tau = 0.97$ to 1.000 the expression $1 - \tau^2$ becomes so small as to be very much influenced by the errors in measurements of the critical temperature. Hence, in this small region the equation is not expected to hold with the same accuracy as in the other parts of the curve. The second point is always to be chosen as close as possible to midway between the two extreme points. This was found by experience to be the best procedure. (4) To choose the intervals between the points 1 and 2 and the points 2 and 3 as large as possible, which is in accordance with the mathematical theory of equations. In a few cases one or more of these conditions could not be observed, for lack of corresponding density data. In such cases the calculated constants were considered slightly inaccurate and in Table III they are enclosed in parentheses.

Accuracy of the Proposed Equation.—In the two columns preceding the last of Table III we have given the averages of the actual and the percentage differences of the function $\ln v_g/v_l$. We see upon examining the differences that they vary from substance to substance. This variation is to be expected since the equation

$$\ln v_g/v_l = k \frac{(1 - \tau^2)^m}{\tau^n} \tag{5}$$

TABLE III

SUMMARY OF RESULTS

A = number of atoms. The substances in this table are arranged in the ascending order of the curves.

	Substance	[a]	T_{cr}, °K.	Mol. wt.	A	$\ln v_g/v_l$ obsd. for $\tau = 0.600$
1	Helium	(1)	5.19	4.00	1	3.35
2	Hydrogen	(2)	33.18	2.0156	1	4.100
3	Neon	(3)	44.38	20.18	1	5.03
4	Argon	(2)	150.65	39.94	1	5.10
5	Oxygen	(2)	154.19	32.00	2	5.25
6	Carbon monoxide	(4)	132.89	28.00	2	5.40
7	Nitrogen	(2)	125.99	28.02	2	5.43
8	Ethylene	(5)	282.6	28.03	6	5.56
9	Ethane	(6, 12)	405.3	30.05	8	5.67
10	Hydrogen chloride	(6)	324.6	36.46	2	5.85
11	Nitrous oxide	(6)	309.6	44.02	3	5.87
12	Acetylene	(6)	309.1	26.02	4	Below triple point
13	Methyl ether	(6)	400.0	46.05	9	6.00 (extrap.)
14	Carbon tetrachloride	(7)	556.2	153.83	5	6.05
15	Benzene	(7)	561.6	78.05	12	6.17
16	*i*-Pentane	(7)	460.6	72.09	17	6.20
17	*n*-Pentane	(7)	470.3	72.09	17	6.30
18	Monofluorobenzene	(7)	559.6	96.04	12	6.37
19	Sulfur dioxide	(8)	430.3	64.06	3	6.38
20	Ammonia	(9)	406.1	17.03	4	6.43
21	Methyl formate	(7)	487.1	60.03	8	6.45
22	Ethyl ether	(7)	466.9	74.08	15	6.49
23	*n*-Hexane	(7)	507.9	86.11	20	6.53
24	Acetic acid	(7)	594.7	60.03	8	6.78
25	Ethyl propionate	(7)	546.0	102.08	17	7.03
26	Sulfur trioxide	(6)	491.4	80.06	4	7.50 (extrap.)
27	Water	(10)	647.2	18.02	3	6.83
28	Methyl alcohol	(7)	513.2	32.03	6	7.75
29	Ethyl alcohol	(7)	516.2	46.05	9	7.95
30	Nitrogen tetroxide	(11)	431.3	92.02	6	8.00 (extrap.)

[a] The numbers in column 3 indicate the corresponding references on orthobaric densities and critical data, given in Table V.

TABLE III (*Concluded*)

$$\ln \frac{v_g}{v_l} = k\,\frac{(1-\tau^2)^m}{\tau^n}$$

		Constants[b]			Average differences actual[c]	Average percentage differences actual[d]	Average percentage deviations estimated[e]
		k	m	n			
1	Helium	2.659	0.4003	0.8215	0.023	0.56	4.0
2	Hydrogen	3.166	.4300	.9000	.014	.54	0.9
3	Neon	3.134	.3735	1.247	.019	.61	1.0
4	Argon	3.297	.3767	1.198	.027	1.5	1.1
5	Oxygen	(3.084)	(.3407)	(1.345)	(.010)	(0.54)	1.0
6	Carbon monoxide	3.251	.3790	1.320	.016	.58	1.0
7	Nitrogen	3.203	.3510	1.315	.012	.37	1.0
8	Ethylene	(3.421)	(.3881)	(1.298)	.020	.52	0.7
9	Ethane	3.345	.3492	1.331	.018	.64	.5
10	Hydrogen chloride	3.623	.3855	1.264	.010	.32	.7
11	Nitrous oxide	3.691	.4068	1.262	.010	.40	.7
12	Acetylene	3.677	.3946	1.331	.012	.40	.7
13	Methyl ether	3.641	.3856	1.353	.017	.50	.5
14	Carbon tetrachloride	3.724	.3896	1.290	.005	.14	.5
15	Benzene	3.798	.3932	1.300	.008	.18	.5
16	*i*-Pentane	3.707	.3863	1.343	.002	.06	.5
17	*n*-Pentane	3.755	.3867	1.352	.004	.18	.5
18	Monofluorobenzene	3.687	.3763	1.397	.004	.10	.5
19	Sulfur dioxide	3.977	.4111	1.257	.027	.80	.5
20	Ammonia	(3.881)	(.3858)	(1.331)	.004	.05	.25
21	Methyl formate	3.807	.3853	1.367	.005	.18	.5
22	Ethyl ether	3.757	.3833	1.403	.010	.24	.5
23	*n*-Hexane	3.837	.3861	1.376	.006	.07	.5
24	Acetic acid	3.960	.3879	1.396	.006	.11	.5
25	Ethyl propionate	3.967	.3842	1.443	.004	.05	.5
26	Sulfur trioxide	(4.297)	(.4012)	(1.102)	.017	.73	.5[f]
27	Water	4.122	.3770	1.338	.017	.26	.25
28	Methyl alcohol	4.329	.3780	1.460	.004	.08	.5
29	Ethyl alcohol	4.266	.3883	1.558	.010	.20	.5
30	Nitrogen tetroxide	(4.910)	(.4197)	(1.240)	.010	.20	.5[f]

[b] Values of the constants **k, m, n** in parentheses are not quite reliable, since the corresponding substances have only a very short range of observed densities. Consequently the intervals between the three reference points are too small. Also, in the case of ethylene, ammonia and nitrogen tetroxide, the third reference point lies below $\tau = 0.96$, *i. e.*, above the characteristic abrupt portion of the curve, because the corresponding vapor densities are not accurately known near T_{cr}. [c] Values are the average of the differences $\ln_{\text{obsd.}} - \ln_{\text{calcd.}}$. [d] Values are the average of the percentage differences $(\Delta \ln v_g/v_l)/(\ln v_g/v_l) \times 100$. [e] Values are estimated deviations based on the assumptions that the effects of errors in v_g and T_{cr} upon $\ln v_g/v_l$ are additive as explained subsequently in the text. [f] The figures given for sulfur trioxide and nitrogen tetroxide in the last 3 columns are for the range of temperatures: 100–218.3° and 0–60°, respectively.

is influenced largely by errors in the measurements of critical temperature and to some extent by errors in the measurements of vapor density; and these errors are not the same in all cases.

The effect of an error in τ can be obtained by differentiation of equation (5) whence

$$\frac{\Delta \ln v_g/v_l}{\ln v_g/v_l} = -\frac{\Delta\tau}{\tau}\left(\frac{2m\tau^2}{1-\tau^2} + n\right) \qquad (7)$$

One finds that for a given absolute error in τ, the corresponding proportional error in $\ln v_g/v_l$ is large either for $\tau = 0$ or 1 and is a minimum between these values, while for a given proportional error in τ, the corresponding proportional error in $\ln v_g/v_l$ is n times as large when $\tau = 0$ and infinite when $\tau = 1$.

In this connection we should like to point out the following: although in general the temperature can be measured very accurately, yet at the critical point the procedure is a very difficult one. It follows from the survey of critical data by Pickering[6] that even the most careful observers do not always check each other, since for some substances the critical temperature values differ by one or more degrees. Therefore, we believe it is fair to assume that the critical temperature is known accurately to within ±0.1–0.5° only. The effect of an error in T_{cr} upon τ is obviously

$$\Delta\tau/\tau = \Delta T_{cr}/T_{cr} \qquad (8)$$

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(6) Pickering, *Bur. Standards Sci. Papers*, No. 541, p. 598 (1926).

or the proportional error in τ is equal to the proportional error in T_{cr}.

On the basis of equations (7) and (8) we can figure out the effect of an error in the measurement of the critical temperature upon the calculation of $\ln v_g/v_l$. Taking ten representative substances we get the results tabulated in Table IV.

TABLE IV

Substance	Crit. temp., T_{cr}, °K.	Error in crit. temp., ΔT_{cr}, °K.	Effect upon $\ln v_g/v_l$ $\frac{\Delta \ln v_g/v_l}{\ln v_g/v_l} \times 100$, % $\tau = 0.5$	0.75	0.9	1.0
Helium	5.19	0.1	2.0	3.6	9.6	∞
Hydrogen	33.18	.1	1.2	2.0	4.5	∞
Neon	44.38	.2	0.5	0.6	1.5	∞
Nitrogen	125.99	.5	.5	.6	1.5	∞
Ethylene	282.6	.5	.25	.35	0.70	∞
Ammonia	406.1	.2	.08	.12	.23	∞
Sulfur dioxide	430.3	.5	.16	.23	.46	∞
n-Hexane	507.8	.5	.13	.18	.37	∞
Acetic acid	594.7	.5	.12	.17	.35	∞
Water	647.2	.3	.08	.12	.23	∞

The effect of separate errors in the measurements of v_g and v_l upon the $\ln v_g/v_l$ can be shown to be

$$\frac{\Delta \ln v_g/v_l}{\ln v_g/v_l} = \frac{\Delta v_g/v_g + \Delta v_l/v_l}{\ln v_g/v_l} \qquad (9)$$

The liquid density can be measured very easily to 1 part in 2000 or better, so that the term $\Delta v_l/v_l$ is usually negligible and (9) reduces to

$$\frac{\Delta \ln v_g/v_l}{\ln v_g/v_l} = \frac{\Delta v_g/v_g}{\ln v_g/v_l} \qquad (10)$$

which involves only the error in the vapor volume.

For large values of $\ln v_g/v_l$ and a given proportional error in v_g the corresponding proportional error in $\ln v_g/v_l$ is small, while at the critical temperature where $\ln v_g/v_l = 0$, the corresponding proportional error in $\ln v_g/v_l$ is infinite.

In applying equation (10) we must have knowledge of the proportional error $\Delta v_g/v_g$ for each individual case. The most accurate work is probably that of the Bureau of Standards for ammonia and water where the errors in v_g do not exceed a few tenths of one per cent.[7] In Young's work on organic liquids the vapor density is known to 0.0001 which amounts to about 2% in the neighborhood of the normal boiling point and to only about a few tenths of one per cent. as we approach the critical point.[8]

The Leiden laboratory gives only two significant figures for the vapor densities of hydrogen, nitrogen and oxygen in the region below the boiling point.[9] We assume, therefore, that the accuracy of their data is of the same order as Young's density measurements for the range normal boiling point to critical point.

We see that for most substances the proportional error in v_g for $\tau = 0.6$ is of the order 2 to 3% and decreases with increasing τ until at $\tau = 0.95$ it is about 0.3–0.5%. From Fig. 1 it is evident that the least value of $\ln v_g/v_l$ for $\tau = 0.6$ is 3.25 for helium, and the greatest value is 7.95 for ethyl alcohol, while for $\tau = 0.95$ the values range from 1.0 for helium to 1.7 for ethyl alcohol; therefore from equation (10) the proportional error in $\ln v_g/v_l$ will be between 0.25–0.50% for $\tau = 0.6$ and between 0.2–0.5% for $\tau = 0.95$. For water and ammonia because of the high accuracy of the v_g data the proportional error in $\ln v_g/v_l$ will not exceed 0.1% for the same range of τ. The above shows that the proportional error in $\ln v_g/v_l$ is practically constant for $\tau = 0.6$–0.95, and can be taken as equal to 0.1% for water and ammonia, and equal to 0.3% for the remaining substances.

We can now estimate the total effect of errors in the measurement of critical temperature and of vapor volumes upon the calculated values of $\ln v_g/v_l$. It is obvious that the total proportional error in $\ln v_g/v_l$ will not exceed the sum of the two effects: effect *a* due to error in the critical temperature as shown in Table IV and effect *b* due to errors in the vapor volumes as discussed above.

For each substance we estimated effect *a* as a percentage difference for intervals of τ equal to 0.05 and obtained the average. Effect *b* was considered constant and equal to 0.1% for water and ammonia and 0.3% for the remaining substances; these values were added to the average of effect *a* in the respective cases. The sums thus obtained, we believe, represent fair estimates of the upper limits of the proportional errors in $\ln v_g/v_l$ arising from errors of experimentation. They give a view of the reliability of the proposed equation (5) for the range melting point to 0.95 critical point and therefore are included in Table III (last column)

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(7) The Bureau of Standards data for v_g are calculated from the measured latent heat of evaporation. For details, see Bur. Standards Circ. No. 142, 1923; and Osborn, Stimson and Ginnings, *Mech. Eng.*, **57**, 162 (1935).

(8) Correspondingly, we find only two significant figures at the normal boiling point in Young's vapor densities as given by "Int. Crit. Tables," Vol. III, 1928, p. 244. Other observers usually give less accurate measurements. For the estimate of error in density measurements of Young and others, see J. Timmermans, *ibid.*, p. 244.

(9) The density tables and the discussion of experimental errors are given in the papers by Mathias and co-workers: *Ann. phys.*, **17**, 416–474 (1922).

for comparison with the percentage differences actually found.

Both the actual and estimated deviations refer to temperature ranges for which the vapor densities are accurately known, namely, measured or calculated from a reliable equation of state. Some of the substances investigated by Young, such as benzene, carbon tetrachloride, etc., have vapor densities roughly extrapolated (by Young) in the region below the boiling point. The corresponding values of ln v_g/v_l are unreliable and were not taken into account in making the computations.

We see upon examination of the table that twenty-seven substances show smaller actual deviations than the estimated, while three, argon, sulfur dioxide and sulfur trioxide, show greater.

A few words should be said regarding sulfur trioxide and nitrogen tetroxide. Each of these substances gives a curve which in part follows the typical shaped curves shown in Fig. 1 and in part deviates more or less as shown by the dotted lines in Fig. 2.

In the case of sulfur trioxide the explanation of this behavior seems to be that part of the data (100–218.3°) was observed[10] while the rest of the data (44–100°) was apparently calculated by means of an equation involving mean density.[11] In plotting the ln values against τ we find that the observed values (100–218.3°) give the typical shape while the calculated values (44–100°) depart from it. The constants k, m and n in Table III were evaluated from the observed data; accordingly we find upon applying the proposed equation (5) that it holds fairly well only for the range (100–218.3°) and not at all for the range (44–100°).

As to nitrogen tetroxide, its densities have been observed all along the saturation line by Mittasch and co-workers (0 to 55°),[12] and by Bennewitz and Windish (30 to $t°$ crit.).[12] In constructing the corresponding curve we find that the portion (0 to 60°) falls right along that of ethyl alcohol, but the portion (60 to 158.2°) is very unusually shaped (Fig. 2 dotted line). We expected our equation to fit in the range (0–60°) and this was found to be the case with very good agreement, but above 60° the deviation from observed values of ln is very large. It is possible that this discrepancy is caused by partial dissociation of $N_2O_4 \longrightarrow 2NO_2$ under saturation pressure[13] which is probably small below 60° and hence does not affect the corresponding value of ln $v_{\text{gas}}/v_{\text{liq}}$.

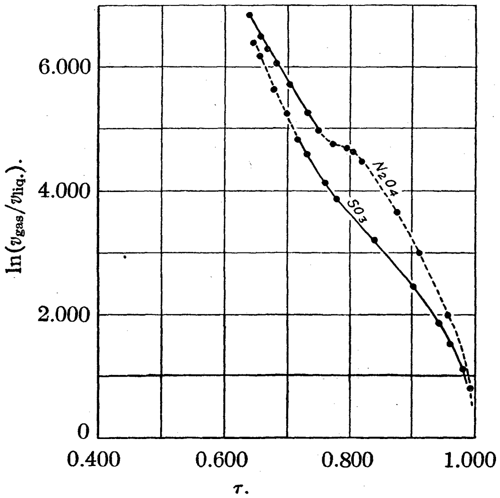

Fig. 2.—――――― Part of experimental curve which follows equation; - - - - - - part of experimental curve which deviates from equation.

Comparison of the Constants k, m **and** n.—When we compare the values of the three constants for different substances given in Table III, we see that each of them varies but little in comparison with the wide variation in physical and chemical properties.

Thus k increases from about 3.2 to 4.3 with the two exceptions helium, $k = 2.66$; nitrogen tetroxide, $k = 4.9$.

m ranges from 0.347 to 0.420 and for many organic substances it is equal to about one-tenth of k.

n ranges from 0.821 to 1.558.

The curves are described accurately by the proposed equation and consequently the order of arrangement should bear close relationship to the corresponding values of the constants k, m and n. We find that m and n do not show any striking regularity, but k is quite characteristic. It increases regularly in about the same order in which the curves succeed each other with a few exceptions. Further, we observe that in general closely adjacent curves such as those for nitrogen and carbon monoxide, or normal and i-pentane, have almost identical values of k.

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(10) Berthoud, *Helv. Chim. Acta*, **5**, 513 (1922); *J. chim. phys.*, **20**, 77 (1923).

(11) "Int. Crit. Tables," Vol. III, 1928, p. 228; see bottom line of the sulfur trioxide table.

(12) Mittasch, Kuss and Schleuter, *Z. anorg. Chem.* **159**, 29 (1927); Bennewitz and Windish, *Z. physik. Chem.*, **A166**, 401 (1933).

(13) Nitrogen tetroxide dissociates partially under saturation pressure as is indicated in the corresponding pressure–temperature table (bottom line). See "Int. Crit. Tables," Vol. III, 1928, p. 229.

The close parallelism between the values of k and the location of the curve $\ln v_g/v_l$ suggests at once that the constant k itself is a function of the physical and chemical properties of substances.

This supposition proves to be correct. We find that both the position of the curve and the value of the constant k depend very closely on the properties of substances in the critical state, namely, on their critical constants.

Relation between the Constant k and the Critical Coefficient.—Upon examining the values for k we find that they are almost identical with the critical coefficient for gases K_{cr} defined by the equation

$$K_{cr} = RT_{cr}d_{cr}/Mp_{cr} \qquad (11)$$

In Table V we give the results of this comparison. The thirty substances studied are the same as before. They are arranged in the ascending order of the curves. In columns 3–5 we give the number of atoms in the molecule and the values of k and K_{cr}. The ratio K_{cr}/k is calculated for each substance and is given in column 6.

TABLE V

A = number of atoms. $k = [\ln d_l/d_g]/[(1 - \tau^2)^m/\tau^n]$. $K_{cr} = RT_{cr}d_{cr}/Mp_{cr}$.

The substances in this table are arranged in the order of ascending position of curves

	Substance[a]	A	k	K_{cr}	Ratio K_{cr}/k	Literature
1	Helium	1	2.659	3.270	1.230[b]	(1)
2	Hydrogen	1	3.166	3.276	1.035	(2)
3	Neon	1	3.134	3.249	1.037	(3)
4	Argon	1	3.297	3.425	1.039	(2)
5	Oxygen	2	(3.084)	3.346	1.085	(2)
6	Carbon monoxide	2	3.251	3.395	1.044	(4)
7	Nitrogen	2	3.203	3.420	1.068	(2)
8	Ethylene	6	(3.421)	3.524	(1.030)	(5)
9	Ethane	8	3.345	3.587	1.072	(12)
10	Hydrogen chloride	2	3.623	3.801	1.049	(6)
11	Nitrous oxide	3	3.691	3.630	0.9835	(6)
12	Acetylene	4	3.677	3.635	.9886	(6)
13	Methyl ether	9	3.641	3.719	1.022	(6)
14	Carbon tetrachloride	5	3.724	3.680	0.9882	(7)
15	Benzene	12	3.798	3.755	.9887	(7)
16	*i*-Pentane	17	3.707	3.735	1.007	(7)
17	*n*-Pentane	17	3.755	3.766	1.003	(7)
18	Monofluorobenzene	12	3.687	3.796	1.030	(7)
19	Sulfur dioxide	3	(3.977)	3.600	(1.140)[b]	(8)
20	Ammonia	4	(3.881)	4.125	(1.067)	(9)
21	Methyl formate	8	3.807	3.922	1.030	(7)
22	Ethyl ether	15	3.757	3.798	1.011	(7)
23	*n*-Hexane	20	3.837	3.830	0.9982	(7)
24	Acetic acid	8	3.960	4.991	1.260[b]	(7)
25	Ethyl propionate	17	3.967	3.923	0.9889	(7)
26	Sulfur trioxide	4	(4.297)	3.805	(0.8855)[b]	(6)
27	Water	3	4.122	4.234	1.027	(10)
28	Methyl alcohol	6	4.329	4.559	1.053	(7)
29	Ethyl alcohol	9	4.266	4.026	0.9437	(7)
30	Nitrogen tetroxide	6	(4.910)	4.385	(0.8727)[b]	(11)

[a] The value for $K_{cr} = RT_{cr}d_{cr}/Mp_{cr}$ is calculated from the corresponding critical data. The bibliography is given below. [b] Values show disagreement between k and K_{cr}.

BIBLIOGRAPHY ON EXPERIMENTAL DATA

Orthobaric Densities and Critical Data; References

(1) Helium: Leiden Lab. Comm. No. 172b (1925); 179c (1926).
(2) H_2, A, O_2, N_2: *Ann. phys.*, [9] **17**, 416 (1922).
(3) Neon: *ibid.*, [9] **19**, 231 (1923).
(4) Carbon monoxide: Leiden Lab. Comm. No. 221b (1932).
(5) Ethylene: *Ann. phys.*, [9] **11**, 343 (1929).
(6) Acetylene, hydrogen chloride, methyl ether, nitrous oxide, sulfur trioxide, ethane: Tables and references, see "Int. Crit. Tables," Vol. III, 1928, pp. 228–236.

(7) Carbon tetrachloride, benzene, monofluorobenzene, *i*- and *n*-pentanes, *n*-hexane, methyl formate, ethyl propionate, methyl and ethyl alcohols, and acetic acid: see original tables of Young, *Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

(8) Sulfur dioxide: observed volumes—(0°C. to *t*° Crit.) also critical data tables and references, see "Int. Crit. Tables," Vol. III, 1928, p. 236. Liquid volumes and vapor volumes (calcd. by means of equation of state between −40 and 0°). See the SO_2 table, "Refrigerating Data Book," 1934. Also original paper by Fiske, *Refrigerating Eng.*, December, (1924).

(9) Ammonia: observed volumes (−59 to +53°), tables and references; also critical data, see Bur. Standards, *Circ.*, No. 142, 1923.

(10) Water: observed liquid volumes: (0 to 30°) see Keenan Steam Tables, ed. 1930. Observ. liquid volumes (+30 to +360°); also crit. vol. and *t*° crit., Smith and Keyes, *Proc. Am. Acad. Arts Sci.*, **69**, 285 (1934). Vapor volumes (0 to +360°) calcd. from observed latent heat and pressure with the aid of liquid volume data of Keyes and Smith. See prelim. report of the Bur. Standards (Osborn, Stimson and Ginnings), *Mech. Eng.*, **57**, 162 (1935). Critical pressure for water, see Keyes, Smith and Gerry, *Proc. Am. Acad. Arts Sci.*, **69**, 139 (1934).

(11) Nitrogen tetroxide: observed densities (+3 to +55°) see Mittasch, *et al.*, *Z. anorg. Chem.*, **159**, 29 (1927). Observed densities (+60°C. to *t*° crit.). Also critical data, see Bennewitz and Windish, *Z. physik. Chem.*, **A166**, 401 (1933).

(12) Critical data for ethane by Cardozo, see Pickering's table, "Int. Crit. Tables," Vol. III, 1928, p. 248.

The agreement between k and K_{cr} is as follows:

% Difference	0.5–6	6–10	10–15	23–26
Number of substances	21	4	3	2

The deviations from unity can in part be accounted for by errors in the critical coefficients, these errors being mostly due to errors in the determination of the critical density. Beattie and co-workers[14] discuss this question and assign an estimate of error of about 1–2% for the best values of critical volumes; however, it must be said that in some of the earlier work the critical volumes are probably in error by as much as 5–10%. It appears, therefore, that for the large majority of cases the ratio of K_{cr} to k is very nearly equal to unity.[15] This fact leads to an important conclusion.

The theory of corresponding states requires that the critical coefficient be a constant for all substances and all known equations of state lead to a constant value of K_{cr}, independent of the nature of the substance.[16] (Thus van der Waals' equation gives $K_{cr} = 2.67$; Dieterici's and Wohl's equations lead to the values $K_{cr} = 3.69$ and 3.75, respectively.)

Actually, however, the critical coefficient is far from being a constant. Table V shows that it changes from about 3.0 for monoatomic to about 4.0 for polyatomic substances and in some cases it is greater than 4.0. In general organic substances have an almost constant value of K_{cr} averaging 3.7. These substances are considered normal.[16]

As to the values of K_{cr} departing from the constant value 3.7, the corresponding substances are classed as abnormal. It is customary to explain these departures as being due to the association of the given liquid.[16] As far as we know, a rational treatment of this question has not yet been attempted.

The investigation of the ratio of orthobaric densities here presented leads to another view of this matter.

Comparing the values of k and K_{cr} we see that they change quite parallel to each other as we go from substance to substance. Since the ratio K_{cr}/k is close to unity and both factors in the ratio are established by independent methods, it follows that K_{cr} cannot be a constant. Its gradual rise follows the order of the curves ($\ln v_g/v_l$) in the coördinate system. Therefore, it appears to be a normal phenomenon not at all indicative of the molecular association of the given liquid. It further appears that a correct equation of state should take account of the variation of K_{cr} from substance to substance.

We should like to express our appreciation to Mr. David L. Fiske, Editor of the Refrigerating Data Book, New York, for many valuable suggestions and for his interest in this work. We should also like to thank Dr. Henry Fleishmann and the Educational Alliance, New York, for the financial assistance given to one of us (C. S.) during this work.

Conclusions

1. The ratio of orthobaric densities is a function of reduced temperature and consequently

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[14] Beattie, Poffenberger and Hadlock, *J. Chem. Phys.*, **3**, 96 (1936).

[15] With respect to the five discrepant cases, where k and K_{cr} differ by more than 10%, namely helium, sulfur dioxide, acetic acid, sulfur trioxide and nitrogen tetroxide, we can offer no explanation at present.

[16] A collection of the best known equations of state and a discussion of the critical coefficient are given in the "Handbuch der Experimental-Physik," Vol. VIII (2), 1929, pp. 224–234.

the vapor volume can be expressed as a function of reduced temperature and liquid volume along the saturation line, namely

$$\ln v_g/v_l = k\,\frac{(1-\tau^2)^m}{\tau^n} \qquad (5)$$

$$v_g = v_l \exp.\, k\,\frac{(1-\tau^2)^m}{\tau^n} \qquad (12)$$

2. The constant k of the suggested equation is almost identical with the critical coefficient K_{cr}, their ratio being nearly equal to unity for most substances investigated.

The critical coefficient is not a constant but varies from substance to substance, increasing with the order of curves ($\ln v_g/v_l$) in the coördinate system.

3. There seems to be a definite similarity in the mechanism of evaporation of substances as shown by the fact that the respective expansion curves can be expressed by one and the same equation and that the constants of this equation have values very close to each other for substances of the most diverse chemical and physical properties.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Kinetics of Thermal *Cis-Trans* Isomerization. VI

BY G. B. KISTIAKOWSKY AND WALTER R. SMITH

In one of the earlier papers[1] of the present series, evidence was presented indicating that the first order rate of isomerization of methyl cinnamate began to fall off at a pressure of 6 mm. Unfortunately, due to the analytical method employed, it was not feasible to study the reaction at still lower pressures. This compound and dimethyl maleate[2] have been the only two in a series of geometric isomers in which this phenomenon, characteristic of unimolecular reactions, has been observed.

In β-cyanostyrene the number of contributing degrees of freedom could be expected to be appreciably less than in methyl cinnamate, because of substitution of a CN group for the $COOCH_3$ group. Hence, with β-cyanostyrene the rate might begin to fall off at a higher pressure and an extensive study of the rate–pressure dependence could be made.

The present paper describes a number of experiments on the rate of isomerization of β-cyanostyrene performed at various temperatures and over an extensive range of pressures.

Experimental Details

Preparation of β-Cyanostyrene.—The nitrile was prepared according to the method of Ghosez[3] by the condensation of benzaldehyde and cyanoacetic acid in the presence of pyridine. Sixty per cent. of the theoretical yield was obtained.[4]

The resulting mixture of the geometric isomers was distilled in an all glass still 3 m. tall and 18 mm. in diameter, packed with Pyrex glass spirals.[5] A 20–1 reflux ratio was used. Two fractions were obtained, one boiling at 139.1° at 30 mm. and the other at 152° at 30 mm. The high boiling fraction was further purified by freezing and allowing it to melt at 20°. The solid portion remaining was distilled at 122° at 2 mm. in a Claisen flask. The weight ratio of high to low boiling isomers was 62:38. Ghosez[3] obtained 63% high boiling compound.

The high boiling isomer melted at 22° and had $n^{20.2}D$ 1.6031. For the low boiling isomer the melting point was −4.4° and $n^{20.2}D$ 1.5843. According to Ghosez and in conformity with other evidence[6] the low boiling isomer must be assigned the *cis* configuration. This is also in agreement with equilibrium data presented below.

Analytical Method.—The appreciable difference in the refractive indices of the two isomers provided a rapid and convenient method of analyzing the reaction mixtures. An Abbé refractometer, thermostated to 20.2° and employing a sodium vapor lamp, was calibrated with a series of known mixtures of the isomers. A strictly linear relationship between composition and refractive index was found. It was possible to detect 0.5% of either isomer.

The melting points of these mixtures were also determined by means of a single junction copper–constantan thermocouple. The couple was used sometimes to check the values obtained from the refractometer, as described below.

The apparatus was of the usual static type. Both it and the experimental procedure have already been described elsewhere.[2]

Some of the earlier runs were analyzed both by the refractive index method and the freezing point. In all cases the two methods gave analyses agreeing to 1%, which is to be regarded as indicating the absence of side reactions.

The reaction was further established by connecting the nitrile to cinnamic acid. The product from a run on the

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[1] Kistiakowsky and Smith, THIS JOURNAL, **57**, 269 (1935).

[2] Kistiakowsky and Nelles, *Z. physik. Chem.*, Bodenstein Festband, 369 (1931), and THIS JOURNAL, **54**, 2208 (1932).

[3] Ghosez, *Bull. soc. chim. Belg.*, **41**, 477 (1932).

[4] We are greatly indebted to Dr. George F. Wright for preparing the compound for us.

[5] Kistiakowsky, *et al.*, THIS JOURNAL, **57**, 877 (1935).

[6] Wright, *ibid.*, **57**, 1993 (1935).

high boiling isomer gave a refractive index indicating the presence of 21% low boiling isomer; 1.69 g. of this product was refluxed for twenty-four hours with 25 cc. of an aqueous 7% sodium hydroxide solution. The solution was then neutralized with dilute hydrochloric acid and the precipitated cinnamic acid was washed free of chloride ion and dried. An 82% yield was obtained. The product melted at 133°. A sample of pure high boiling isomer gave a yield of 81% cinnamic acid, melting at 133°. This evidence, together with the agreement of the refractive index and the melting point methods, indicates clearly that the reaction studied is primarily isomerization.

Experimental Results

No real pressure change could be noted in any of the runs. The product of all runs, except those at the lowest pressure, was clear and colorless. In the latter case a slight grayish turbidity appeared. This settled out on standing and did not interfere with the refractometer readings.

The position of thermal equilibrium at 352° was determined by heating known mixtures of the isomers, in the gas phase, for varying lengths of time. The results of these experiments are reproduced in Fig. 1. At 352° equilibrium exists at 63% high boiling isomer.

A few runs on the low boiling isomer at 352° and at a pressure of 390 mm. gave average velocity constants of 4.03×10^{-5} sec.$^{-1}$. The average constant for the high boiling isomer at these conditions is 2.89×10^{-5} sec.$^{-1}$. The equilibrium concentration of 60% high boiling isomer obtained from these values is in satisfactory agreement with the more accurate value obtained above.

Since these values are nearly identical with the value obtained in preparing the compound at temperatures lower than 100°, it is obvious that the value of ΔH is too small to be determined by studying the equilibrium over any convenient temperature range.

The results of all runs on the high boiling (*trans*) isomer are presented in Table I. The velocity constants have all been calculated allowing for equilibrium at 63% high boiling isomer.

Runs were made over a pressure range of 450 to 20 mm. At the lower pressures there is a marked increase in the velocity constants. At the lowest temperature this increase is nearly threefold. At the highest temperature the constants are nearly identical at all pressures. Runs in a packed flask with about six times the surface gave a marked increase in the constants at the lowest pressure, while such an increase was not noted at the higher pressures.

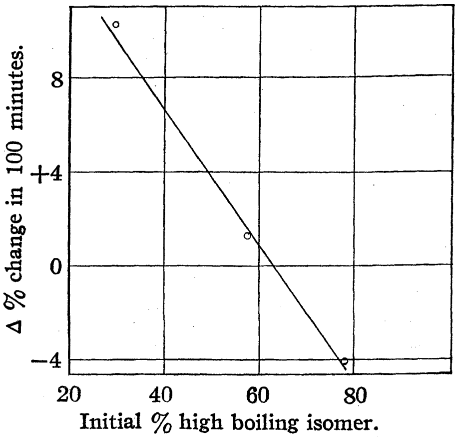

Fig. 1.—Equilibrium composition at 352°.

It is evident that at the lower pressure a wall reaction occurs to some extent. It does not interfere with the rate measurements of the homogeneous reaction at higher pressures, but makes very uncertain the detection of a possible falling off of the rate constant with pressure. Hence the originally intended study of the falling off was abandoned and only the high pressure rate studied.

TABLE I

Run	Temp., °K.	Press., mm.	Time, min.	% HB isomer	*k* corr. sec.$^{-1}$
6	581.3	372	1020	89.8	1.52×10^{-6}
7	581.3	380	1371	89.0	1.59
32	597.4	413	960	79.0	5.30×10^{-6}
31	597.0	399	1031	78.0	5.40
34	596.0	154	1180	78.4	4.58
35	596.3	155	1266	75.8	5.17
36	597.4	20.1	1119.5	64.6	17.3×10^{-6}
38	598.0	19.0	1180	64.0	18.9
12	626.4	364	91	84.2	3.78×10^{-5}
10	625.0	391	109	84.8	2.99
8	623.7	379	195	81.0	2.28
9	625.0	390	338	71.0	2.80
13	626.9	36	213	72.8	3.85
11	625.1	36	399	66.2	3.79
21	625.2	17.5	163	75.0	4.02
19	625.2	18.2	229	69.0	4.90
20	624.6	18.6	258.5	66.8	5.43
23	650.2	446	34.5	80.6	1.33×10^{-4}
24	650.6	458	21.0	84.2	1.64
41[a]	651.2	334	63.0	69.4	1.72
25	650.6	153	61.0	73.1	1.31
26	651.2	156	31.5	82.8	1.22
27	651.0	37	31.5	77.4	1.85
28	651.0	38	64.0	68.3	1.87
29	651.2	19.5	32.5	77.4	1.79
30	650.2	20.0	60.5	73.1	1.32
39[a]	650.2	21.0	30.8	74.8	2.29
40[a]	651.2	20.0	66.5	66.8	2.11

[a] Six times surface.

Figure 2 shows the temperature dependence of the rate of isomerization. Only the runs at the highest pressures have been used. The activation energy is found to be 46,000 ± 1000 cal., which is somewhat higher than those obtained earlier for other *cis–trans* isomerizations involving phenylethylene groups.[1] With this value for the activation energy, the reaction rate constant at high pressures receives the form

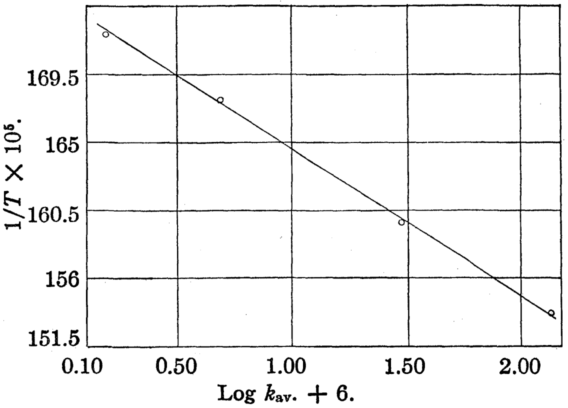

Fig. 2.—Log k–$1/T$ plot of the first order isomerization rate constant.

$$k = 10^{11.6 \pm 0.4}\, e^{-(46{,}000 \pm 1000)/RT}$$

Little new can be added to the comments which were made in earlier papers on the *cis–trans* isomerization, but we wish to point out once more that apparently in all reactions involving rotations of heavy groups, the "A" factor is considerably lower than the "normal" value, 10^{13}, to be expected from statistical considerations.

The Eyring[7] theory, which in a simplified version, possibly applicable to the present case, gives the rate constant as

$$k = \nu e^{-E/RT}$$

ν being here presumably the frequency of the torsional vibration around the double bond, leads to values of this frequency which are of the order of 1–10 cm.$^{-1}$, hence rather too small.

Summary

1. The rate of isomerization of β-cyanostyrene has been studied and found to be of the first order. The velocity constant at higher pressures is given by

$$k = 10^{11.6 \pm 0.4}\, e^{-(46{,}000 \pm 1000)/RT} \text{ sec.}^{-1}$$

2. The equilibrium mixture at 352° contains 63% high boiling (*trans*) isomer. The equilibrium composition appears to be practically independent of temperature.

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(7) Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

CAMBRIDGE, MASS. RECEIVED OCTOBER 7, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RHODE ISLAND STATE COLLEGE]

Some Characteristics of the Residue from the Cracking of Castor Oil[1]

BY ARTHUR A. VERNON AND HALKEY K. ROSS

Much work has been done to determine the chemical nature of castor oil and the results of Krafft,[2] Walden[3] and Kasansky[4] have shown that it consists mainly of the glyceride of ricinoleic acid. More recently Eibner and Münzing[5] have shown that the fatty acid content of castor oil is 95%; 80% is ricinoleic acid and the remaining 15% is a mixture of oleic, linoleic, stearic and dihydroxystearic acids. The structural formula indicates that the probable place of breaking under the influence of heat would be between the twelfth and thirteenth carbon to yield an aldehyde as is the case with hydroxy acids. The glyceryl portion of the molecule[6] should rupture readily to give acrolein and such is experimentally found to be true on this basis. The third product of decomposition should be undecylenic acid but in actual practice the residue from atmospheric cracking, after removal of heptaldehyde and acrolein, is a complex mixture. Perkins and Cruz[7] found that the distillation at 400° under a pressure of 50 mm. produced a distillate composed of about 40% heptaldehyde and 20% of undecylenic acid. Roy[8] studied the changes in castor oil when heated to 140° in the presence of oxygen and nitrogen. The viscosity, iodine number, acid number and index of refraction were found to

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(1) From a thesis submitted by Halkey K. Ross to the faculty of Rhode Island State College in partial fulfilment of the requirements for a Master of Science degree.

(2) Krafft, *Ber.*, **10**, 2034 (1877).

(3) Walden, *ibid.*, **27**, 3471 (1894).

(4) Kasansky, *J. soc. phys. chim. russe*, **32**, 149 (1901).

(5) Eibner and Münzing, *Chem. Umschau Fette, Öle, Wachse Harze*, **32**, 166–176 (1925).

(6) Charles D. Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, Chapter 15.

(7) Perkins and Cruz, THIS JOURNAL, **49**, 1073 (1927).

(8) Roy, *Compt. rend.*, **196**, 1423–1424 (1933).

increase in the presence of oxygen. It was felt that an investigation of the properties of the products of the pyrolysis of castor oil might give information concerning the mechanism of the breakup under the influence of heat and therefore an investigation was made of the acid value, saponification value, acetyl value and iodine number of the residue. Barbot[9] has suggested a molecular rearrangement as the way in which the molecule may break up under the influence of heat and the results of this work may be of value for his interpretations.

Apparatus.—The castor oil was allowed to flow at a constant rate into a heated silica tube 65 cm. long and 2 cm. inside diameter and the product condensed in a water-cooled condenser. The temperature inside the tube was measured with a chromel–alumel thermocouple enclosed in glass.

Material.—The castor oil was Baker chemical grade with these constants: acid value, 12.5; saponification number, 178.3; acetyl value, 152.1; iodine value, 87.13.

Procedure.—The tube was heated to the desired temperature and the oil allowed to flow into the tube at a rate of 505 g. per hour. The first 10–15 cc. of the cracked product was discarded and then about 150 cc. of the material was collected.

This substance was steam distilled until the removal of heptaldehyde was complete. The remaining material was washed, then dried with anhydrous sodium sulfate in an oven at about 100°. According to Woodman[10] this is the customary method of drying oils and fatty acids. Samples were then analyzed to determine the chemical constants.

The acid and saponification values were determined according to the A. O. A. C. Book of Methods.[11]

The acetyl values were made according to the method of Andre-Cook.[12] The iodine numbers were found according to the Wijs Method.[11]

TABLE I

DATA CONCERNING THE RESIDUE

Temp., 0°	Acid number	Saponification number	Acetyl value	Iodine value
299	3.46	178	151.0	85
340	12.40	176	140.0	92
405	55.30		130.5	107
410		164		
450	148.80	82	93.8	
475	155.50	79	41.3	113
510	170.00	70	33.2	
540	171.20			117
620	187.50	48	23.5	119
675	217.00	42		124
750				123

The results of the determinations are summarized in Table I.

The results of the acid number, saponification number and acetyl value determinations are plotted in Fig. 1 to show how these three characteristics vary with the temperature of pyrolysis.

It was noted that dark brown fumes were emitted and that there was no smell of acrolein in the distillate above 800°. A decomposition took place above 800° which resulted in the production of some aromatic compounds.

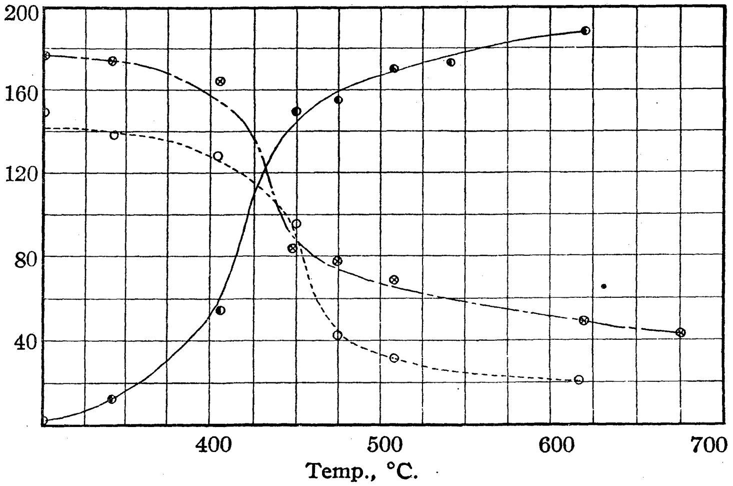

Fig. 1.—Variation of characteristics of castor oil residue with temperature of pyrolysis: ◐, free acid value; ⊗, saponification number; ○, acetyl value.

In order to determine the place of undecylenic acid in the pyrolysis, a test was made in which it was subjected to the same temperatures as castor oil at the same rate of 505 g. per hour, and the iodine value of the residue was determined. The results of this experiment are shown in Table II.

TABLE II

IODINE VALUE OF UNDECYLENIC ACID

Temp., °C.	Iodine value
135	126.6
214	127.2
280	126.9
355	129.0
505	127.8
565	135.0
640	142.0
735	113.6

A plot of the values of Table II appears in Fig. 2 together with the determinations of the iodine number of cracked castor oil.

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(9) Barbot, *Compt. rend.*, **197**, 65–67 (1933).

(10) A. G. Woodman, "Food Analysis," McGraw-Hill Book Co., Inc., New York, 1931, p. 174.

(11) Association of Official Agricultural Chemists, Book of Methods, Second Edition, XX, 19–20, 288 (1925).

(12) Andre-Cook, *J. A. O. A. C.*, 326 (1927).

Discussion of Results

Figure 1 shows a sharp drop in saponification value at about 425° and this would indicate that the glyceryl portion of the molecule is broken off at this temperature. Figure 1 also shows an increase in the acid value at the same temperature, which is added evidence for the formation of free acid. It would seem from this that the first pyrolytic action to occur is the decomposition of the glyceryl portion and the production of acrolein. Figure 1 further shows that the acetyl value drops at 465°, which means that the hydroxyl grouping of the castor oil disappears at this point. This would indicate the formation of heptaldehyde and undecylenic acid. A valuable check on this hypothesis can be made if the characteristics of the residue after the removal of heptaldehyde and acrolein can be shown to be similar to the characteristics of the product of the pyrolysis of undecylenic acid alone. If the acetyl value of the castor oil residue is taken at some temperature and the amount of undecomposed castor oil is calculated, then the amount of iodine number contributed by that undecomposed castor oil can be calculated. If the remainder of the iodine value is attributed to undecylenic acid and its decomposition products, this value can be obtained from Fig. 2 at the corresponding temperature. The sum of these two values should agree with the corresponding iodine value of the castor oil residue.

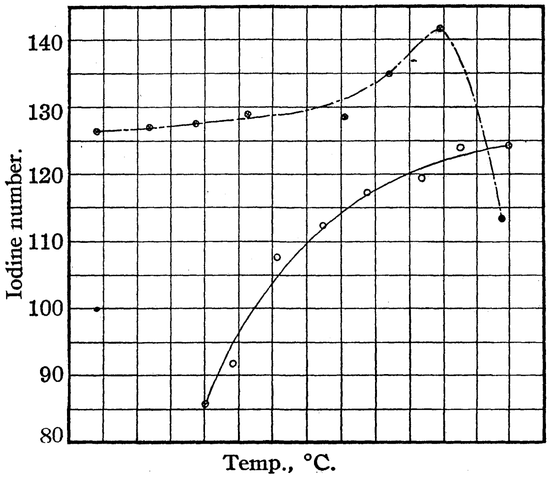

Fig. 2.—Variation of iodine number with temperature of pyrolysis: ⊗, undecylenic acid; ○, castor oil.

The agreement shown in the table is within the precision of the iodine number determinations.

TABLE III

CALCULATED AND OBSERVED IODINE VALUE OF THE CASTOR OIL RESIDUE

Temp., °C.	Calcd. iodine value of residue	Observed value of residue
300	85	85
450	104.7	110
475	115.7	113
500	117	115
550	123.4	118
600	126.6	120.5
650	130	122
700	125	123
725	114.5	121

Ho, Wan and Wen[13] have shown that the iodine value is influenced by the amount of excess iodine solution used for a given sample. The weight of the sample taken for these determinations was always approximately the same, and the iodine solution added was always the same. Since the unsaturation of the samples varied, therefore the iodine excess must have been greater in some samples than in others. This undoubtedly influenced the values obtained. Part of the discrepancy might be attributed to the 20% of the other substances present in castor oil.

The most favorable yield of heptaldehyde obtained was 28.9% by weight of castor oil while the theoretical yield would be 34%.

Work is at present in progress to determine quantitatively the amounts of acrolein and heptaldehyde which are produced at various temperatures. It is hoped that in this way a careful check can be made on the possible mechanism which seems to be indicated by the results obtained. These would be valuable since Shepard[14] has stated that ricinoleic acid has not been cracked successfully to give heptaldehyde. However, the conditions of the pyrolysis in the cracking of castor oil may not be the same as the chemical condition when ricinoleic acid is pyrolyzed.

Summary

1. Castor oil was submitted to pyrolysis at various temperatures in a heated silica tube. The acrolein and heptaldehyde were removed and the iodine number, acetyl value, saponification value and acid value of the residue was determined.
2. Undecylenic acid was submitted to pyrolysis under the same conditions.
3. The results may be explained by assuming

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[13] K. Ho, C. S. Wan and S. H. Wen, *Ind. Eng. Chem., Anal. Ed.*, **7**, 97 (1935).

[14] M. G. Shepard, private communication.

that acrolein splits off first and then the molecule breaks down to give heptaldehyde. The latter reaction requires a higher temperature.

KINGSTON, R. I. RECEIVED JULY 21, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MISSOURI, AND THE NEW MEXICO NORMAL UNIVERSITY]

The Lead–Uranium Ratio of Henvey Cyrtolite[1]

BY O. B. MUENCH

In September, 1931, Dr. H. V. Ellsworth of the Department of Mines, Canada, sent a lump of cyrtolite obtained from the Besner Mine, Henvey Township, Ontario, to the University of Missouri. At that time work on the Hybla Cyrtolite[2] was planned and partly under way, so it was found impossible to do more than a little preliminary work on the Henvey Cyrtolite. Work on this cyrtolite was carried to definite results during the summer of 1935. A lead–uranium ratio on this cyrtolite is interesting for comparison with the one on a Besner Uraninite[3] which has been available for some time.

The occurrence of this cyrtolite and its mineral associates are described by Spence[4] and also Ellsworth[3] (p. 173).

The Sample.—The sample was mostly in one large piece with feldspar at one end. It was very homogeneous, of black pitchy luster and seemed to be altered very little, if any. Only the black homogeneous part was taken, and pulverized in an iron mortar until all of it passed through an 80-mesh sieve. This sieve had no solder from which contamination might be derived. The pulverized sample of cyrtolite weighed 242 g.

Methods of Analysis

In general, the procedure followed in the determination of the uranium, after the sample was in solution was as follows. The zirconium and hafnium were removed as phosphates in acid solution, and then after the removal of the iron, etc., as sulfides in ammonium carbonate solution, the uranium was precipitated as the phosphate in a solution slightly acid with acetic acid. The phosphate method was used because phosphate had been introduced in the removal of the zirconium and hafnium and it was therefore the most direct method to follow. The thorium, after the sample was in solution, and the zirconium and hafnium had been removed by precipitation as phosphates in sulfuric acid solution, was precipitated as the oxalate in oxalic acid solution. Two different methods were followed from this point on. In the peroxide method, the oxalate was converted to the nitrate and the thorium precipitated with hydrogen peroxide from a neutral solution of ammonium nitrate. The precipitate on ignition changes to the oxide. In the iodate method, the oxalate was first converted to the nitrate, and then precipitated with potassium iodate in strong nitric acid solution. The iodate precipitate was dissolved in hydrochloric acid and the thorium precipitated with ammonium hydroxide. Finally this precipitate was dissolved in hydrochloric acid and then the thorium precipitated with oxalic acid. The oxalate was ignited to the oxide and weighed. The lead was determined by the usual procedure of separation as a sulfide, conversion to a sulfate, extraction with ammonium acetate and final precipitation as a chromate.

Uranium.—One-gram samples were fused with sodium peroxide (which oxidized all the carbon) in a nickel crucible. The fused samples were then dissolved in hydrochloric acid, baked in a porcelain dish, taken up with dilute hydrochloric acid and filtered. The residue, after volatilization with hydrofluoric and sulfuric acids, was added to the filtrate. The solution was made alkaline with pure ammonium hydroxide. After three precipitations with pure ammonium hydroxide, the precipitate was dissolved in 30 ml. of concd. sulfuric acid. From this point on, the procedure as given in the paper, "The Age of a Canadian Cyrtolite,"[2] near the bottom of p. 489 was followed.

Thorium.—Five-gram samples were taken for analysis. The method as given in the above

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[1] This work is a portion of a project assisted financially in part by a grant from the National Research Council.

[2] Muench, *Am. J. Sci.*, **25**, 487 (1933).

[3] Ellsworth, "Rare-element Minerals of Canada," Geological Survey, Department of Mines, Canada, Series, No. 11, 1932, p. 268.

[4] Spence, *Am. Min.*, **15**, 11, 513 (1930).

paper[2] was followed, except that after the treatment with hydrofluoric acid the samples were treated with nitric and sulfuric acids and heated to fuming in order to remove carbon. After the samples were taken to the point described at the bottom of p. 491, two samples were analyzed by the iodate method.[5] The third sample was analyzed by Fenner's[6] modification of the peroxide method. His method was followed for this sample from p. 376, when the residue is taken up with 100 ml. of 20% ammonium nitrate solution.

RESULTS OF ANALYSES

Uranium

Sample, g.	$(UO_2)_2P_2O_7$, g.	Uranium, %
1.0068	0.0268	1.77
1.0090	.0283	1.87
1.0025	.0278	1.85
1.0002	.0273	1.82
2.0003	.0545	1.83
	Average	1.83

Thorium

Sample, g.	ThO_2, g.	Thorium, %
5.0100	0.0007	0.01
5.0010	.0008	.01
5.0012	.0007	.01
	Average	.01

Lead

Sample, g.	$PbCrO_4$, g.	Lead, %
30.0000	0.0165	0.035
10.0000	.0059	.037
10.0000	.0058	.037
10.0000	.0057	.036
	Average	.036

SULFUR DETERMINATIONS (SUMMARY)[7]

Total sulfur, %S	Soluble sulfates, as %S	Insoluble sulfides, pyrite, etc., %S	By difference soluble sulfides and insol. sulfates as %S
0.079	0.007	0.006	0.066
Loss at 110°, three hours		.46	
Loss on ignition		9.79	

Lead-uranium ratio,

$$\frac{\text{Ra G}}{\text{U} + 0.36\text{Th}}, \frac{0.036}{1.83 + 0.36 \times 0.01} = 0.019$$

Lead.—The method used for the lead determination was essentially that described in the paper "The Age of a Canadian Cyrtolite."[2]

Recoveries of lead were made on the filtrates and are included in the weights of the lead chromate precipitates. Carefully tested, lead-free reagents were used.

Approximate Age of the Mineral.—We have no atomic weight determination of the lead from this cyrtolite. Assuming the absence of ordinary lead, the approximate age calculated from the above lead-uranium ratio is

$$\frac{0.019 \times 1.15 \text{ million years}}{1.57 \times 10^{-4}} = 139 \text{ million years.}$$

Acknowledgment.—The writer wishes to express his gratitude to Dr. H. Schlundt for his interest in this work and also the use of the Laboratories and other facilities of the University of Missouri. The author is indebted to Dr. A. C. Lane for his many suggestions and to Dr. H. V. Ellsworth for furnishing the mineral sample. Thanks are here expressed to the National Research Council for financial aid.

Conclusion

As pointed out by Lane,[7] the lead ratio is abnormally low and only about a sixth of that of the uraninite from the same mine. He gives a possible explanation of this.

Practically the entire sample was used for the determinations described in this paper, leaving an insufficient amount for an atomic weight determination of the lead. The approximate age of this mineral in the absence of an atomic weight determination of the lead, is calculated from the analysis as one hundred and thirty-nine million years.

The amount of thorium is so small that no critical test of the two methods is indicated by the results.

The percentage of sulfur is higher in this cyrtolite than in the other cyrtolites which were analyzed at the same time for sulfur.

LAS VEGAS, N. M.

RECEIVED OCTOBER 14, 1936

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(5) Method of Meyer and Speter as given by Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 420.

(6) Fenner, *Am. J. Sci.*, **16**, 369 (1928).

(7) Muench, *Am. Min.*, **21**, 374 (1936).

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 565

On the Application of the Raman–Krishnan Theory to Dipole Moment Measurements by the Dilute Solution Method

BY H. O. JENKINS AND S. H. BAUER

It has been suggested by Le Fèvre and Le Fèvre[1] that the Raman–Krishnan theory of anisotropic dielectrics[2] provides an explanation of the effect of the medium on the determination of the moment by the dilute solution method. We wish to point out that strong theoretical objections to the Raman–Krishnan treatment itself can be raised and to demonstrate empirically that the particular application is not useful since accurate predictions cannot be made by means of it.

To begin with, it is difficult to justify the expression given by the latter investigators for the local field (equation 11, note 2) when the parameters are given the meaning they intend them to have. An extended argument for the model they had in mind is presented by Krishnan and Rao,[3] who attempt to show that the field at the center of an ellipsoidal cavity of the dimensions of a single molecule immersed in a medium of uniform polarizability is the proper value to be taken for the local field. We should like to draw attention to the restrictions to which the equations used in obtaining the field in a cavity are subjected, *viz.:* the cavity must be so large that it contains many of the volume elements over which the necessary integrations are to be performed and hence must contain many molecules, while at the same time it must be sufficiently small so that the polarization does not vary appreciably across it. As the cavity is made smaller quadrupole and higher order terms should be taken into consideration, and when its dimensions approach those of a single molecule the integration of the polarization over the surface of the cavity should further be replaced by a summation. If these latter troublesome evaluations are to be avoided, the cavity must be made of dimensions of the order of thousands of molecules and then, obviously, the local field will be independent of the shape chosen.

Hence, as far as we can see, for solutions one cannot escape calculating the contribution to the local field of the material inside the cavity (called F_3), which requires that special assumptions be made regarding the distribution of charges around the dipole in question. To emphasize the complexity of the situation we shall list the factors which must be taken into consideration in expressing the mean volume polarization of a sufficiently dilute solution (one in which dipole–dipole interactions may be neglected) in terms of molecular constants: (a) the effect of the impressed field upon the solvent molecules; (b) the effect of the dipoles on the solvent molecules in their immediate vicinity; (c) the effects of solvent molecules on each other (usually quite small); (d) the effect of the impressed field upon the solute molecules; (e) the effect of the polarization of the solvent on the solute molecules (due to factors a, b and c); (f) the statistical fluctuations in the above effects (those of a and c are usually considered; the others are neglected). Since a rigorous treatment of all the above factors would be indeed a formidable task,[4] an empirical or semi-empirical method of approach seems the most promising at present. It is encouraging to note that F. E. Hoecker[5] has obtained highly accurate measurements on extremely dilute solutions of ethyl alcohol in various non-polar solvents and found that in the usual treatment an apparently anomalous behavior often takes place at great dilutions. By slightly modifying the analysis he was able to perform the extrapolation to zero concentration to obtain for the electric moment a value which agreed very well with the accepted one for the gas.

Since the ultimate value of a theory may best be ascertained by investigating its usefulness in predicting the results of experiments, we assumed the final form of the R–K formula (equation 23) and made the following empirical test. It was, however, first necessary to derive from the latter an expression which is applicable to a dilute solution. [We here wish to indicate that the Le Fèvre equation is not the one which is obtained

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(1) C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1747 (1935), and subsequent papers in the same journal.

(2) C. V. Raman and K. S. Krishnan, *Proc. Roy. Soc.* (London), **A117**, 589 (1927).

(3) K. S. Krishnan and S. R. Rao, *Indian J. Physics*, **4**, 39 (1929).

(4) Lars Onsager, THIS JOURNAL, **58**, 1486 (1936), considered some of these factors but restricted his discussion to spherical isotropic molecules immersed in an isotropic medium.

(5) F. E. Hoecker, *J. Chem. Phys.*, **4**, 431 (1936).

through the strict application of the theory since it gives only the most significant term but omits others which may be appreciable (see tables below); also that one should keep in mind that two assumptions must be made in attempting the suggested application: (a) the volume polarizations of the components are additive (*i. e.*, no interactions between solute and solvent molecule takes place which will alter their moments); (b) the new constants entering into the formulation are to be characteristic of the molecules themselves and not of the state of aggregation.] Under this circumstance

$$\frac{\epsilon_{12}-1}{\epsilon_{12}+2}\,\frac{M_1f_1+M_2f_2}{\rho_{12}} = \frac{4\pi N}{3}\left\{\left(\frac{a_{ii}+a_{jj}+a_{kk}}{3}\right)_1 f_1 + \left(\frac{a_{ii}+a_{jj}+a_{kk}}{3}\right)_2 f_2\right\} + N\,\frac{\epsilon_{12}-1}{\epsilon_{12}+2}\,(\psi_1f_1+\psi_2f_2) + \frac{N}{3kT}\left\{\frac{4\pi}{3}\,\mu^2 + \frac{\epsilon_{12}-1}{\epsilon_{12}+2}\,\theta_2\right\} f_2 \quad (1)$$

(suffix $_1$ refers to solvent; $_2$ to solute; $_{12}$ to solution), and M, f, N, ρ, k, T have their usual significance.

$\theta_2 = (\mu_i^2\sigma_i + \mu_j^2\sigma_j + \mu_k^2\sigma_k + \text{negligible cross terms})_2$

with $\sigma_i = p_i - \dfrac{4\pi}{3}$

$\mu_{i,j,k}$ are the components of the permanent electric moment of the solute molecule resolved along the principal axes of electric polarizability

$p_{i,j,k}$ are the factors determining the polarization field acting along any particular axis when the external field is along that axis

$\psi_2 = \dfrac{1}{3}\,(a_{ii}\sigma_i + a_{jj}\sigma_j + a_{kk}\sigma_k)_2$

and similarly for ψ_1

where $a_{ii,jj,kk}$ are the diagonal elements of the induced moment tensor.

The ψ's and θ_2 are therefore measures of the anisotropy of the molecules composing the mixture.[6] Equation (1) may be rewritten

$$(P_{12}) \equiv (P_1^{\text{g}})f_1 + (P_2^{\text{g}})f_2 = \frac{4\pi N}{3}\left\{\left(\frac{a_{ii}+a_{jj}+a_{kk}}{3}\right)_1 f_1 + \left(\frac{a_{ii}+a_{jj}+a_{kk}}{3}\right)_2 f_2 + \frac{\mu^2}{3kT}f_2\right\} = \frac{\epsilon_{12}-1}{\epsilon_{12}+2}\left\{\frac{M_1f_1+M_2f_2}{\rho_{12}} - N(\psi_1f_1+\psi_2f_2) - \frac{N}{3kT}\,\theta_2f_2\right\} \quad (2)$$

from which it may appear that one may solve for P_2^{g} from the value of ϵ_{12} at any concentration provided the molecular anisotropy constants are known. The molecular polarization symbols are therefore placed in parentheses to indicate that this is not legitimate as dipole–dipole and other interactions have not been taken into consideration in equation (2). The usual procedure of extrapolating to infinite dilution must be resorted to. Since in the range of concentrations used it has been experimentally verified that[7]

$$\begin{aligned}\epsilon_{12} &= \epsilon_1(1+K_1f_2+K_2f_2^2)\\ \rho_{12} &= \rho_1(1+R_1f_2+R_2f_2^2)\end{aligned} \quad (2a)$$

one finds

$$(P_2^{\text{g}})_\infty = \frac{\epsilon_1-1}{\epsilon_1+2}\,\frac{M_1}{\rho_1}\left\{\frac{M_2}{M_1} - R_1 + \frac{3\epsilon_1K_1}{(\epsilon_1-1)(\epsilon_1+2)}\right\} - \frac{3\epsilon_1K_1N}{(\epsilon_1+2)^2}\,\psi_1 - \frac{\epsilon_1-1}{\epsilon_1+2}\,N\left(\psi_2+\frac{1}{3kT}\,\theta_2\right) \quad (3)$$

which is an expression for the "gas" value of the polarization obtained by extrapolating data on dilute solutions using the R–K equation. But the first term of the right member of (3) is equal to P_2^{sol};[8] whence

$${}_\infty P_2^{\text{sol}} = (P_2^{\text{g}})_\infty + \frac{\epsilon_1-1}{\epsilon_1+2}\,N\left\{\psi_2+\frac{\theta_2}{3kT}\right\} + \frac{3\epsilon_1NK_1}{(\epsilon_1+2)^2}\,\psi_1 \quad (4)$$

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(6) One may indicate at this point why the R–K equation as applied for the purpose at hand breaks down. Although in the first paper on the subject written by these authors it is stressed that the ψ's and θ's are to depend on the state of aggregation as well as on the characteristics of the particular molecules, in the subsequent work, however, these quantities were treated consistently as molecular constants and, in fact, must be so considered if their values are to be calculated theoretically.

(7) The use of a quadratic form is somewhat unusual. It is, however, a simple matter to show that this is essential in a number of cases. The authors wish to stress particularly that the graphical methods of extrapolation which are almost universally employed in this work are not sufficiently sensitive to detect deviations from linearity which may introduce as much as five per cent. error in the values of K_1 and R_1. Thus, for nitrobenzene in *n*-hexane, the K_1 derived from measurements on a solution for which $f_2 = 0.046$, was 7.566 when a linear relation was used but reduced to 7.232 when a quadratic one was assumed.

(8) With the aid of (2a), an expansion results in the following analytic expression for the quantity usually referred to as

$$P_2^{\text{sol}} = \phi_0 + \phi_1f_2 + \phi_2f_2^2 + \phi_3f_2^3 + \ldots \text{ where}$$

$$\phi_0 = \frac{\epsilon_1-1}{\epsilon_1+2}\,\frac{M_1}{\rho_1} \equiv P_1^{\text{g}}$$

$$\phi_1 = \frac{\epsilon_1-1}{\epsilon_1+2}\,\frac{M_1}{\rho_1}\left\{\frac{M_2}{M_1} - 1 - R_1 + \frac{3\epsilon_1K_1}{(\epsilon_1+2)(\epsilon_1-1)}\right\}$$

$$\phi_2 = \frac{\epsilon_1-1}{\epsilon_1+2}\,\frac{M_1}{\rho_1}\left\{R_1^2 - R_1\left(\frac{M_2}{M_1}-1\right) - R_2 + \frac{3\epsilon_1K_1}{(\epsilon_1+2)(\epsilon_1-1)}\left(\frac{K_2}{K_1}+\frac{M_2}{M_1}-1-R_1-\frac{\epsilon_1K_1}{\epsilon_1+2}\right)\right\} \text{ etc.}$$

It is clear then that although in the final value of ${}_\infty P_2^{\text{sol}}$ the second order coefficients of f_2 do not appear, they do make a contribution to P_2^{sol} and their non-vanishing may introduce significant changes in the values of K_1 and R_1 which will affect the limiting value. Again, for nitrobenzene in *n*-hexane, ϕ_2 varies by approximately 12% in going from $f_2 = 0.046$ to 0.015 (H. O. Jenkins, *J. Chem. Soc.*, 480 (1934)). It is thus of interest to raise the question whether the extrapolations made heretofore on the assumption of a linear variation of P_2^{sol} with f_2 are valid in the range of concentrations investigated. Apparently, even though the slope of the line may vary by large amounts as indicated above, the limiting value actually changes slightly due to the fact that the ratio $\phi_2f_2/(\phi_0+\phi_1)$ is a small quantity.

As a rule, the $\frac{\epsilon_1 - 1}{\epsilon_1 + 2} N\psi_2$ term is of the order of a cc. and may be neglected.[9]

In making the test of the applicability of the theory we calculated values of θ_2 for a number of polar solutes and compared them with the values which one must assume in order to explain the solvent effect. To obtain ψ_1 and θ_2, one must first compute the appropriate σ and a terms. There are several possible sources for these: (1) x-ray diffraction data for the liquid, giving closest distances of approach, as recommended by Krishnan and Rao. We desire to stress that such values are only significant when derived through the use of the Ehrenfest–Keesom equation, within the limitations indicated by Warren;[10] (2) light scattering data on the liquids; (3) the variation of the polarization of the liquids with pressure;[11] (4) molecular geometry as derived through the use of tables of covalent radii[12] and electron diffraction data (published by Pauling, Brockway and others). The eccentricity of the ellipsoidal cavity produced by the removal of the molecule of interest from the body of the medium which is considered as continuous may be assumed to be determined by the molecular dimensions only; the formulas given by Lord Rayleigh[13] are to be used. Method (4) enabled the authors to calculate the σ's while the a's were determined from light scattering data according to the procedure outlined by Krishnan and Rao. The following values were obtained.

TABLE I

Compound	ψ_1	a_{ii}	a_{jj} ($\times 10^{24}$)	a_{kk}	σ_1	σ_2	σ_3
n-Hexane	-2.1×10^{-24}	13.9	10.8	10.8	−1.68	0.82	0.82
Cyclohexane	−1.3	12.0	12.0	10.0	−0.58	−0.58	1.12
Carbon tetrachloride	−0.0						
Benzene	−5.2	12.9	12.9	6.38	−1.18	−1.18	2.32
Carbon disulfide	−7.0	5.74	5.74	13.0	1.47	1.47	−2.92

	θ_2	σ*
Nitrobenzene	-43.4×10^{-36}	−2.46
Chlorobenzene	− 7.6	−2.36
4-Chlorodiphenyl	− 8.9	−3.48
4-Nitrodiphenyl	−68.2	−3.52
α-Nitronaphthalene	−31.6	−1.88
β-Nitronaphthalene	−49.5	−2.46

* In making these calculations, the coördinate system was so chosen as to orient one of the major axes parallel to the direction of the resultant dipole. Then only one σ term appears in the expression for θ_2. The appropriate ones are listed.

By analogy with the corresponding chloro compounds the gas electric moments of α- and β-nitronaphthalene have been assumed to be 4.1 *D* and 4.5 *D*, respectively. The shape of the β-compound was considered to be approximately ellipsoidal while that of the α an oblate spheroid.

The following two tables give the values of θ_2 which are required to explain the experimental facts for nitrobenzene and chlorobenzene. The total polarization of these at 25° in the gas phase are 400 cc. and 91 cc., respectively.[14]

TABLE II

NITROBENZENE IN VARIOUS SOLVENTS

Solvent	$_\infty P^{\text{sol}}$	$\frac{3N\psi_1 K_1\epsilon_1}{(\epsilon_1 + 2)^2}$	$\theta_2 \times 10^{36}$	$\theta'_2 \times 10^{36}$
n-Hexane	372.5	− 3.4	−21.4	−24.4
Cyclohexane	360.0	− 2.4	−30.1	−32.0
Carbon tetrachloride	353.1	− 0.0	−32.7	−32.7
Benzene	353.8	−11.6	−23.5	−31.4
Carbon disulfide	310.0	−19.3	−40.6	−51.6

CHLOROBENZENE IN VARIOUS SOLVENTS

Solvent	$_\infty P^{\text{sol}}$	$\frac{3N\psi_1 K_1\epsilon_1}{(\epsilon_1 + 2)^2}$	$\theta_2 \times 10^{36}$	$\theta'_2 \times 10^{36}$
n-Hexane	86	− 0.7	− 3.8	− 4.4
Cyclohexane	84	− 0.7	− 5.0	− 5.6
Carbon tetrachloride	81	− 0.0	− 7.0	− 7.0
Benzene	81	− 1.7	− 5.6	− 6.8
Carbon disulfide	75	− 2.3	− 7.6	− 9.0

From Table II it can be seen that whether the effect of the solvent has been taken into consideration in the ψ_1 term (column 3) or whether it has been neglected (column 4), within the range of 50% θ_2 is not a molecular constant.[6]

Experiments also indicate that the polarizations of many substances are closely alike in benzene and carbon tetrachloride solutions but since ψ_1 is 5.2×10^{-24} for the former and zero for the

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[9] Le Fèvre and Le Fèvre neglected the term involving ψ_1 as well.

[10] B. E. Warren, *Phys. Rev.*, **44**, 969 (1933).

[11] Data for a number of hydrocarbons are given by Ch. Francke, *Ann. phys.*, **77**, 177 (1925).

[12] L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[13] Scientific Papers, Vol. 4, p. 307.

[14] H. Müller, *Physik. Z.*, **34**, 689 (1933); H. O. Jenkins, *J. Chem. Soc.*, 480 (1934).

latter, the theory predicts that a difference should always exist. For nitrobenzene this difference is predicted to be 11 cc. but only 1 cc. has been found experimentally. The theory also indicates the presence of considerable divergences in the behavior of substituted diphenyl and naphthalene derivatives from that of the corresponding benzene compounds. That this is unlikely is demonstrated by the fact that the polarization of 4-chlorodiphenyl in benzene is close to that of chlorobenzene; further experimental work will be undertaken shortly to test this point.

Acknowledgments.—The authors wish to express their thanks to Professors Pauling and Houston and to Dr. Wheland for the many discussions relating to the material here presented. One of us (H. O. J.) is indebted to the Commonwealth Fund for a fellowship.

Summary

Theoretical objections to the Raman–Krishnan theory of anisotropic dielectrics are raised.[15] Empirical tests further indicate that the application of the above theory to dielectric constant measurements of dilute solutions of polar solutes in non-polar media would enable one to predict the difference between the moments as determined by the dilute solution method and those derived from gas measurements only as to order of magnitude.

[15] Subsequent to the submittal of this manuscript to the Editor a paper by Hans Mueller appeared [*Phys. Rev.*, **50**, 547 (1936)] in which essentially similar conclusions were reached through the use of arguments quite unlike those presented here.

PASADENA, CALIF. RECEIVED SEPTEMBER 4, 1936

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE NEW YORK STATE EXPERIMENT STATION]

The Influence of Neutral Salts on the Optical Rotation of Gelatin. V. Rotatory Dispersion of Gelatin in Sodium Bromide Solutions[1]

BY D. C. CARPENTER AND F. E. LOVELACE

Previous work from this Laboratory[2] has shown that a single term Drude equation $[a]_\lambda = k/(\lambda^2 - \lambda_0^2)$ expressed the rotatory dispersion of gelatin dissolved in sodium iodide solutions and that the dispersion was governed by an absorption band at 2200 Å. At 40° the rotatory dispersion constant k was linearly related to sodium iodide concentration and at 0.5° was found to be expressed by the sum of two equations, $C_{\mathrm{NaI}} = k \log [a/(1 - a)] - \log (1/K)$ and the linear equation $K_{0.5°} = K - k_0 C_{\mathrm{NaI}}$. It was concluded that the tremendous effect of sodium iodide on the rotation of gelatin at 0.5° was due to an association or dissociation of the gelatin molecule.

The purpose of the present investigation was to continue the rotatory dispersion studies using sodium bromide solutions as solvent and ascertain if the above equations were applicable to other alkali metal halide systems.

Experimental

The procedure for preparing the solutions and for the measurement of rotations, density, *p*H, etc., was the same as has been described before.[3]

The specific rotations of gelatin solutions at 0.5 and 40° were measured at five different wave lengths in the visible spectrum, *viz.*: red lithium line, $\lambda = 6707.86$ Å.; sodium D line, $\lambda = 5892.617$ Å. (optical mean); yellow mercury line, $\lambda = 5780.13$ Å. (optical mean); green mercury line, $\lambda = 5460.73$ Å.; and the deep blue mercury line, $\lambda = 4358.34$ Å. The various light filters employed have been described. The gelatin concentration of the solutions was 0.7824 g. per 100 g. of solution.

Discussion and Conclusions

In Tables I and II are given our data for 0.5 and 40°, respectively, for the wave lengths employed. In Figs. 1 and 2 these data are graphed, plotting the reciprocal of specific rotation against the squares of the wave lengths at which the rotations were obtained. The relationship is linear, which means that a single-term Drude equation adequately expresses the results.

As with sodium iodide solutions of gelatin, the straight lines cut the x-axis at the same point, corresponding to $\lambda_0 = 2200$ Å., the location of the absorption band of gelatin. The same value for λ_0 was obtained by solving our data mathematically by the method used before. The values of k, numerator in the Drude equation, were calculated for each concentration of sodium bromide and appear in Table III and are graphed in Fig. 3. At 40° the k values bear a linear relation to

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[1] Approved by the Director of the New York State Experiment Station for publication as Journal Paper No. 153.

[2] Carpenter and Lovelace, THIS JOURNAL, **57**, 2342 (1935).

[3] Carpenter, *J. Phys. Chem.*, **31**, 1873 (1927); Carpenter and Kucera, *ibid.*, **35**, 2619 (1931); Carpenter and Lovelace, THIS JOURNAL, **57**, 2337 (1935).

TABLE I

SPECIFIC ROTATION OF GELATIN SOLUTIONS CONTAINING SODIUM BROMIDE AT 0.5° FOR DIFFERENT WAVE LENGTHS OF LIGHT

Soln.	Concn. of NaBr, molal	Density at 25°	pH	Levo degrees λ 6707.86 Å. (a)	[α]	λ 5892.62 Å. (a)	[α]	λ 5780.13 Å. (a)	[α]	λ 5460.73 Å. (a)	[α]	λ 4358.34 Å. (a)	[α]
1	0.00	1.0023	6.50	3.83	248.01	5.14	332.84	5.38	348.38	6.15	398.24	10.86	703.23
2	.50	1.0414	6.28	3.94	241.80	5.30	325.27	5.54	339.99	6.33	388.47	11.18	686.11
3	1.01	1.0869	6.18	3.91	229.89	5.25	308.68	5.49	322.79	6.28	369.24	11.09	652.05
4	1.34	1.1186	6.21	3.78	215.98	5.08	290.25	5.31	303.39	6.08	347.39	10.72	512.60
5	1.65	1.1490	6.14	3.49	194.13	4.70	261.43	4.91	273.11	5.62	312.61	9.91	551.22
6	1.95	1.1790	6.09	3.02	163.17	4.06	220.10	4.24	229.85	4.85	262.92	8.57	464.58
7	2.20	1.2048	5.90	2.54	134.74	3.41	180.89	3.57	189.38	4.08	216.43	7.19	381.42
8	2.45	1.2321	6.02	2.18	113.07	2.93	151.97	3.06	158.71	3.50	181.53	6.18	320.53
9	2.68	1.2608	5.88	1.94	98.33	2.61	132.29	2.73	138.37	3.12	158.14	5.50	278.77
10	3.05	1.3050	5.93	1.71	83.74	2.29	112.15	2.40	117.54	2.74	134.19	4.84	237.04
11	3.40	1.3518	6.04	1.61	76.11	2.17	102.59	2.26	106.85	2.59	122.45	4.57	216.19
12	4.20	1.4626	5.67	1.48	64.67	1.99	86.95	2.08	90.88	2.38	104.00	4.20	183.52

TABLE II

SPECIFIC ROTATION OF GELATIN SOLUTIONS CONTAINING SODIUM BROMIDE AT 40° FOR DIFFERENT WAVE LENGTHS OF LIGHT

Soln.	Concn. of NaBr, molal	Density at 25°	pH	Levo degrees λ 6707.86 Å. (a)	[α]	λ 5892.62 Å. (a)	[α]	λ 5780.13 Å. (a)	[α]	λ 5460.73 Å. (a)	[α]	λ 4358.34 Å. (a)	[α]
1	0.00	1.0023	6.50	1.71	110.73	2.30	148.94	2.41	156.06	2.75	178.07	4.86	314.71
2	.50	1.0414	6.28	1.72	105.56	2.31	141.76	2.42	148.52	2.77	170.00	4.88	299.48
3	1.01	1.0869	6.18	1.70	99.95	2.28	134.05	2.39	140.52	2.73	160.51	4.82	283.40
4	1.34	1.1186	6.21	1.68	95.98	2.26	129.13	2.36	134.84	2.70	154.27	4.77	272.54
5	1.65	1.1490	6.14	1.66	92.33	2.23	124.04	2.34	130.16	2.67	148.51	4.71	261.99
6	1.95	1.1790	6.09	1.64	88.90	2.21	119.80	2.31	125.22	2.64	143.11	4.66	252.62
7	2.20	1.2048	5.90	1.62	85.93	2.18	115.64	2.28	120.95	2.61	138.49	4.60	244.02
8	2.45	1.2321	6.02	1.59	82.46	2.14	110.99	2.24	116.18	2.56	132.78	4.52	234.43
9	2.68	1.2608	5.88	1.59	80.59	2.14	108.47	2.24	113.54	2.56	129.76	4.52	229.10
10	3.05	1.3050	5.93	1.57	76.89	2.11	103.33	2.20	107.74	2.52	123.41	4.45	217.93
11	3.40	1.3518	6.04	1.54	72.80	2.07	97.86	2.17	102.59	2.48	117.25	4.38	207.07
12	4.20	1.4626	5.67	1.48	64.67	1.99	86.95	2.08	90.88	2.38	104.00	4.20	183.52

concentration of sodium bromide as given by the equation

$$k_{40^\circ} = 44.517 - 4.415C_{\mathrm{NaBr}} \qquad (1)$$

At 0.5° the curve for the k values is made up of two simultaneously occurring effects, the one a linear relationship to concentration of sodium bromide

$$k_{0.5^\circ} = 46.330 - 4.8476C_{\mathrm{NaBr}} \qquad (2)$$

similar to the one above except for the fact that the constants are slightly different in magnitude from those at 40°, and a second relationship

$$C_{\mathrm{NaBr}} = \frac{1}{1.33}\log\left(\frac{a}{1-a}\right) - \log\,(1/K) \qquad (3)$$

where a represents the fraction dissociated as shown by the change in magnitude of the dispersion constants $k_{0.5^\circ}$. In Table III are given the a values for the dissociated fraction and the calculated values obtained for log $(1/K)$. The latter agree very well with one another and indicate a mean value of 2.002. The factor 1/1.33 preceding the dissociation term regulates how rapidly the dissociation or association takes place.

TABLE III

ROTATORY DISPERSION CONSTANTS AT 0.5 AND 40°

Soln.	Concn. NaBr, molal	$k_{0.5^\circ}$	a	Log $(1/K)$	k_{40°
1	0	99.541	..	...	44.517
2	0.50	97.117	..	...	42.407
3	1.01	92.261	0.045	2.010	40.110
4	1.34	86.723	.116	1.995	38.553
5	1.65	78.023	.254	2.002	37.122
6	1.95	65.723	.458	2.005	35.756
7	2.20	54.064	.654	1.992	34.548
8	2.45	45.375	.795	2.008	33.167
9	2.68	39.502	.884	2.016	32.411
10	3.05	33.558	.962	1.993	30.842
11	3.40	30.568	.987	2.002	29.275
12	4.20	25.971	1.000	...	25.974

$k_{0.5} = 99.541 - XC_{\mathrm{NaBr}}$ where $X = 4.8476$
$k_{40} = 44.517 - XC_{\mathrm{NaBr}}$ where $X = 4.4149$
Mean log $(1/K) = 2.002$.

Attention is called to the identity of the ratio, for the salts sodium iodide and sodium bromide, between the respective constants for the linear equation (eq. 1 and 2); $k_{40}/k_{0.5^\circ} = 0.92$ for sodium iodide and 0.91 for sodium bromide. Attention

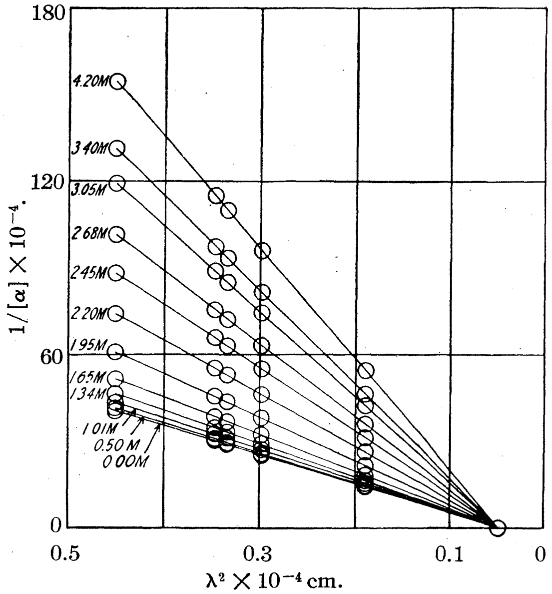

Fig. 1.—Graph of reciprocal of specific rotation *versus* wave length squared at 0.5°.

is also directed to the change in the value of the constant preceding the logarithmic term, log $[a/(1 - a)]$ (eq. 3), in going from sodium iodide to the bromide. With sodium bromide this constant (1/1.33) is exactly double that found for sodium iodide (1/2.66). Our preliminary experiments with sodium chloride indicate a value of 1/0.67, a further doubling of the value of this constant. The log $(1/K)$ term meanwhile changes from 0.9983 for sodium iodide to 2.002 for sodium bromide, an almost exact doubling; a preliminary value of 4.0 is indicated for sodium chloride, again a doubling. It is clear that for all the sodium halides the various log $(1/K)$ terms can be rewritten now as a common constant k' log $(1/K)$ of value 2.66, k' being the reciprocal of the former k.

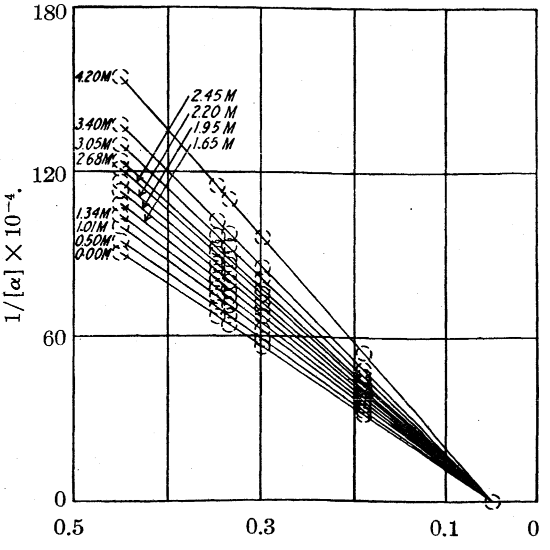

Fig. 2.—Graph of reciprocal of specific rotation *versus* wave length squared at 40°.

It is clear that in our experiments the influence of salts on the optical rotation cannot be explained as the polarization of the optically active molecules in an ionic atmosphere. According to Debye and Hückel, such an effect would require a greater effect for ions with small radii and large charges. If this were the case chlorides would be expected to have a greater effect on the rotation than iodides, which is contrary to fact.

It is not at present clear as to why the k constants preceding the dissociation term (1/0.67, 1/1.33 and 1/2.66) bear this mathematical regularity, respectively, for chlorides, bromides and iodides. It is pointed out that the sixth power of the ionic radii of the halogens as recorded by Wasastjerna[4] (Cl = 1.72; Br = 1.92; I = 2.19 Å.) gives a ratio 26:49:109, almost exactly the 1:2:4 ratio given by the respective denominators of the above k constants. While the principal effect of neutral salts on gelatin at 0.5° is no doubt due to the anion of the salt, nevertheless, the cation has a slight influence which is not accounted for in the sixth power relationship mentioned above.

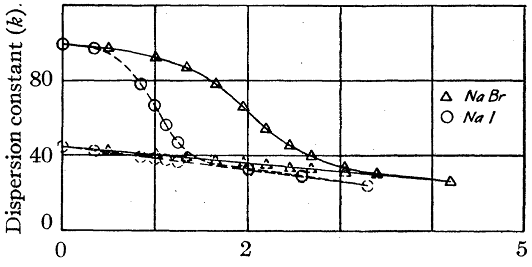

Fig. 3.—Rotatory dispersion constant of gelatin in sodium bromide solutions at 0.5 and 40°.

Smith[5] concluded that the effect of heating gelatin was to cause a bimolecular reaction to take place in which two molecules of the original protein were united together into one molecule at elevated temperatures. We have noted before[6] that heating to 40° caused a doubling of the molecular weight of the simplest species of casein. Weber and Stover[7] record osmotic pressure data

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[4] Wasastjerna, *Soc. Sci. Fennica Commentationes Phys. Math.*, **38**, 1 (1923).

[5] C. R. Smith, THIS JOURNAL, **41**, 135 (1919).

[6] Svedberg, Carpenter and Carpenter, *ibid.*, **52**, 241, 701 (1930)

[7] Weber and Stover, *Biochem. Z.*, **259**, 269 (1933).

giving the molecular weight of muscle protein as 81,000 in water solution and as 300,000 in ammonium thiocyanate solution. We have shown[3] that potassium thiocyanate has the same sort of effect on the optical rotation of gelatin at 0.5° and of about the same magnitude as potassium iodide and that the effect of the sodium halides follows the dissociation (association) formulation stated before. The effect of the halide salts on the rotation at 0.5° also appears to be the same effect as that of raising the temperature, recorded by Smith. It seems fairly well established that the influence of the halide salts on gelatin at low temperatures is to cause an association of the protein molecule.

On applying the Lucas formulation[8] for two optically active components

$$k = \left[\frac{[\alpha]_1 - [\alpha]_2}{[\alpha]_1 - [\alpha]_n}\right]_{\lambda_a} = \left[\frac{[\alpha]_1 - [\alpha]_2}{[\alpha]_1 - [\alpha]_n}\right]_{\lambda_b} = \left[\frac{[\alpha]_1 - [\alpha]_2}{[\alpha]_1 - [\alpha]_n}\right]_{\lambda_c} \text{etc.} \quad (4)$$

to our data, the constants given in Table IV were obtained for the various combinations employed. It is obvious that a constant is actually obtained for any combination for a series of different wave lengths, as is required for a mixture of two optically active substances. We conclude therefore that the behavior of gelatin at 0.5° in the presence of sodium bromide is entirely analogous to its behavior with sodium iodide, that two and only two optically active species are present and that one optically active form is converted to the other by the action of the neutral salt and that one active form is the associated form of the other.

TABLE IV

CALCULATION OF THE LUCAS CONSTANT FOR GELATIN-SODIUM BROMIDE SYSTEM CONTAINING TWO OPTICALLY ACTIVE COMPONENTS (0.5°)

Combination[a]	λ 6708 Å.	λ 5893 Å.	λ 5780 Å.	λ 5461 Å.	λ 4358 Å.
1-2/1-12	0.0338	0.0307	0.0325	0.0332	0.0329
1-3/1-12	.0988	.0982	.0993	.0985	.0984
1-4/1-12	.175	.173	.175	.173	.175
1-5/1-12	.294	.290	.292	.291	.292
1-6/1-12	.463	.459	.460	.460	.459
1-7/1-12	.618	.618	.617	.618	.619
1-8/1-12	.736	.736	.737	.737	.734
1-9/1-12	.816	.816	.816	.816	.817
1-10/1-12	.896	.898	.896	.897	.897
1-11/1-12	.938	.937	.938	.937	.937

[a] The numbers in this column refer to corresponding soln. no. in Table I.

Summary

The rotatory dispersion of gelatin has been examined in various concentrations of sodium bromide at 0.5 and 40°, at five different wave lengths in the visible spectrum.

As was previously shown with sodium iodide solutions, a single term Drude equation expressed the experimental results. An absorption band at 2200 Å. governed the dispersion.

The rotatory dispersion constants of gelatin at 40° follow the linear equation $k_{40°} = 44.517 - 4.415\, C_{\text{NaBr}}$.

The rotatory dispersion constants at 0.5° were found to be expressed by the sum of two equations

$$C_{\text{NaBr}} = \frac{1}{1.33} \log \left(\frac{a}{1-a}\right) - \log (1/K)$$

and the linear equation

$$K_{0.5°} = 46.330 - 4.8476 C_{\text{NaBr}}$$

It was concluded that the great change in rotation caused by halides at 0.5° is due to an association of the gelatin molecule.

Based on the Lucas formulation, two and only two optically active species exist in gelatin solutions and gels.

GENEVA, N. Y. RECEIVED JULY 31, 1936

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(8) Lucas, *Ann. phys.*, [10] **9**, 381 (1928); *Trans. Faraday Soc.*, **26**, 418 (1930).

[Contribution from the Laboratories of the R. & H. Chemicals Department, E. I. du Pont de Nemours & Co., Inc.]

Sodium Naphthalene. I. A New Method for the Preparation of Addition Compounds of Alkali Metals and Polycyclic Aromatic Hydrocarbons

By N. D. Scott, J. F. Walker and V. L. Hansley

The direct reaction of alkali metals with certain aromatic hydrocarbons has been reported previously in the literature, the reaction of sodium with anthracene in ethyl ether solution[1] being an example. Efforts to extend this reaction to simpler hydrocarbons such as naphthalene and diphenyl have met with very limited success. Schlenk and Bergmann were able to cause lithium to react with these hydrocarbons to a sufficient extent to make some examination of the products[2] but reported no detectable reaction with sodium under similar conditions.

A solution of sodium in liquid ammonia also has been used to bring about the addition of sodium to naphthalene but in this case the reaction is complicated by the rapid ammonolysis of the products.[3] Liquid ammonia as a solvent has the added disadvantage of reacting with carbon dioxide, interfering with the use of this reagent in characterizing the sodium compounds.

We have found that when methyl ether is used as the solvent medium the previously known sodium reactions take place many times faster than in ethyl ether. Furthermore, with this solvent it is possible to increase the scope of the reaction to include naphthalene and diphenyl as well as many other aromatic hydrocarbons. This striking difference of methyl ether compared with ethyl ether is more than a difference in the rate of the reaction, for if ethyl ether is added to a solution of sodium naphthalene in dimethyl ether the rate of formation of the sodium compound is gradually decreased. If sufficient ethyl ether is added the formation of the sodium compound is inhibited completely and the compound already formed decomposes with the liberation of the original hydrocarbon and elementary sodium. With concentrated solutions of hydrocarbons in pure methyl ether it is possible to dissolve one or two gram atoms of sodium per liter in two hours or less. It is already known that the first member of most homologous series of organic compounds shows the more characteristic properties of the series to a unique degree but the surprising difference between methyl ether and ethyl ether has not been fully appreciated by previous investigators. Methyl ethyl ether is the only other monoether in which these reactions occur readily. The formation of sodium naphthalene is slow but detectable in the methyl propyl ethers.[4]

In seeking for suitable solvents that are liquid at ordinary temperatures, we discovered that the dimethyl ether of ethylene glycol (b. p. 85°) is substantially equivalent to dimethyl ether as a solvent for sodium reactions. Contrary to the conclusions that might have been drawn from the behavior of monoethers it was found that all fully alkylated glycols and polyhydric alcohols are effective solvents for sodium addition reactions.[5] It was also found that trimethylamine and a few other amino compounds are effective although they offer little advantage over the ethers.

For most purposes dimethyl ether and the dimethyl ether of ethylene glycol are the most suitable solvents for the reaction, and the latter is the more convenient by reason of its boiling point. It is, however, slowly attacked by sodium naphthalene at room temperature with the formation of methyl vinyl ether, presumably in accordance with the equation

$$C_{10}H_8Na_2 + 2CH_3OCH_2CH_2OCH_3 \longrightarrow C_{10}H_{10} + 2CH_3ONa + 2CH_3OCH{=}CH_2$$

The methyl vinyl ether was identified by its boiling point and unsaturation toward bromine.

The presence of the special solvent is required not merely for the initiation of the reactions but for the existence of sodium naphthalene. This can be shown by preparing a solution of sodium naphthalene in dimethyl ether and then completely evaporating the ether at room temperature. The dark green solution deposits a very dark green solid which changes to gray in color with loss of the last traces of ether. The solid will then on treatment with water evolve nearly the theoretical amount of hydrogen as such. When sodium naphthalene solution is treated with water no hy-

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(1) Schlenk, Appenrodt, Michael and Thal, *Ber.*, **47**, 479 (1914).

(2) Schlenk and Bergmann, *Ann.*, **463**, 91 (1928).

(3) Wooster and Smith, This Journal, **53**, 179–187 (1931).

(4) Scott, U. S. patent 2,019,832 (1935).

(5) Scott, U. S. patent 2,023,793 (1935).

drogen is evolved. If the solid be extracted with heptane a residue is obtained consisting almost entirely of sodium. For most purposes the isolation of sodium naphthalene in the solid state is not attempted since its reactions are conveniently carried out in solution.

The special solvents which are effective for the reaction of sodium with naphthalene can be used in similar fashion with the other alkali metals. In place of naphthalene one may use methyl naphthalenes, acenaphthene, diphenyl or phenanthrene, none of which react with sodium in ethyl ether solution. The special solvents also have a striking effect in facilitating the addition reactions of sodium with anthracene and with benzophenone, causing much more rapid reaction than occurs in ethyl ether. The special solvents do not appear to facilitate the reaction of sodium with hydrocarbons such as triphenylmethane, fluorene, or acetylene where the characteristic reaction is one of substitution.

Solutions of sodium naphthalene display many unusual properties. The solutions are dark green in color and have good electrical conductivity. No quantitative measurements have been made of the heat of the reaction by which they are formed, but it is not large. This is consistent with the ease of dissociation of the compound either by removing the ether solvents by evaporation or by dilution with a large volume of hydrocarbon solvent, or by removing the sodium, for example by shaking with mercury. The amount of sodium which will dissolve readily in a solution of naphthalene or diphenyl is only one atom per molecule of hydrocarbon. Inasmuch as many of the reactions of the solution correspond with a disodium naphthalene addition compound, this raises the question of the formula of the compound. The formula $C_{10}H_8Na_2{\cdot}C_{10}H_8$ correctly represents the proportions of sodium and naphthalene while avoiding the question of structure. Discussion as to structure will largely be deferred to later papers dealing more fully with the reactions.

The reactions of sodium naphthalene can be divided into two classes. In the first the naphthalene is recovered unchanged, the solution behaving much like dissolved sodium. In this class one may mention the reactions with mercury, with oxygen, and with benzyl chloride. In the second class of reactions the naphthalene is reduced to dihydronaphthalene or its derivatives depending on the reagent used. With water, alcohols or the wide range of organic compounds capable of forming sodium derivatives where sodium replaces hydrogen, the products are dihydronaphthalene and the sodium compound of the material used as source of hydrogen. For example with acetylene the reaction can be represented by the equation

$$C_{10}H_8Na_2{\cdot}C_{10}H_8 + 2C_2H_2 \longrightarrow C_{10}H_{10} + C_{10}H_8 + 2C_2HNa$$

This is a convenient method for the preparation of a variety of sodium derivatives.

In general, the only requirements for the formation of sodium naphthalene and related compounds in dimethyl ether and other active ether solvents are that the solvent be pure and dry and that the hydrocarbon be reasonably pure. It is also imperative that a clean surface of alkali metal be exposed to initiate the reaction. Once started, the reaction thoroughly cleans any metal surface that was not originally clean. When pieces of sodium that are reacting come in contact in the reaction mixture, they fuse together, even at −30° and lower. Impurities such as water, methanol and carbon dioxide prevent the reaction from starting by forming products which coat the surface of the alkali metal as soon as it is exposed. If they are only present in traces, however, persistent scratching of the metal surface will eventually lead to their destruction and the reaction will proceed.

Experiments

Preparation of Sodium Naphthalene Solutions

A. In Dimethylglycol Ether.—One liter of a molal solution of naphthalene in pure dry dimethyl glycol ether is placed in a two-liter three-necked flask equipped with a mercury-sealed stirrer in which an atmosphere of pure dry nitrogen is maintained. About 25 g. of sodium is then added, the metal being cut in the form of sticks 2–3 cm. long and 3–5 mm. square on the end. After the sodium has been added the mixture is agitated mechanically. The stirring should be rapid at the start but should be decreased considerably after the reaction has commenced. With a good grade of dimethylglycol ether the reaction should start in one to three minutes. Some cooling is required, and this can be accomplished safely by the use of a methanol cooling bath to which solid carbon dioxide is added as required. The reaction mixture should be kept between −10 and +30°. At temperatures below −10° the reaction rate falls off considerably in dimethylglycol ether. At 20–25° the reaction is complete in about two hours. Unreacted sodium which is usually stuck together in a single piece can then be removed easily from the mixture with forceps.

The progress of the reaction can be measured from time to time by removal of small samples of the reaction mixture and determination of their sodium content, after dilution with alcohol, by titration with standard acid using methyl red. This does not discriminate between sodium naphthalene and other suspended or dissolved alkaline sodium compounds in the solution but when pure solvent is used it gives a close approximation of the sodium naphthalene that has been formed.

B. In Dimethyl Ether.—The preparation of sodium naphthalene in dimethyl ether is carried out in much the same way as in dimethylglycol ether except for the changes occasioned by the low boiling point (−25°). The flask in which the reaction is to be carried out is cooled to about −50° in a bath of solid carbon dioxide and methanol, and the solvent is led in as a gas from a cylinder and condensed. The reaction is best carried out at a temperature of −30°. The nature of the solvent makes it difficult to make analyses in this case, but an approximate measure of the reacted sodium can be obtained easily by weighing the unreacted sodium recovered after the completion of the reaction.

Dimethylglycol Ether.—This reagent was prepared by the methylation of the monomethyl ether of ethylene glycol. It must be purified and thoroughly dried for use in alkali metal reactions. It is a colorless fluid with a characteristic ether-like odor boiling at 85°.

Dimethyl Ether.—This ether was sufficiently pure as obtained from the Ammonia Department of E. I. du Pont de Nemours & Company, Inc.

Summary

The reaction of aromatic hydrocarbons with sodium is so greatly facilitated by employing dimethyl ether or dimethylglycol ether as the solvent, in place of diethyl ether, that with the use of these special solvents even such hydrocarbons as naphthalene and diphenyl can be converted easily into sodium compounds.

NIAGARA FALLS, N. Y. RECEIVED SEPTEMBER 23, 1936

[CONTRIBUTION FROM THE BURROUGHS WELLCOME AND CO., U. S. A., EXPERIMENTAL RESEARCH LABORATORIES]

The Separation of Primary Aryl Amines from Secondary Alkylaryl Amines

BY CLAYTON W. FERRY AND JOHANNES S. BUCK

In the course of the preparation of a series of unsymmetrical alkylaryl ureas and thioureas[1,2] a number of secondary alkylaryl amines, substantially free from primary aryl amines, was required (small amounts of tertiary amines are unimportant, since they form no ureas). When alkoxy and certain N-alkyl groups are present in the secondary amine, the usual methods of preparation (*e. g.*, *via* the acyl derivatives, nitroso compounds, etc.) are not satisfactory[2] and it is necessary to alkylate the primary aryl amine directly and to remove unchanged primary amine from the product. A method for carrying out this removal, suggested by the work of Eibner and by several patents[3] and outlined by DeBeer, Buck, Ide and Hjort[2] is here described, whereby the primary amine is removed readily by shaking the crude secondary amine with benzaldehyde–sodium bisulfite compound and water. The primary amine combines with the reagent and is recoverable, while the secondary amine remains unattacked.

Experimental

Twenty grams each of primary aryl amine and secondary alkylaryl amine (the secondary amines mentioned in this report were all purified *via* the nitroso compound) were mixed and shaken mechanically with water and benzaldehyde–sodium bisulfite compound at room temperature. The mixture was then filtered from the solid with suction, the solid well washed with ether and the filtrate extracted with ether. The total ether was washed with brine, the ether evaporated and the residual amine tested for primary amine.

In the first series of experiments, designed to investigate the conditions of reaction, the above process was repeated until tests showed the absence of any appreciable amount of primary amine (< 0.5%). In the first treatment 50 cc. of water and one mol of bisulfite compound (calculated on the primary amine present) were used. In the second treatment 30 cc. of water and 0.5 mol of bisulfite compound and in the third and subsequent treatments, 30 cc. of water and 0.25 mol of bisulfite compound were used. In all cases the shaking was for two hours per treatment.

When this method was applied to mixtures of methyl aniline, *n*-butylaniline, ethyl-*m*-toluidine, ethyl-*p*-toluidine and ethyl-*o*-phenetidine, with the corresponding primary amine, over 80% of the secondary amine, containing less than 0.5% of the primary amine was obtained after the third treatment. Similar mixtures from ethyl-*p*-phenetidine and isopropyl-*p*-anisidine required, respectively, four and five treatments, about 54% of the secondary amine being recovered. A mixture from ethyl-*o*-toluidine was not purified to less than 10% of primary amine, even after five treatments.

The second series of experiments was carried out in order to simplify the process practically, and to reduce the losses in manipulation. It was found that, using the same mixture (20 g. primary amine, 20 g. secondary amine), efficient separation could be obtained by six hours of shaking

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[1] Buck, Hjort and DeBeer, *J. Pharmacol.*, **54**, 188 (1935).

[2] DeBeer, Buck, Ide and Hjort, *ibid.*, **57**, 19 (1936).

[3] German Patent 181,723, 132,621, 157,909; Eibner, *Ann.*, **316**, 89 (1901).

with two mols (calculated on the primary amine present) of bisulfite compound and 140 cc. of water. The yield also was much improved. Thus, with mixtures of methylaniline, *n*-butylaniline, ethyl-*m*-toluidine, ethyl-*p*-toluidine and ethyl-*p*-phenetidine with the corresponding primary amine, the content of primary amine was reduced to 0.5% or less. The recovery was, respectively, 80, 94, 92, 90 and 78% of the secondary amine taken. In practice, 50% of primary amine in a mixture is rarely encountered and the amount is usually much less, so that the separation would be correspondingly facilitated.

The major part of the primary amine may be recovered from the aqueous liquors from the extractions and from the solid filtered off, by adding to these 200 cc. of water containing 25 cc. of concd. sulfuric acid and steam-distilling the mixture. Benzaldehyde comes over and may be largely recovered. The acid liquid in the flask is then made alkaline with 30% sodium hydroxide solution and the steam distillation continued, the receiver being changed. The primary amine may be recovered by saturating the distillate with salt and extracting four times with ether. After drying, the ether is evaporated and the residual amine distilled. From the mixtures cited above there was recovered aniline, 92%; aniline 87%; *m*-toluidine, 88%; *p*-toluidine, 90%; and *p*-phenetidine, 75%, respectively.

The boiling points of the recovered secondary amines were the same as those of authentic specimens[4] (the yields throughout refer to distilled amines of the correct boiling point). As an additional check the recovered secondary amines from the first series of experiments were converted into the α-naphthyl ureas and these were compared with specimens prepared from authentic amines. The melting points of the ureas from the recovered amines were in general only two or three degrees lower than those of the corresponding purified ureas, except in the cases of ethyl-*o*-phenetidine and ethyl-*p*-phenetidine, where the melting points were, respectively, eight and five degrees lower. The yields, in all cases, were substantially the same from either recovered or authentic amine.

α-Naphthyl Ureas.—Three cc. of α-naphthyl isocyanate (20–25% excess) was added to 2 cc. of amine (weighed) in 15 cc. of hexane. The oil which separated soon crystallized, and was filtered off and well washed with petroleum ether and its melting point determined. The ureas (from authentic amines), recrystallized from alcohol, form small, glistening, granular crystals, readily soluble in hot alcohol and in hot benzene, that from ethyl-*o*-toluidine being considerably more soluble than the others. The α-naphthyl ureas, not previously described, are tabulated below.

α-ALKYL-α-ARYL-β-(α-NAPHTHYL) UREAS

α-Groups	Formula	M. p., °C.	Analyses, %N Calcd.	Found
Methyl, phenyl	$C_{18}H_{16}ON_2$	99	10.14	10.29
n-Butyl, phenyl	$C_{21}H_{22}ON_2$	99	8.80	9.03
Ethyl, *o*-tolyl	$C_{20}H_{20}ON_2$	85.5	9.21	9.27
Ethyl, *m*-tolyl	$C_{20}H_{20}ON_2$	95.5	9.21	9.39
Ethyl, *p*-tolyl	$C_{20}H_{20}ON_2$	103	9.21	9.51
Isopropyl, *p*-anisyl	$C_{21}H_{22}O_2N_2$	147	8.38	8.48
Ethyl, *o*-phenetyl	$C_{21}H_{22}O_2N_2$	136.5	8.38	8.43
Ethyl, *p*-phenetyl	$C_{21}H_{22}O_2N_2$	111	8.38	8.43

Benzaldehyde–sodium bisulfite compound was prepared in the usual manner and well washed with water. The product is satisfactory for ordinary purposes, but for the present work it was recrystallized from water, then washed with ether when dry.

Primary amines were tested for by a spot method, an adaptation of the method of Cumming, Hopper and Wheeler,[5] using both "R" salt and (better) "H" salt and comparing the colors produced with those given by known mixtures. The carbylamine reaction, also used, was carried out in the usual manner, with alcoholic potassium hydroxide and chloroform. Both tests readily showed the presence of 0.5% primary amine.

In attempting to purify ethyl-*o*-toluidine several bisulfite compounds were tried (from anisaldehyde, *m*-nitrobenzaldehyde, and salicylaldehyde) but without much improvement. The reaction of ethyl-*o*-toluidine with isocyanates is relatively sluggish, and this fact allows a fair separation from primary amine to be made. A specimen of ethyl-*o*-toluidine, containing 10% *o*-toluidine, in 4 volumes of petroleum ether was well cooled and phenyl isocyanate (1.5 times calcd. for the primary amine present) added in one lot. After two and one-half minutes strong ammonium hydroxide was added (twice the volume of the amine), the whole chilled and the crystalline material filtered off and washed with petroleum ether. The total petroleum ether, after washing with water and drying (potassium hydroxide) was evaporated and the residual amine distilled. There was obtained in 80% yield, ethyl-*o*-toluidine, b. p. 103–104.5° (16 mm.), containing about 1% *o*-toluidine.

The recovered secondary amines usually contain small amounts of benzaldehyde, which can be readily removed if necessary by dissolving the amine in acid. Estimated as acid-insoluble material, the benzaldehyde varied, with different amines, between 0.3 and 1.7%, but was usually close to the lower figure.

Attempts to extend the method to the separation of aliphatic amines were finally abandoned. In general the solubility of the amines in water, the instability of the azomethine compounds usually formed and the solubility of these compounds in organic solvents render a practical separation not feasible. The use of formaldehyde–sodium bisulfite compound helps matters somewhat, but the method still is not practical.

Summary

An expeditious method for separating mixtures of primary aryl amines with secondary alkylaryl amines is here described. The method depends on the preferential combination of benzaldehyde–sodium bisulfite compound with primary aryl amines, and is very generally applicable. An alternative method, involving the use of phenyl isocyanate, is suggested for mixtures of *o*-toluidine and ethyl-*o*-toluidine. Some α-naphthyl ureas derived from the secondary amines are described.

TUCKAHOE, N. Y. RECEIVED OCTOBER 10, 1936

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(4) Hjort, DeBeer, Buck and Ide, *J. Pharmacol.*, **55**, 152 (1935), and to be published later.

(5) Cumming, Hopper and Wheeler, "Systematic Organic Chemistry," 2d ed., D. Van Nostrand Co., New York, 1928, p. 501.

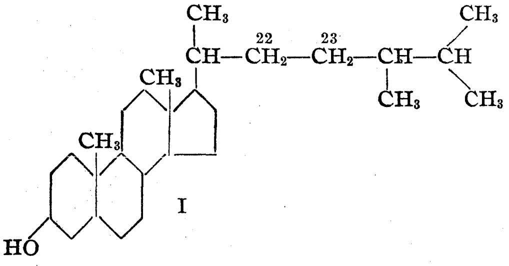
[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

α-Sitosterol

BY EVERETT S. WALLIS AND E. FERNHOLZ[1]

It can now be stated with a fair degree of certainty that the structural formulas of cholesterol, ergosterol and stigmasterol are well established. Our knowledge, however, of the most common plant sterol, sitosterol, is still unsatisfactory. This is due to the fact that sitosterol is in reality a mixture of several sterols, and that their separation is effected with great difficulty. This observation was first made by Anderson, Shriner and Burr.[2] These investigators showed that sitosterol obtained from various sources is not a homogeneous substance but that it contains dihydrositosterol and at least three other sterols. They named these latter compounds α, β- and γ-sitosterol. γ-Sitosterol, which is the least soluble, was isolated by them in nearly a pure state. The purification of β-sitosterol was not so complete. The α-sitosterol was obtained only in a very impure condition; no satisfactory method for its purification was discovered.

Recently certain information has become available regarding the constitution of β- and γ-sitosterol. Bengtsson[3] has compared derivatives of β-sitostanol with stigmastanol. From his experiments he has come to believe that these compounds are identical, and that, therefore, β-sitosterol is in reality 22-dihydrostigmasterol (I).



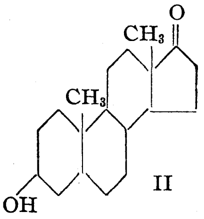
I

This conclusion has indeed a high degree of probability.

A valuable contribution to our knowledge of γ-sitosterol has been made recently by Oppenauer.[4] This investigator prepared dehydroandrosterone (II) from sitosterol If we assume that a sufficiently pure γ-sitosterol was used in these experiments, this fact proves that the ring system of both β- and γ-sitosterol is the same, and that they differ only in the structure or stereochemical arrangement of the side chain.

In this connection mention should be made also of certain other observations. Bonstedt[5] has reported that γ-sitostane and stigmastane, when mixed together, give a strong depression of the melting point. This fact supports the idea that β- and γ-sitosterol are different compounds, and not more or less impure specimens of the same substance. Anderson[2] expresses the opinion that the different sitosterols are isomers.

In this paper we wish to report certain experiments which show that such a conclusion cannot be reached for the most soluble fraction of the sitosterol complex, called by Anderson and co-workers,[2] α-sitosterol.[6] From recrystallization of 500 g. of a sitosterol obtained from wheat germ oil we separated 36 g. of a material rich in α-sitosterol. A method of purification of this material had to be developed since Anderson and his co-workers[2] were unsuccessful in effecting a separation by crystallization of the acetates, and by bromination. Preliminary experiments showed that this could be accomplished by means of a fractional crystallization of the corresponding benzoates. Accordingly this mixture of sterols (36 g.) was converted into the corresponding benzoates. By a single crystallization 23 g. of a benzoate, m. p. 144°, which was mainly β-sitosteryl benzoate, was removed. The α-sitosteryl benzoate remained in the mother liquor. This more soluble benzoate was then hydrolyzed and converted into the corresponding m-dinitrobenzoate. By fractional crystallization two new dinitrobenzoates were isolated in a pure state. The least soluble α_1-sitosteryl m-dinitrobenzoate was obtained in a yield of 1 g. The more soluble α_2-sitosteryl m-dinitrobenzoate, which seems to be the more plentiful constituent, was obtained only in a yield of 0.4 g. It is possible that other



II

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(1) Merck Fellow in Organic Chemistry.

(2) R. J. Anderson, R. L. Shriner and G. O. Burr, THIS JOURNAL, **48**, 2987 (1926); see also Anderson and Shriner, *ibid.*, **48**, 2987 (1926); Anderson, *ibid.*, **46**, 1450 (1924).

(3) B. E. Bengtsson, *Z. physiol. Chem.*, **237**, 46 (1935).

(4) R. V. Oppenauer, *Nature*, **135**, 1039 (1935).

(5) Bonstedt, *Z. physiol. Chem.*, **205**, 137 (1932).

(6) Burian [*Monatsh.*, **18**, 551 (1897)], who also observed the difference in the solubility of this fraction from the bulk of the sitosterol, named it para-sitosterol.

sterol *m*-dinitrobenzoates were present in the mother liquors.

The properties of α_1- and α_2-sitosterol and their derivatives are given in the table.

Derivative	α_1-Sitosterol		α_2-Sitosterol	
	M. p., °C.	$[\alpha]^{25}_D$	M. p. °C.	$[\alpha]^{25}_D$
Sterol	166	-1.7	156	$+3.5$
Acetate	137	$+29$	126	$+17$
Benzoate	172	$+42$	166	$+27$
m-Dinitrobenzoate	222	$+37$	206	$+26$

We also wish to report certain other important observations. These two new sterols are *not* isomers of β- and γ-sitosterol. α_1-Sitosterol is an isomer of stigmasterol, $C_{29}H_{48}O$, and α_2-sitosterol is in all probability a homolog, $C_{30}H_{50}O$. Titration with perbenzoic acid shows that two double bonds are present in both sterols. Both sterols give the same color reaction (Liebermann). The final color is a dark blue with a reddish tint. The Salkowski reaction for both α_1- and α_2-sitosterol is similar to that of ergosterol; the sulfuric acid layer becomes colored, while the chloroform stays colorless. The opposite is true for cholesterol, γ-sitosterol, and stigmasterol; α_1- and α_2-sitosterol are precipitated by digitonin.

Experimental Part

Five hundred grams of sitosterol,[7] isolated from wheat germ oil (m. p. 134–137°, $[\alpha]^{20}_D$ $-30°$ in chloroform), was subjected to a systematic crystallization from a mixture of alcohol and benzene, and from alcohol. The most soluble fractions were collected. They had a total weight of 36 g., and melted unsharply at 141°, $[\alpha]^{20}_D$ $-24°$.

The shape of these crystals is different from those of the main portion. They are small needles. β- and γ-sitosterol crystallize in large leaflets.

This material (36 g.) was dissolved in 150 cc. of pyridine and to the solution was added 30 cc. of benzoyl chloride. The mixture was kept on a boiling water-bath for an hour. The benzoate, so formed, was taken up in ether, and recrystallized from a mixture of benzene and alcohol. Twenty-three grams of a benzoate was obtained in well-defined leaflets which melted at 144°. This is mainly β-sitosteryl benzoate. Ten grams of a crude benzoate, m. p. 115–140°, was also isolated from the mother liquors. This latter fraction was hydrolyzed with 5% alcoholic potassium hydroxide solution. It yielded 7.5 g. of a sterol which melted unsharply at 150°. This sterol was dissolved in 50 cc. of pyridine and treated with 7 g. of *m*-dinitrobenzoyl chloride. The mixture was kept on a boiling water-bath for one hour. The dinitrobenzoate was taken up in ether, and the solution decolorized with animal charcoal. On evaporation of the solvent, 10.8 g. of material, m. p. 170–180°, was obtained.

Isolation of α_1-Sitosteryl *m*-Dinitrobenzoate.—The crude dinitrobenzoate described above was dissolved in 100 cc. of hot ethyl acetate. The solution was allowed to cool; 3.4 g. of yellowish brittle plates crystallized, m. p. 197–207°. This material was recrystallized from the same solvent until the melting point and rotation were constant. The pure crystals melted at 222°. 25.8 mg. dissolved in 2 cc. of chloroform solution gave α^{24}_D $+0.48$; $[\alpha]^{24}_D$ $+37.2°$.

Anal. Calcd. for $C_{36}H_{50}N_2O_6$: C, 71.24; H, 8.31; N, 4.62. Found: C, 71.16; H, 8.31; N, 4.78.

α_1-Sitosteryl *m*-Dinitrobenzoate Dioxide.—Twenty-five and eight-tenths milligrams of the above dinitrobenzoate was kept for three days at 0° with an excess of a chloroform solution of perbenzoic acid. The substance consumed 1.33 mg. of oxygen (theoretical amount for 2 atoms of oxygen is 1.36 mg.). The chloroform solution was washed with sodium carbonate solution. The dioxide was recrystallized from a mixture of benzene and petroleum ether. Small needles were obtained which melted at 209–212°.

Anal. Calcd. for $C_{36}H_{50}N_2O_8$: C, 67.67; H, 7.89; N, 4.39. Found: C, 67.70; H, 8.00; N, 4.44.

α_1-Sitosteryl Benzoate.—The above *m*-dinitrobenzoate was hydrolyzed and the free sterol so obtained was dissolved in pyridine and treated with benzoyl chloride. The mixture was kept on a boiling water-bath for one hour. After working up the product in the usual manner a benzoate was obtained which crystallized from alcohol and benzene in the form of flat needles; m. p. 168–172°; $[\alpha]^{27}_D$ $+41.8°$ (28.2 mg. in 2 cc. chloroform solution gave α^{27}_D $+0.59°$).

Anal. Calcd. for $C_{36}H_{52}O_2$: C, 83.68; H, 10.15. Found: C, 83.93; H, 10.16.

α_1-Sitosterol.—The pure benzoate (m. p. 172°) was hydrolyzed by refluxing it for one hour with a 5% alcoholic solution of potassium hydroxide. The sterol was then precipitated by the addition of water. Purification was accomplished by crystallization from alcohol. Needles were obtained which melted at 164–166°; $[\alpha]^{28}_D$ $-1.7°$ (23.6 mg. in 2 cc. of chloroform solution gave α^{28}_D $-0.02°$). α_1-Sitosterol is precipitated by digitonin.

Anal. Calcd. for $C_{29}H_{48}O$: C, 84.38; H, 11.73. Found: C, 83.8;[8] H, 11.5.

α_1-Sitosteryl Acetate.—This acetate was prepared by heating a sample of α_1-sitosterol for one hour on the water-bath with acetic anhydride. The acetate crystallized on cooling. Recrystallization from alcohol gave leaflets which melted at 137°; $[\alpha]^{28}_D$ $+28.6°$ (27.3 mg. in 2 cc. of chloroform solution gave α^{28}_D $+0.39°$).

Anal. Calcd. for $C_{31}H_{50}O_2$: C, 81.87; H, 11.09. Found: C, 81.95, 81.68; H, 10.98, 11.05.

α_2-Sitosteryl *m*-Dinitrobenzoate.—The mother liquor obtained from the first crystallization of α_1-sitosteryl *m*-dinitrobenzoate was concentrated, and alcohol was added until needles started to crystallize from the boiling solution. The material so obtained (m. p. 180–190°) was recrystallized several times from ethyl acetate and alcohol, and from acetone until the melting point, and rotation re-

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[7] The sitosterol used in these experiments was purchased from the University of Iowa.

[8] As is so often the case with sterols, α_1-sitosterol seems to retain a small amount of solvent of crystallization. This is very difficult to remove completely and lowers the value for the percentage of carbon.

mained unchanged. The yield of pure α_2-sitosteryl *m*-dinitrobenzoate was only 0.4 g. An attempt to increase the yield by recrystallization of the material in the mother liquors was unsuccessful.

α_2-Sitosteryl *m*-dinitrobenzoate melted at 206°. It is much more soluble than α_1-sitosteryl *m*-dinitrobenzoate, and forms needles which are white with a yellowish tint. It gives a depression of the melting point when mixed with the α_1-*m*-dinitrobenzoate; $[\alpha]^{30}\text{D}$ +26.4° (24.2 mg. in 2 cc. of chloroform solution gave $\alpha^{30}\text{D}$ +0.32°).

Anal. Calcd. for $C_{37}H_{52}N_2O_6$: C, 71.57; H, 8.45; N, 4.51. Found: C, 71.70, 71.71; H, 8.24, 8.20; N, 4.81.

Titration with Perbenzoic Acid.—Twenty-four and two-tenths milligrams took up 1.38 mg. of oxygen on standing for four days at 0° with an excess of perbenzoic acid. This is equivalent to 2.26 atoms of oxygen. In another experiment 34.4 mg. took up 1.65 mg. of oxygen on standing for two days at 0°. This is equivalent to 1.82 atoms of oxygen. These values are not as good as in α_1-sitosteryl *m*-dinitrobenzoate. They do show, however, the presence of two double bonds.

α_2-Sitosterol.—The *m*-dinitrobenzoate described above was hydrolyzed on the water-bath with a 5% alcoholic solution of potassium hydroxide. The free sterol was recrystallized from alcohol and petroleum ether.

α_2-Sitosterol melts at 156°. It is soluble in the common solvents; $[\alpha]^{25}\text{D}$ +3.5° (22.6 mg. in 2 cc. of chloroform solution gave $\alpha^{25}\text{D}$ +0.04°).

Anal. Calcd. for $C_{30}H_{50}O$: C, 84.43; H, 11.82. Found: C, 84.40; H, 11.91.

α_2-Sitosteryl Benzoate.—α_2-Sitosterol was dissolved in pyridine and treated with benzoyl chloride. The solution was kept on the water-bath for one hour. The product was worked up in the usual manner. The benzoate was purified by recrystallization from a mixture of benzene and alcohol.

α_2-Sitosteryl benzoate is very soluble in benzene, and sparingly soluble in alcohol. It forms needles which melt at 164–166°. The melting point is not depressed by α_1-sitosteryl benzoate. $[\alpha]^{26}\text{D}$ +27.4° (25.6 mg. in 2 cc. chloroform solution gave $\alpha^{26}\text{D}$ +0.35°).

Anal. Calcd. for $C_{37}H_{54}O_2$: C, 83.71; H, 10.26. Found: C, 83.59, 83.39; H, 10.19, 10.32.

α_2-Sitosteryl Acetate.—α_2-Sitosterol was converted into its acetate by heating with acetic anhydride for one hour in a boiling water-bath. The acetate was recrystallized from alcohol. It forms small leaflets which melt at 124–126°. It is soluble in most solvents, but only sparingly soluble in methyl alcohol $[\alpha]^{27}\text{D}$ +16.5° (24.2 mg. in 2 cc. of chloroform solution gave $\alpha^{27}\text{D}$ + 0.20°).

Anal. Calcd. for $C_{32}H_{52}O_2$: C, 81.98; H, 11.19. Found: C, 81.75, 81.83; H, 11.07, 11.28.

We wish to express our thanks to Merck and Company, Inc., Rahway, N. J., for all the analyses in this article and for a grant-in-aid for this work.

Summary

Two new double unsaturated sterols have been isolated in a pure state from the most soluble fraction of the sitosterol complex obtained from wheat germ oil and formerly named by Anderson α-sitosterol.

The acetates, benzoates and *m*-dinitrobenzoates of these two sterols have been prepared and characterized.

α_1-Sitosterol is an isomer of stigmasterol.

α_2-Sitosterol is probably a homolog.

PRINCETON, N. J. RECEIVED OCTOBER 19, 1936

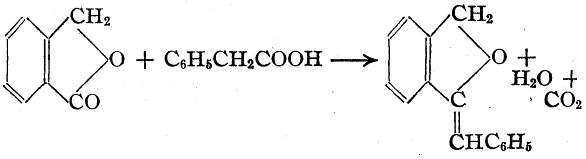
[CONTRIBUTION FROM THE PEDIATRIC RESEARCH LABORATORY OF THE JEWISH HOSPITAL OF BROOKLYN]

The Synthesis of Benzalphthalane

BY SAMUEL NATELSON AND AARON PEARL

In a recent paper[1] the relationship between benzalphthalide and certain naturally occurring materials was pointed out and a procedure for its conversion to compounds related to this series was demonstrated.

Since the hitherto unknown benzalphthalane offered promise of becoming a valuable intermediate in this field of research, its synthesis appeared desirable. An unsuccessful attempt was made to obtain this product by condensation of phthalide with phenylacetic acid as follows



In this reaction carbon dioxide and water, along with large yields of phthalide and toluene, were formed. Since phenylacetic acid under similar conditions does not evolve carbon dioxide, benzalphthalane was probably the initial reaction product but immediately hydrolyzed in accordance with the equation

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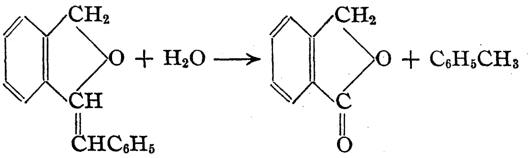
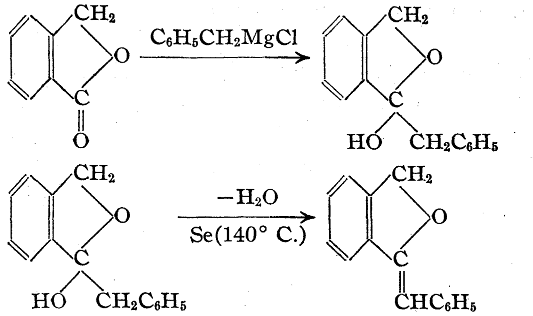
(1) Natelson and Gottfried, THIS JOURNAL, **58**, 1432 (1936).



However, a very satisfactory synthesis was effected by conversion of phthalide through a Grignard synthesis, employing benzylmagnesium chloride, to 1-benzyl-1-hydroxyphthalane, followed by dehydration of this product with the use of selenium.



Benzalphthalane is observed to be split readily, to yield phthalide, by numerous acidic or basic reagents, or even on exposure to air for several months. Because of this instability and the excellent results now obtained with derivatives of benzalphthalide, the application of the former in synthesis has been abandoned in favor of the latter.

Reaction between Phthalide and Phenylacetic Acid.—In four experiments 27 g. of phthalide, 27.5 g. of phenylacetic acid, 2 g. of freshly fused sodium acetate, and a pinch of pumice were heated in a sand-bath until the melt reached 140, 160, 180 and 230°, respectively. At 140° some water and carbon dioxide were evolved and at 180° all of the carbon dioxide was evolved. Even when a temperature of 230° was maintained for three hours, the reaction mixture, recrystallized from carbon bisulfide, yielded 25 g. of phthalide (m. p. 74.5°). (*Anal.* Calcd. for $C_8H_6O_2$: C, 71.64; H, 4.55. Found: C, 71.73; H, 4.61.) Distillation of the filtrate gave a fraction of b. p. 110° which was identified as toluene. In no case was benzalphthalane obtained.

In confirmation of the assumption that benzalphthalane is an intermediary product in the above reactions, it was found that phenylacetic acid either alone or admixed with fused sodium acetate does not evolve carbon dioxide when heated to 180°.

1-Benzyl-1-hydroxyphthalane.—An ether solution of benzylmagnesium chloride, prepared by dissolving 10 g. of magnesium in a solution of 60 g. of benzyl chloride in 300 cc. of anhydrous ether was added drop by drop with vigorous stirring to a cooled suspension of 52 g. of phthalide, prepared by the method of Russert,[2] in 200 cc. of anhydrous ether. As the Grignard reagent hits the phthalide suspension a vigorous reaction ensues and an orange color appears which disappears on stirring. After the addition was complete the reaction mixture was stirred for thirty minutes longer and then allowed to stand well corked overnight. Crushed ice and 380 cc. of 10% sulfuric acid were then added, the mixture was well shaken and the ether layer separated. The lower layer was again washed with ether and the combined ether washings were dried over anhydrous sodium sulfate and evaporated on a steam-bath. The oily residue crystallizes on stirring and cooling with alcohol and petroleum ether mixture and may be recrystallized from alcohol or from carbon bisulfide in long white needles; m. p. 137° yield 50 g.; insol. petroleum ether, sol. alcohol and carbon bisulfide.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.64; H, 6.19. Found: C, 79.33; H, 6.44.

Benzalphthalane. Method 1.—Fifty grams of 1-benzyl-1-hydroxyphthalane is ground with 5 g. of selenium and heated on a sand-bath to 140°. The water given off is collected through a bent tube into a graduated cylinder. When the water ceases to come off, the material is allowed to cool and is recrystallized from alcohol, in which it is rather insoluble when cold. Benzalphthalane crystallizes as wedge-shaped golden crystals, m. p. 94°; yield 42 g.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.53; H, 5.77. Found: C, 86.33; H, 5.93.

Method 2.—To 50 g. of 1-benzyl-1-hydroxyphthalane was added 20 g. of cold concd. sulfuric acid. The mixture was shaken and then gently warmed to 40° for a few minutes. The mixture was allowed to come to room temperature and washed free of sulfuric acid with water and recrystallized from alcohol; m. p. 94°; yield 10–18 g.

Summary

1. Benzalphthalane is prepared by dehydration of 1-benzyl-1-hydroxyphthalane formed by the action of benzylmagnesium chloride on phthalide.

2. The reaction between phthalide and phenylacetic acid in the presence of sodium acetate is studied and a rationale proposed for the inability to obtain benzalphthalane from this reaction mixture.

NEW YORK, N. Y. RECEIVED AUGUST 1, 1936

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[2] Russert, *Ber.*, **46**, 1489 (1913).

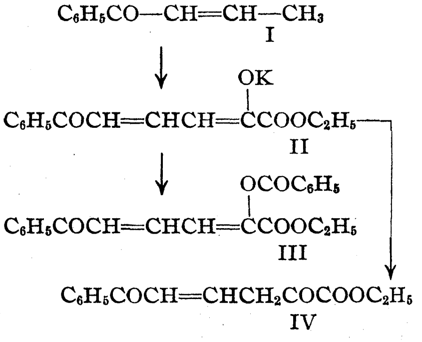
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Condensation of Propenyl Ketones with Ethyl Oxalate

BY REYNOLD C. FUSON, R. E. CHRIST[1] AND G. M. WHITMAN

Propenyl ketones and their higher vinylogs[2] might be expected to exhibit the properties characteristic of methyl ketones. Thus condensation with ethyl oxalate would lead to the synthesis of substances of the type $\mathrm{RCO(CHCH{=})_{\mathit{n}}{-}CH_2COCOOC_2H_5}$ analogous to the unsaturated keto esters of the type $\mathrm{RO_2C(CH{=}CH)_{\mathit{n}}CH_2{-}COCOOR}$ derived from crotonic ester and its vinylogs.[3] The realization of this expectation would open the way to the preparation of keto acids of the type $\mathrm{RCO(CH{=}CH)_{\mathit{n}}COOH}$.

As a first step in this process we have studied the action of ethyl oxalate on two propenyl ketones—phenyl propenyl ketone (I) and mesityl propenyl ketone (V). Phenyl propenyl ketone was treated with ethyl oxalate in ether solution, potassium ethoxide being employed as a catalyst. The reaction led to the formation of the potassium salt (II); this demonstrates that the methyl group of I possesses the activity which was to be predicted.



$$\mathrm{C_6H_5CO{-}CH{=}CH{-}CH_3}\quad \text{I}$$

$$\downarrow$$

$$\mathrm{C_6H_5COCH{=}CHCH{=}\overset{OK}{C}COOC_2H_5}\quad \text{II}$$

$$\downarrow$$

$$\mathrm{C_6H_5COCH{=}CHCH{=}\overset{OCOC_6H_5}{C}COOC_2H_5}\quad \text{III}$$

$$\mathrm{C_6H_5COCH{=}CHCH_2COCOOC_2H_5}\quad \text{IV}$$

When treated with benzoyl chloride, the salt was converted into the benzoate (III). The free keto ester (IV) was produced by dissolving the potassium salt in water and acidifying with acetic acid. This is a somewhat unstable substance. As first obtained, it is a light yellow crystalline compound. Upon exposure to air, it assumes a brilliant orange color and finally changes to a reddish oil. Its alcoholic solution is colored a light brown by ferric chloride, showing that it exists to some extent, at least, in its enolic form. It is readily soluble in alkali.

Phenyl propenyl ketone was found to give a positive iodoform test; however, the production of iodoform is slow. Undoubtedly, the alkali employed in this reaction is capable of splitting the ketone into acetophenone and acetaldehyde, both of which would give the iodoform reaction. At any rate, the hydrolytic cleavage of the double bond conjugated with the carbonyl group was accomplished by refluxing the ketone with potassium carbonate solution. The acetophenone was actually isolated and characterized, but the aldehyde underwent condensation in the presence of the carbonate solution. This is in accord with the results of Meyer[4] on the hydrolytic cleavage of similar unsaturated ketones.

Mesityl propenyl ketone (V), a new compound, was prepared from crotonyl chloride and mesitylene, employing the Friedel–Crafts synthesis.

$$\mathrm{(CH_3)_3C_6H_2{-}CO{-}CH{=}CH{-}CH_3}$$

V

$$\mathrm{(CH_3)_3C_6H_2{-}CO{-}CH{=}CH{-}CH_2{-}CO{-}COOC_2H_5}$$

VI

$$\mathrm{(CH_3)_3C_6H_2COOH}$$

VII

This ketone was condensed with ethyl oxalate in an alcoholic solution, using potassium ethoxide as a catalyst. The product isolated was the expected keto ester (VI). It is a light yellow crystalline substance, which, unlike the corresponding phenyl compound, is quite stable in air. It is readily soluble in alkali, showing that it exists in its enolic form. Oxidation with hydrogen peroxide leads to the formation of β-isodurylic acid (VII).

Experimental

Crotonyl Chloride.—This substance was prepared by a slight modification of the method of Kohler.[5] Crotonic acid and thionyl chloride were used instead of sodium crotonate and phosphorus oxychloride.

One mole (86 g.) of crotonic acid was heated under reflux with 300 cc. of thionyl chloride in a 1-liter, three-necked flask, equipped with a stirrer and reflux condenser, until the evolution of hydrogen chloride ceased. The mixture was then fractionally distilled from a modified Claisen flask. The excess thionyl chloride distilled at 75–80°. The temperature then rose rapidly to 124°, where the crotonyl chloride began to distill. The yield was 90 g., b. p. 124–126°, or 86% of the theoretical amount.

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(1) Du Pont Post-doctorate Fellow, 1935–1936.

(2) Fuson, *Chem. Rev.*, **16**, 1 (1935).

(3) Kuhn and Grundmann, *Ber.*, **69**, 1757 (1936).

(4) Meyer, *Helv. Chim. Acta*, **18**, 461 (1935).

(5) Kohler, *Am. Chem. J.*, **42**, 395 (1909).

Phenyl Propenyl Ketone.—The directions of Kohler[5] were used to prepare this ketone with the modification that benzene was substituted for carbon disulfide as solvent.

Two hundred grams of aluminum chloride was placed in a 1-liter, three-necked flask with 600 cc. of benzene. The mixture was cooled to 0° and exposed to the rays of a mercury vapor lamp. With vigorous stirring, 146 g. of crotonyl chloride was run in over a period of thirty minutes. There was brisk evolution of hydrogen chloride and the deposition of a colorless aluminum chloride complex. After fifteen minutes, the contents was poured into an ice–hydrochloric acid mixture, extracted with ether, washed with 10% sodium hydroxide solution, dried and distilled under reduced pressure. The fraction having a boiling point of 90–95° (2 mm.) was collected as the desired ketone. The total weight was 124 g., representing a 61% yield; $n^{26}\text{D}$ 1.5475.

The residue in the flask solidified upon cooling. Recrystallization from alcohol gave 65 g. of a product having a melting point of 74°. This was the product ($C_6H_5CH(CH_3)CH_2COC_6H_5$) obtained by Kohler by the condensation of two molecules of benzene with one of crotonyl chloride.

Hydrolytic Cleavage of Phenyl Propenyl Ketone.—In an all-glass refluxing apparatus were placed 4.0 g. of phenyl propenyl ketone, 10 g. of potassium carbonate and 50 cc. of water. To the top of the reflux condenser was attached a tube leading into a solution of 4 g. of semicarbazide hydrochloride and 4 g. of sodium acetate dissolved in 50 cc. of water. The object of this was to collect any acetaldehyde which might be formed from the hydrolysis. The solution was refluxed for a period of twenty-one hours. Twice during this time, the water was removed from the condenser to allow a small amount of vapor to pass over into the semicarbazide solution. It was hoped that in this way any acetaldehyde would be detected. However, the semicarbazone isolated proved to be that of acetophenone; m. p. 201°.

The solution remaining in the flask was extracted twice with ether, washed and then dried over calcium chloride. Upon distillation, 2.11 g. of product was obtained, having a boiling point of 196–203°. About 0.5 g. of higher boiling material remained in the flask. The semicarbazone of the 196–203° fraction was prepared, and was found to have a melting point of 200°. A mixed melting point with an authentic sample of acetophenone semicarbazone (m. p. 202°) was found to be 201°. This proved that acetophenone was formed by the hydrolytic cleavage of the phenyl propenyl ketone. The other product, which would have to be acetaldehyde, was not isolated. It probably underwent condensation in the presence of alkali, accounting for the residue remaining in the distilling flask.

Iodoform Reaction with Phenyl Propenyl Ketone.—In this test the reagent of Fuson and Tullock[6] was used. A small amount of iodoform was obtained.

Condensation of Ethyl Oxalate with Phenyl Propenyl Ketone.—Twenty-six grams of finely cut potassium was placed in a flask with 170 cc. of dry ether and cooled to 0°; 116 cc. of absolute alcohol was added, with shaking.

To the ether solution of potassium ethoxide was then added 48.8 g. of ethyl oxalate dissolved in 20 cc. of ether. Fifteen minutes later, 48.8 g. of phenyl propenyl ketone dissolved in 20 cc. of ether was added, with continued shaking. The color of the solution began to darken after a period of time. The mixture was allowed to stand in an ice box for twenty-four hours; a heavy layer of brilliant orange crystals of the potassium salt (II) settled out.

The mixture was filtered rapidly, and the potassium salt was then washed several times with dry ether. Afterward it was dried in a desiccator for twelve hours under reduced pressure. The weight of the final product was 77 g.; yield 81.3%.

Reaction of the Potassium Salt (II) with Benzoyl Chloride.—Ten grams of the salt was mixed with 5.3 g. of benzoyl chloride dissolved in 75 cc. of ether and allowed to stand for a period of twelve hours at room temperature.

The solution was practically colorless by this time, and a precipitate of potassium chloride crystals was on the bottom of the flask. After addition of water, the insoluble ether layer was separated and washed several times. The solvent was then evaporated, leaving a yellow crystalline mass of the benzoyl derivative. This was collected on a filter, washed with 10% sodium hydroxide to remove any benzoyl chloride or benzoic acid present and then recrystallized three times from alcohol.

The final product was a light yellow crystalline substance having a melting point of 123°. The total weight was 5.28 g., representing a 43% yield.

Anal. (semi-micro) Calcd. for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 71.75; H, 5.30.

Preparation of the Keto Ester (IV) from the Potassium Salt.—Ten grams of the salt was dissolved in 100 cc. of water. The addition of an excess of 2 *N* acetic acid caused a yellow semicrystalline mass to be thrown out of solution. The weight of crude material, obtained by filtering and drying by suction, amounted to 7.8 g.

The keto ester is somewhat unstable. Even during the crystallization a change appears to take place. The best solvent was found to be alcohol to which a few drops of acetic acid had been added. The crystals, as first obtained, have a faintly yellow color and melt at 106°, with decomposition. Upon exposure to air, they assume a brilliant orange color, and finally melt to form a reddish oil. When the compound is stored in a desiccator at reduced pressure, no change occurs. The compound dissolves in alkali, giving a light yellow coloration.

Anal. (semi-micro) Calcd. for $C_{14}H_{14}O_4$: C, 68.26; H, 5.73. Found: C, 68.14; H, 5.79.

Preparation of Mesityl Propenyl Ketone.—This is a new compound. It was prepared from crotonyl chloride and mesitylene by use of the Friedel–Crafts synthesis.

Two hundred eighty grams of aluminum chloride was placed in a 2-liter, three-necked flask with 800 cc. of carbon disulfide. The mixture was cooled to 0° and exposed to the rays of a mercury vapor lamp. With vigorous stirring, 209 g. of crotonyl chloride and 240.2 g. of mesitylene dissolved in 200 cc. of carbon disulfide were run in slowly over a period of two hours. There was a vigorous evolution of hydrogen chloride. The solution was stirred for an additional two hours at room temperature. The contents were then poured into iced hydrochloric acid solution, extracted with ether, washed with alkali, dried over calcium chloride and distilled under reduced pressure. A total of

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[6] Fuson and Tullock, THIS JOURNAL, **56**, 1638 (1934).

284 g. of the desired ketone was obtained; b. p. 128° (5 mm.); n^{20}_{D} 1.5330; d^{20}_{4} 0.9819. This represents a yield of 75%.

Anal. (semi-micro) Calcd. for $C_{13}H_{16}O$: C, 82.92; H, 8.57. Found: C, 82.61; H, 8.46.

Condensation of Mesityl Propenyl Ketone with Ethyl Oxalate.—A total of 6.5 g. of finely cut potassium was placed in a flask with 45 cc. of dry ether. Absolute alcohol (29 cc.) was added, with shaking, to convert the potassium to potassium ethoxide.

To the ether solution was then added 12.2 g. of ethyl oxalate dissolved in 15 cc. of ether. Fifteen minutes later, 15.7 g. of mesityl propenyl ketone dissolved in 15 cc. of ether was added, with continued shaking. The color of the solution soon changed to a dark red. The mixture was allowed to stand for a period of twenty hours in an ice box.

The solution was then treated with water and neutralized with acetic acid. The ether layer was separated and dried. Evaporation of the solvent left a crystalline mass. Crystallization from alcohol gave 22 g. of beautiful light yellow crystals which melted, with decomposition, at 156°; yield 90%.

Anal. (micro) Calcd. for $C_{17}H_{20}O_4$: C, 70.78; H, 6.99. Found: C, 70.74; H, 6.96.

Oxidation with Hydrogen Peroxide.—One gram of the ester was placed in a flask with 20 cc. of 10% sodium hydroxide solution and 100 cc. of 3% hydrogen peroxide solution. The mixture was allowed to stand for a period of twelve hours at room temperature.

The solution was then acidified with acetic acid. The precipitate which formed was collected on a filter and redissolved in alkali. It was then thrown out of solution again by the addition of more acetic acid. Recrystallization from a mixture of benzene and low-boiling petroleum ether gave 0.34 g. of beautiful colorless crystals of β-isodurylic acid; m. p. 152°.

Summary

Phenyl propenyl ketone (I) has been prepared from crotonyl chloride and benzene by use of Friedel–Crafts synthesis. The ketone was condensed with ethyl oxalate in ether solution, potassium ethoxide being employed as a catalyst.

The potassium salt (II) was converted into the benzoate (III) by treatment with benzoyl chloride. When the salt was acidified with acetic acid, the free keto ester (IV) was produced.

Mesityl propenyl ketone (V) has been prepared in an analogous manner. It was, likewise, condensed with ethyl oxalate, producing a keto ester (VI).

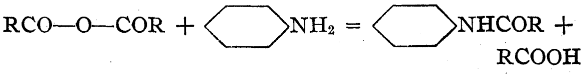
URBANA, ILL. RECEIVED OCTOBER 5, 1936

[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS & COMPANY]

Quantitative Determination of Anhydrides of Carboxylic Acids

BY DONALD MILTON SMITH AND W. M. D. BRYANT

Organic acid anhydrides ordinarily are estimated analytically either by hydrolysis followed by titration of both acidic groups, or by the use of a reaction which converts one acidic residue into a neutral substance leaving only one carboxyl as a measure of the anhydride present. While both analytical schemes are bases of accepted methods, it is apparent that neither alone is sufficient to differentiate sharply between anhydrides and free acids. However, by using the two principles in combination, it becomes possible to determine the –CO–O–CO– content of a mixture, even though the exact nature and composition of the mixture is unknown. Radcliffe and Medofski[1] have made a careful investigation of the above-mentioned procedures as applied to acetic anhydride. The majority of these procedures make use of the fact that an anhydride reacts with aniline to form a mole each of anilide and acid, respectively[2]



The action of alcoholates of the alkali metals upon anhydrides is analogous to that of aniline, a mole of ester and a mole of alkali salt resulting from the reaction carried out as a titration.[3]

Except for the closely related work of Holde[4] on the titration of higher fatty acid anhydrides with alcoholic sodium hydroxide, little use has been made of the above reaction in an analytical way.

In the present investigation a standard solution of sodium methylate was used in place of aniline,

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[1] Radcliffe and Medofski, *J. Soc. Chem. Ind.*, **36**, 628 (1917).

[2] Menschutkin and Vasiliev, *J. Russ. Phys.-Chem. Soc.*, **21**, 190 (1889).

[3] Caudri, *Rec. trav. chim.*, **48**, 778 (1929).

[4] Holde and Smelkus, *Ber.*, **53**, 1889 (1920); Holde and Tacke, *ibid.*, **53**, 1898 (1920).

since it offered the advantage of combining into a single step the cleavage and neutralization processes of the older method while sharing its high reactivity. Total acidity was determined on a separate sample by titration with aqueous sodium hydroxide. In this connection it was found that the addition of a large amount of pyridine just before titration greatly accelerated the hydrolysis of anhydrides rendering it in most cases instantaneous. The two basic reactions involved are

$$\mathrm{RCO{-}O{-}COR} + \mathrm{CH_3ONa} = \mathrm{RCOOCH_3} + \mathrm{RCOONa} \tag{1}$$

and

$$\mathrm{RCO{-}O{-}COR} + 2\mathrm{NaOH} = 2\mathrm{RCOONa} + \mathrm{H_2O} \tag{2}$$

It is readily apparent that in mixture with other acidic materials the distinctive measure of anhydride present is the amount of acyl radical rendered unavailable as ester, or the equivalent difference between the titers of the above reactions. The initial presence of free acids is without effect upon this determination.

A group of ten anhydrides selected for wide differences in structure were analyzed by this method with an average precision of ±0.2%. The method is stoichiometric within this limit as shown by results obtained with glutaric, phthalic and camphoric anhydrides, the substances obtained in the highest purity. All of the compounds except camphoric anhydride were titrated directly in the cold. Due to steric hindrance arising from the presence of an adjacent tertiary carbon atom, the latter material required thirty minutes of heating at 60° with an excess of reagent, followed by back-titration with standard acid. The analytical data are given in Table I.

TABLE I

ANALYTICAL DATA FOR ANHYDRIDES

Anhydride	Millimoles per gram sample NaOH (a)	NaOCH$_3$ (b)	–CO–O–CO– (a–b)		% of theoretical –CO–O–CO–	
Acetic	19.61	9.88	9.73	(4)[a]	99.3	± 0.2
Propionic	15.40	7.79	7.61	(3)	99.0	.2
n-Heptylic	8.21	4.21	4.00	(1)	96.9	
Succinic	19.83	10.35	9.48	(4)	94.8	.2
Maleic	20.20	10.22	9.98	(2)	97.8	.0
Glutaric	17.42	8.67	8.75	(2)	99.8	.1
Camphoric	10.99	5.49	5.50	(2)	100.2	.4
Benzoic	8.84	4.45	4.39	(2)	99.3	.1
Phthalic	13.50	6.75	6.75	(2)	99.9	.3
Furoic	9.61	4.97	4.64	(4)	95.6	.2

[a] Figures in parentheses indicate number of individual determinations.

The matter of interfering substances was also investigated and as the probable titration behavior of lactones was in doubt several examples of this class were examined and the results recorded in Table II. Ordinary esters and stable lactones like phthalide and coumarin are inert toward the reagents as ordinarily employed, hence do not interfere. Readily hydrolyzed compounds of these classes such as alkyl formates and glucono-δ-lactone although unaffected by sodium methylate undergo hydrolysis in aqueous solution and so lead to ambiguous results in mixtures. β-Methylumbelliferone, a substituted coumarin, reacts as an acid with both reagents, hence does not affect the determination of anhydrides.

TABLE II

ANALYTICAL DATA FOR LACTONES

Lactone	Millimoles per gram sample NaOH (a)	NaOCH$_3$ (b)	Δ (a − b)
Glucono-δ-lactone	5.65	0.05	5.60
Phthalide[a]	0.11	.02	0.09
Coumarin	.05	.02	.03
β-Methylumbelliferone	5.63	5.62	.01

[a] Obtained from British Drug House, Ltd.; remaining lactones Eastman products.

Experimental

Compounds Investigated.—With two exceptions all of the anhydrides studied in the present research were Eastman products, and were used without further purification. **Phthalic anhydride** ("Aero" Brand) was obtained from American Cyanamide and Chemical Corp., and **glutaric anhydride** was prepared from the acid by the method of Mol.[5] In this connection, evidence was obtained that solid anhydrides adsorb large quantities of water vapor on short exposure to moist air. Decomposition is not instantaneous but takes place to a serious extent during subsequent storage. To minimize this difficulty, samples for analysis were dispensed by means of a simple "dry manipulator."

Analytical Procedure

One to three grams of sample is weighed into a dry 250-cc. g. s. volumetric flask (calibration unnecessary) or similarly designed vessel. If the sample is a solid, 20 to 30 cc. of dry methanol or acetone is added, warming if necessary to complete solution. The solution is then titrated directly with 0.5 *N* sodium methylate in methanol to a phenolphthalein or thymol blue end-point. The indicator should be made up in dry dioxane or acetone (an alcohol solution would be unsuitable for use in the next step). This titer is a measure of the anhydride plus any free acid present.

A second weighed sample is mixed with 25 cc. of C. P. pyridine and titrated with 0.5 *N* aqueous sodium hydroxide to the indicator previously employed. Alcohol should be omitted in order to avoid ester formation. This titer is a measure of the total acidity of the sample. The true anhydride content is measured by the difference between the two titers expressed in moles per gram of sample.

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[5] Mol, *Rec. trav. chim.*, **26**, 373 (1907).

The sodium methylate solution is prepared by dissolving the required amount of metallic sodium in dry c. p. methanol. Although precautions should be taken to keep the solution dry, the presence of up to 1% of water introduces only a small error. The two alkalies should be compared frequently with standard 0.5 *N* acid. Anhydrides that are unreactive because of steric hindrance, may be heated with an excess of either alkali and back titrated cold with standard acid. In such cases, however, esters must be absent to avoid interference. Camphoric anhydride was the sole example of this class encountered.

Summary

1. A rapid and precise method for the determination of anhydrides of carboxylic acids based on sodium methylate titration has been developed. The method has been applied successfully to the following anhydrides: acetic, propionic, *n*-heptylic, succinic, glutaric, maleic, camphoric, benzoic, phthalic and furoic.

2. In connection with the above method, the hydrolytic cleavage of anhydrides was found to be accelerated by the use of pyridine.

3. The interference of lactones has been investigated. Phthalide and coumarin do not react. β-Methylumbelliferone reacts but does not interfere. Glucono-δ-lactone interferes with anhydride determinations.

Wilmington, Del. Received October 7, 1936

[Contribution from the Kedzie Chemical Laboratory, Michigan State College]

The Surface Tensions, Densities, Free Surface Energies and Parachors of Some Derivatives of Benzylated Phenols[1]

By D. T. Ewing and Frances W. Lamb

In this paper data are presented for the measurement of the surface tension and density at different temperatures of a series of new organic compounds, which are derivatives of benzylated phenols. From these values the molal free surface energy and parachors have been calculated. Although these physical factors have been evaluated for a number of organic compounds, reliable surface tension values of only four diphenyl and two triphenyl compounds have been reported previously.

The compounds used in these investigations were those prepared by R. C. Huston and associates in a series of investigations in this Laboratory. These substances were found to be of sufficient purity to warrant direct measurement without further purification. In each case the compounds had been carefully distilled many times.

Density measurements were made at different temperatures with a pycnometer which was essentially a bulb of glass blown on a capillary. A special pycnometer was made partly because in several cases the sample of liquid was limited to a few ml. and partly because the best density bulb is one which is spherical in form with only a fine capillary opening. In each case the pycnometer was carefully calibrated with water at the several temperatures. Density measurements were made at 25, 35 and 50°. For this purpose the substances were equilibrated in constant-temperature water-baths which did not vary in temperature more than 0.005°.

Surface tension measurements were made with a metal drop weight apparatus[2] supported on a heavy concrete pillar free from the floor of the laboratory to avoid any vibration. The radius of the tip was carefully determined with a Gaertner comparator and found to have a value of 0.26740 cm. The drop weight assembly with the liquid was lowered below the surface of the water in the thermostat and allowed to remain until the temperature of the liquid was a constant when the drop weight determinations were made. For each liquid, when the volume available permitted, 25 to 30 drops were formed very slowly into a weighing bottle and from this weight that of the drop was determined.

From the weight of the drop and the density of the liquid the surface tension γ was calculated by the equation

$$\gamma = \frac{mg}{2\pi r f(r/v^{1/3})}$$

where m = mass of drop in grams
g = 981 dynes
r = 0.26740 cm. the radius of the tip
v = volume of the drop

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[1] A portion of Part I of a thesis submitted to the Graduate Faculty of the Michigan State College by Miss Frances W. Lamb in partial fulfilment of the requirements for the Ph.D. degree, June, 1933.

[2] Harkins and Brown, This Journal, **41**, 519 (1919)

TABLE I

	Compound	Temp., °C.	Wt. 1 drop, g.	Surface tension, dynes	d	$(m/d)^{2/3}$ ergs	P, obsd.	P, calcd.	ΔP
1	2-Chlorophenyl benzyl ether, b. p. 178–179°	25	0.042841	41.699	1.15494	1374.4	480.85		
		35	.041732	40.626	1.14607	1345.9	481.41	476.2	+ 5.21
		50	.040147	39.092	1.13338	1304.7	482.13		
2	2-Chlorobenzylphenol ether, b. p. 141–145°	25	.042974	41.836	1.18044	1359.0	470.84		
		35	.041742	40.644	1.17199	1326.6	470.82	476.2	− 5.38
		50	.040096	39.050	1.15764	1285.1	472.91		
3	2-Chloro-4-benzylphenol, b. p. 145–148°	25	.044938	43.722	1.18805	1414.1	473.01		
		35	.043869	42.700	1.17915	1388.0	473.79	476.2	− 2.41
		50	.042228	41.111	1.16653	1346.0	474.40		
4	2-*o*-Chlorobenzylphenol, b. p. 146–151°	25	.044416	43.236	1.21219	1379.8	463.20		
		35	.043782	42.623	1.20494	1365.7	463.42	476.2	−12.78
		50	.042444	41.328	1.19563	1331.1	463.43		
5	Benzoyl ester of 2-*o*-chlorobenzylphenol, b. p. 173–176°	25	.043708	42.551	1.20592	1766.5	683.17		
		35	.043137	41.998	1.19911	1750.0	684.81	693.9	− 9.09
		50	.042014	40.910	1.18696	1716.4	687.30		
6	2-Methyl-4,6-dibenzylphenol, b. p. 225–227°	25	.043630	42.393	1.09866	1737.0	669.21		
		35	.043008	41.796	1.09137	1720.2	671.31	689.9	−18.59
		50	.041870	40.709	1.80043	1686.8	673.86	...	...
7	3-Methyl-2,6-dibenzylphenol, b. p. 216–218°	25	.040410	39.336	1.09552	1614.9	658.72		
		35	.039938	38.878	1.09159	1599.8	659.56	689.9	−30.34
		50	.039112	38.077	1.08133	1576.8	661.93		
8	4-Methyl-2,6-dibenzylphenol, b. p. 236–238°	25	.041760	40.624	1.09651	1666.7	663.44		
		35	.041234	40.119	1.08998	1652.8	665.32	689.9	−24.58
		50	.040249	39.176	1.07990	1623.7	667.54		
9	6-Benzyl-2-phenylphenol, b. p. 193°	25	.044991	43.697	1.11662	1654.4	598.95		
		35	.044092	42.840	1.10926	1629.1	599.91	611.9	−11.99
		50	.042613	41.429	1.09693	1587.2	601.60		
10	4-Benzyl-2-phenylphenol, b. p. 200°	25	.045066	43.775	1.12321	1650.7	595.70		
		35	.044349	43.089	1.11590	1632.0	597.21	611.9	−14.69
		50	.043105	41.903	1.10424	1598.3	599.34		
11	6-Benzyl-4-bromo-2-phenylphenol, b. p. 215°	25	[a]		1.39834				
		35	.044878	43.732	1.39020	1707.1	627.15	662.8	−35.65
		50	.043724	42.615	1.37755	1673.6	628.83		
12	6-Bromo-4-benzyl 2-phenylphenol, b. p. 225°	25	[a]		1.34835				
		35	.044387	43.244	1.34109	1729.0	648.27	662.8	−14.53
		50	.043660	42.539	1.32842	1711.6	651.90	...	...
13	*o*-Hydroxyl-1-diphenylbutane, b. p. 144–146°	25	.038382	37.363	1.04937	1343.0	532.8		
		35	.037729	36.740	1.04072	1328.0	534.97	556.0	−21.03
		50	.036413	35.454	1.03055	1289.8	535.46		

[a] Reliable data not obtained because of high viscosity of compounds at 25°.

The f functions of $r/v^{1/3}$ were those determined by Harkins and Brown.[2]

The thirteen compounds investigated are as follows: 2-chlorophenylbenzyl ether and 2-chloro-4-benzylphenol, both prepared by G. W. Warren,[3] 2-chlorobenzylphenyl ether, 2-*o*-chlorobenzylphenol and the benzoyl ester of 2-*o*-chlorobenzylphenol, all prepared by P. S. Chen,[4] 2-*m*-methyl-4,6-dibenzylphenol prepared by Huston, Swartout and Wardwell,[5] 3-methyl-2,6-dibenzylphenol as prepared by Huston and Houk,[6] 4-methyl-2,6-dibenzylphenol prepared by Huston and Lewis,[7] 6-benzyl-2-phenylphenol, 4-benzyl-2-phenylphenol, 6-benzyl-4-bromo-2-phenylphenol and 6-bromo-4-benzyl-2-phenylphenol, all prepared by G. W. Warren,[8] and *o*-hydroxy-1,1-diphenylbutane by Strickler.[9]

The values obtained for the surface tension and density at the three temperatures are tabulated for each of the compounds. The molal free sur-

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(3) G. W. Warren, Master's thesis, 1931.

(4) P. S. Chen, Master's thesis, 1930.

(5) Huston, Swartout and Wardwell, THIS JOURNAL, **52**, 4484 (1930).

(6) Huston and Houk, *ibid.*, **54**, 1506 (1932).

(7) Huston and Lewis, *ibid.*, **53**, 2379 (1931).

(8) G. W. Warren, Senior report, 1930.

(9) Strickler, Master's thesis, 1927.

face energies $\gamma(m/d)^{2/3}$ and the parachors are evaluated from these experimental values and also tabulated. The parachor observed is calculated from Sugden's formula $P(\text{obsd.}) = m/d\gamma^{1/4}$ in which m is molecular weight, d the density and γ the surface tension.

In Table I it should be noted that compounds 1, 2, 3 and 4 are isomeric and have a molecular weight of 218.5. Compounds 6, 7 and 8 are isomeric, and have a molecular weight of 288.2. Compound 9 is isomeric with compound 10 (mol. wt. 260.1), and compound 11 is isomeric with compound 12 (mol. wt. 339.0).

A summary of the molal free surface energies and parachors (observed) at 35° together with the respective names of the liquids is given in the above table. The parachors (calculated) are given, column no. 8. These are obtained by adding the proper atomic and structural parachors for each compound.[10] In the last column the difference ΔP between the parachor (observed) at 35° and parachor (calculated) is tabulated.

In the table it is noted that in general as the molecular weights increase, the differences in the calculated and observed parachors increase. The values for ΔP are negative except in the first case and range from $+5$ to -35. Since the parachor values are proportional to molecular volume these negative values for ΔP would seem to indicate that these molecules are more closely packed together than is accounted for by the present structural parachors. In a calculation of parachor observed and parachor calculated for diphenylmethane[11] and diphenylethane,[1] Harkins and Ewing show negative values for ΔP of the same order as those found here. These results seem to indicate a need for the application of an additional structural parachor for compounds having two or more phenyl groups.

The parachor (calculated) is the same for compounds isomeric with one another; however, it is interesting to note the variation of the values for parachor (observed) for the different isomers. The observed parachor for compound 1, in which the chlorine and CH_2 groups are not on adjacent carbon atoms in the benzene ring, is 481.41 while in compound 2, in which they are on adjacent carbon atoms in the benzene ring, the value is 470.8, a difference of 10.59. Upon comparing compounds 3 and 4 in the same manner, it is noted that compound 4, where the chlorine and CH_2 group are on adjacent carbon atoms of the benzene ring, the value is 463.42, and for compound 3, in which these groups are not on adjacent carbon atoms, the value is 473.79. Here the difference is 10.37 and agrees with the above value of 10.59. Thus it would seem that with sufficient data some important relations could be evaluated for isomeric compounds in regard to their parachors.

The molal free surface energies range from 132.6 to 138.8 ergs for those compounds containing two phenyl groups, while the molal free surface energies for all compounds containing three phenyl groups range from 160 to 175 ergs.

Conclusion

1. Surface tensions and densities of 13 new derivatives of benzylated phenols have been determined, and their molal free surface energies and parachors have been evaluated.

East Lansing, Mich. Received October 12, 1936

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[10] Sugden, *J. Chem. Soc.*, **125**, 1177 (1924).

[11] Harkins and Ewing, This Journal, **41**, 1977 (1919).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

The Potentiometric Iodide–Silver Titration at Extreme Dilutions

BY I. M. KOLTHOFF AND J. J. LINGANE

In a study of the solubility of slightly soluble (10^{-3} to 10^{-5} N) silver salts in solutions of various electrolytes and in water it was necessary to develop an accurate method for the determination of very small amounts of dissolved silver. We have found that the potentiometric titration of silver with iodide is very suitable for this purpose, and as little as one part of silver in twenty million parts of solution (5×10^{-7} N) may be titrated with an accuracy of a few per cent. when 500 ml. of the solution is taken for analysis. At this high dilution the potentiometric method is more accurate than any other method of analysis, especially in the presence of large amounts of indifferent electrolytes.

Experimental

Apparatus and Materials.—The potentiometric apparatus and the general technique of the iodide–silver titration have been described already.[1] Silver iodide electrodes were used, since our experience has shown that these are somewhat more satisfactory than plain silver electrodes. A saturated calomel electrode, with a saturated potassium nitrate bridge, was used as reference electrode. Titrations were performed in the absence of light in the one liter titration beaker previously described.[1] The potassium iodide titrating solution was delivered from a 10-ml. microburet, with which volumes could be read easily to ±0.005 ml.

The nitric acid, water and salts were purified carefully by the usual methods. Mallinckrodt reagent quality potassium iodide (ground and dried at 200°) was used in most of the experiments since in titrating the very dilute silver solutions it gave the same results as the carefully synthesized salt.[1]

Approximately 0.01 N stock solutions of silver nitrate and potassium iodide were prepared by weighing out the dried salts. The more dilute solutions were prepared by diluting the stock solutions in carefully calibrated volumetric apparatus. The potassium iodide titrating solutions varied in concentration from 10^{-3} to 5×10^{-5} N, depending on the concentration and volume of silver solution to be titrated. These solutions were stable for several weeks when made up in pure water that was entirely free from traces of copper and stored in the dark. The concentrations of the various solutions were known to ±0.1%.

Data of the Titrations.—For the purpose of illustrating a typical titration we may consider the case of the most dilute silver solution that was titrated, which was only 5.15×10^{-7} N in silver. The data obtained in this titration are given in Table I and Fig. 1. These data show that the

TABLE I

DATA OF TYPICAL TITRATION AT EXTREME DILUTION

500 ml. of 5.15×10^{-7} N silver nitrate, containing 2 ml. of concd. nitric acid, titrated with 4.99×10^{-5} N potassium iodide at room temperature in presence of air.

4.99×10^{-5} N KI, ml.	E, v.	$\Delta E/\Delta V$, mv. per 0.4 ml.
0	+0.1824	
1.0	.1766	
2.0	.1695	
3.0	.1600	
3.8	.1490	
4.2	.1412	78
4.6	.1307	105
5.0	.1138	169
5.4	.0882	256
5.8	.0648	234
6.2	.0505	143
6.6	.0410	95
7.0	.0330	80
8.0	.0203	
9.0	.0115	

$$V = 5.0 + \frac{256 - 169}{(256 - 169) + (256 - 234)} \times 0.4 = 5.32$$

ml.; calcd. = 5.16 ml. Error, +3.2%.

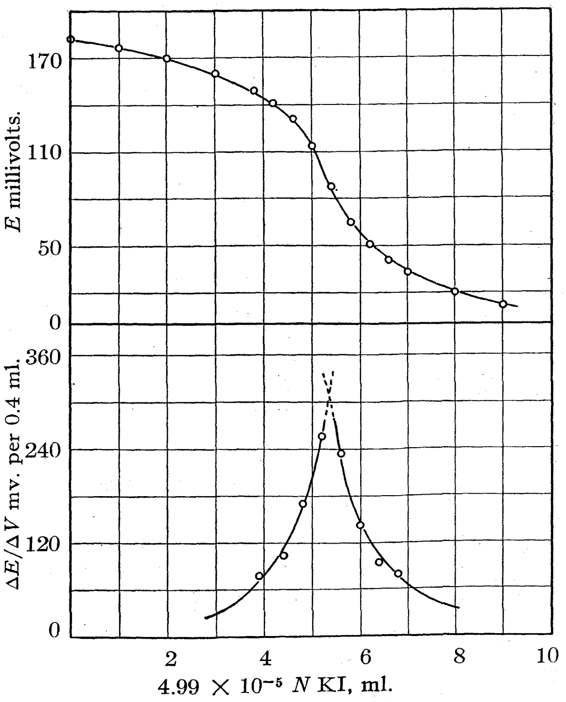

Fig. 1.—Titration of 500 ml. of 5.15×10^{-7} N silver nitrate with 4.99×10^{-5} N potassium iodide (data from Table I).

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[1] I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **58**, 1524 (1936).

TABLE II

SUMMARY OF TITRATIONS

500-ml. sample of solution containing 2 ml. of concd. nitric acid in all experiments

Series no.	Concn. of $AgNO_3$, N	No. of titrations	Other salts, g.	Av. error, %	Av. $E_{E.P.}$, v.	Remarks[a]
1	1.029×10^{-5}	6	....	±0.14	0.099	R. T. in air
2	1.029×10^{-5}	1	....	− .64	.097	R. T. in CO_2
3	1.030×10^{-6}	3	....	+2.3	.095	R. T. in air
4	1.030×10^{-6}	5	....	+1.2	.095	R. T. in CO_2
5	1.030×10^{-6}	2	20 g. $Ba(NO_3)_2$	+1.0	.096	R. T. in CO_2
6	1.030×10^{-6}	2	10 g. $Ba(NO_3)_2$	±1.3	.098	R. T. in CO_2
7	1.030×10^{-6}	1	20 g. K_2SO_4	+8.1	.090	R. T. in CO_2
8	5.15×10^{-7}	1	....	+3.2	.093	R. T. in air
9	2.058×10^{-5}	1	....	−0.32	.098	60° in air
10	1.029×10^{-5}	2	....	− .25	.097	60° in air
11	9.41×10^{-6}	1	....	+ .51	.097	60° in air
12	9.41×10^{-6}	1	....	+ .06	.099	55° in CO_2

[a] R. T. = room temperature.

end-point of the titration (maximum value of $\Delta E/\Delta V$) is still well defined at this extreme dilution, and the error of +3.2% is remarkably small when it is realized that the total amount of silver titrated was only 0.028 mg. in a volume of 500 ml.

A summary of the results obtained in twenty-six titrations in which the concentration of silver titrated was varied between 5×10^{-7} and 10^{-5} N, is given in Table II. Some of these titrations were carried out in the absence of air, by bubbling a rapid stream of carbon dioxide through the solution, in order to see whether atmospheric oxygen had any influence on the accuracy of the titration. Titrations were also made in solutions that contained large amounts of very pure barium nitrate and potassium sulfate. A few titrations were also made at 60°.

The column headed "av. $E_{E.P.}$" in Table II, contains the average values of the e. m. f. at the end-point of the titrations (equivalence potential); the significance of these values will be explained later.

Discussion

Steady e. m. f. readings are obtained relatively rapidly in these "dilute" titrations, except in the immediate vicinity of the end-point where ten to fifteen minutes are required between each addition of the potassium iodide solution. The e. m. f. becomes steady more quickly in these "dilute" titrations than in titrations of ordinary amounts of silver because the amount of solid silver iodide present is so extremely small that adsorption effects are negligible. The time required for the e. m. f. to become steady simply corresponds to the time required to re-establish solubility equilibrium after each addition of potassium iodide. This is substantiated by the fact that the direction of the drift is toward decreasing values of the e. m. f., *i. e.*, toward decreasing silver ion activity.

When the titration is carried out at 60° the e. m. f. becomes steady more quickly, because solubility equilibrium is attained more rapidly at the higher temperature. A titration at room temperature requires about one to one and one-half hours, but at 60° this time is reduced to about one-half. In titrating a 10^{-5} N silver solution at 60° the maximum value of $\Delta E/\Delta V$ is only about one-third as great as at room temperature, but is still sufficiently sharp to allow an accurate determination of the end-point.

An inspection of the data of Table II shows that a 10^{-5} N silver solution can be titrated at room temperature with an accuracy of at least ±0.2%, a 10^{-6} N solution can be titrated with an accuracy of about 1–2% and a 5×10^{-7} N solution with an accuracy of about 3%. Since the percentage error is a linear function of the amount of silver titrated, it is evident that the absolute error is constant and independent of the amount of silver titrated in this range of concentrations.

The data also show that air has no marked effect on the accuracy of the titration, although a comparison of series nos. 3 and 4 and nos. 11 and 12 indicate that somewhat better results are obtained in the presence of carbon dioxide when titrating very small amounts of silver or when titrating at 55–60°.

Large amounts of barium nitrate have no influence on the results. Potassium sulfate (sulfate ion) in large amounts on the other hand causes a large positive error (no. 7). The deleterious influence of the sulfate ion on the behavior of silver electrodes appears to be rather general; it has been observed previously in work with the silver electrode.[2]

The interference of large amounts of sulfate

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(2) I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **119**, 202 (1921); **132**, 117 (1923).

ion at these high dilutions is to be attributed to the reaction

$$Ag^+ + SO_4^= \rightleftharpoons AgSO_4^-$$

which results in a decrease of the silver ion activity, an increase in the solubility of silver iodide, and an asymmetric location of the equivalence point; *i. e.*, the equivalence point no longer corresponds exactly to the maximum value of $\Delta E/\Delta V$.

We have also found that the titration can be carried out with the same degree of accuracy in dilute potassium bicarbonate medium (*p*H about 8.3) as in dilute nitric acid.

The titration may be simplified and made more convenient by simply titrating to the equivalence potential instead of recording the data of the entire titration curve.[3] The average value of the equivalence potential found was +0.097 ± 0.005 v. against the saturated calomel electrode, as shown by the data of Table II. This value is in excellent agreement with that found in the titration of ordinary amounts of silver.[1] We have found that the value of the equivalence potential is practically the same (within ±5 mv.) in dilute potassium bicarbonate medium as in dilute nitric acid, and it is evident from Table II that it is also practically independent of temperature, and the presence of large amounts of barium nitrate. Titrations to the equivalence potential gave identically the same results as by the ordinary method, and are more convenient because the constant attention of the operator is not required.

It is evident from these results that this titration should be a valuable analytical method of investigating the solubility and activity relations of slightly soluble silver salts. We are using the method in a study of the activity of silver chloride and silver iodate in various salt solutions. Obviously the method could also be applied to the determination of very small amounts of iodide by adding an excess of silver nitrate solution to the unknown iodide solution and back-titrating the excess silver.

Acknowledgment.—We wish to express our appreciation to the Graduate School of the University of Minnesota for financial assistance in this work.

Summary

1. The accuracy of the potentiometric iodide–silver titration at extreme dilutions has been investigated. Using a 500-ml. sample, a 10^{-5} *N* silver solution can be titrated with an accuracy of ±0.2%, a 10^{-6} *N* solution with an accuracy of 1–2% and a 5×10^{-7} *N* solution with an accuracy of about 3% at room temperature. Large amounts of barium nitrate have no influence on the results, but a large positive error was found in the presence of high concentrations of sulfate ions.

2. The titration is recommended as an analytical tool in investigations of the solubility and activity relations of slightly soluble silver salts.

MINNEAPOLIS, MINN. RECEIVED SEPTEMBER 28, 1936

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[3] I. M. Kolthoff, *Rec. trav. chim.*, **47**, 397 (1928); I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **57**, 2126 (1935).

[CONTRIBUTION FROM THE EASTMAN LABORATORY OF PHYSICS AND CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Structure of Crystalline Bromine

BY B. VONNEGUT AND B. E. WARREN

Introduction

There is very little crystallographic information available concerning crystalline bromine. The material melts at −7.3° and single crystals are readily obtained from the vapor. It would be expected that the crystalline structure of bromine should be very similar to that of orthorhombic iodine.[1] This has turned out to be the case, and the structure analysis has been considerably simplified by making comparison with the known structure of iodine.

Experimental

Bromine crystals were formed from the vapor on the surface of a round-bottomed flask filled with dry ice and placed over the mouth of a beaker containing liquid bromine. The crystals showed a pronounced elongation along the direction of the *c*-axis, and were thus readily oriented for rotation and oscillation patterns about *c*. They were mounted by being placed upon a smooth surface of dry ice, and cemented to a fine glass rod with a soft vaseline which froze upon cooling. The crystal was maintained at about −150°

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[1] Harris, Mack and Blake, THIS JOURNAL, **50**, 1583 (1928).

during the exposure by being placed in the exhaust stream from a liquid air container. Since the crystal is bathed completely in a stream of dry cold air, there is no trouble from water vapor freezing out upon the crystal. The vapor pressure of the bromine crystal was sufficiently reduced by the cooling, so that a single crystal would last through a twelve-hour oscillation exposure. The experimental arrangement is shown schematically in Fig. 1.

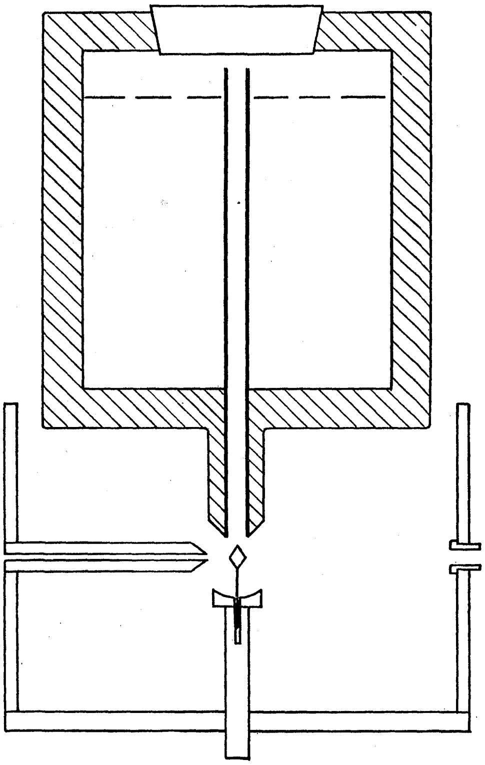

Fig. 1.—Method for producing low temperature x-ray diffraction patterns of bromine by placing crystal in liquid air exhaust.

Three 38° oscillation photographs were made in a cylindrical camera of radius 8.61 cm. The radiation used was Mo Kα with 0.30 mm. aluminum sheet in front of the film to reduce the blackening by fluorescent bromine radiation.

Unit Cell and Space Group.—From the layer line separations on the three oscillation patterns, the length of the c-axis was determined directly as 8.72 Å. By assuming that the axes of bromine would all stand in about the same ratio to the corresponding axes in iodine, tentative values of a and b were obtained which allowed a satisfactory indexing of all the spots on the oscillation patterns. Final values of the axes were then calculated from $h00$ and $0k0$ reflections; a = 4.48 Å., b = 6.67 Å.

All reflections hkl were missing except for $h + k$ = even. In addition, the reflections $0kl$ and $hk0$ were missing except for even indices. These vanishings are consistent with the space group *Ccma* (V_h^{18}) which is the space group found previously for orthorhombic iodine.[1]

Since the isomorphism of the bromine and iodine structures is completely established by the intensity comparisons which are given below, one can assume 8 atoms per unit cell as in iodine and calculate the density of bromine at about −150°.

$$\rho = \frac{8 \times 79.9}{0.606 \times 8.72 \times 6.67 \times 4.48} = 4.05$$

This is in satisfactory agreement with most of the values given in the literature; 4.107 (−194°),[2] 4.13 (−253°).[3] The value 3.4 for the density of crystalline bromine given in the "International Critical Tables" is much too low.

Atomic Arrangement.—The eight atoms in the bromine unit cell are in the 8-fold position f of V_h^{18}. The coördinates are

$x,0,z$	$\bar{x},0,\bar{z}$	$x,\frac{1}{2},\frac{1}{2} - z$	$\bar{x},\frac{1}{2},\frac{1}{2} + z$
$\frac{1}{2} + x,\frac{1}{2},z$	$\frac{1}{2} - x,\frac{1}{2},\bar{z}$	$\frac{1}{2} + x,0,\frac{1}{2} - z$	$\frac{1}{2} - x,0,\frac{1}{2} + z$

Structure factors were calculated for several values of the parameters x and z. The best general agreement between calculated and observed intensities was given for the values x = 0.135, z = 0.110.

The intensities of the spots on the oscillation patterns are given roughly by the relation[4]

$$I \alpha F^2/\xi$$

No attempt was made to apply any correction for temperature motion or absorption in the crystal. By looking for close agreement only among spots in the same row line, the neglect of these factors is not serious. Table I gives a comparison of values of $F/\xi^{1/2}$ calculated for x = 0.135, z = 0.110 and the visually estimated intensities of the spots. The agreement is sufficiently good to substantiate the proposed structure. No serious attempt was made to deduce precise values of the parameters x and z as the absorption in the sample was large, and only low order reflections were present on the oscillation patterns.

Discussion of Structure.—The resulting structure for bromine is shown in Fig. 2, projected on

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(2) Sapper and Biltz, *Z. anorg. Chem.*, **198**, 184 (1931).

(3) W. Heuse, *Z. physik. Chem.*, **A147**, 273 (1930).

(4) ξ is a coördinate in the reciprocal lattice; J. D. Bernal, *Proc. Roy. Soc.* (London), **A113**, 117 (1926).

TABLE I

COMPARISON OF CALCULATED AND OBSERVED INTENSITIES

hkl	Obsd.	$F/\xi^{1/2}$	*hkl*	Obsd.	$F/\xi^{1/2}$	*hkl*	Obsd.	$F/\xi^{1/2}$
200	abs	67	020	vs	780	242	abs	8
201	m	344	022	vw	142	243	m	306
202	abs	13	024	s	640	244	abs	39
203	ms	457	220	abs	59	440	m	252
204	abs	56	221	ms	305	441	abs	40
400	ms	310	222	abs	11	442	abs	45
401	abs	46	223	ms	405	443	abs	53
402	abs	55	224	abs	50	444	w	226
403	abs	64	420	m	272	151	vw	178
404	m	277	421	abs	43	152	m	250
111	s	407	422	abs	51	153	abs	105
112	vs	556	423	abs	59	154	abs	91
113	wm	236	424	m	252	060	m	300
114	w	175	131	w	266	062	abs	54
311	ms	249	132	m	370	064	m	270
312	m	212	133	abs	156	260	abs	33
313	wm	148	134	abs	135	261	w	172
314	abs	78	040	s	680	262	abs	6
511	abs	87	042	abs	79	263	w	236
512	m	212	044	ms	380	264	abs	27
513	abs	54	240	abs	44	080	w	230
514	abs	78	241	m	230	082	abs	43

the 010 plane. Each atom has one nearest neighbor at a distance 2.27 Å., the other member of the Br_2 molecule. The x-ray crystal value of the Br–Br distance 2.27 Å. is to be compared with the band spectrum value[5] 2.28 Å. and the electron diffraction value[6] 2.28 Å. The close agreement is fortuitous as the x-ray value is probably uncertain by ±0.10 Å.

Each atom has three other close neighbors in the same reflection plane (plane of paper) at distances: 3.30, 3.30, 3.75. Eight more neighbors in the planes above and below are at slightly larger distances: 4.00, 4.00, 3.98, 4.10.

Crystalline bromine is definitely a molecular structure, the Br_2 molecule being easily recognized in the crystalline structure from consideration of the observed interatomic distances. The structure of orthorhombic bromine is isomorphous with that of iodine,[1] but apparently different from the structure of crystalline chlorine.[7] The structure of bromine forms one more example of the application of the 8-N law to the structures of the B sub-group elements in columns IV–VII.

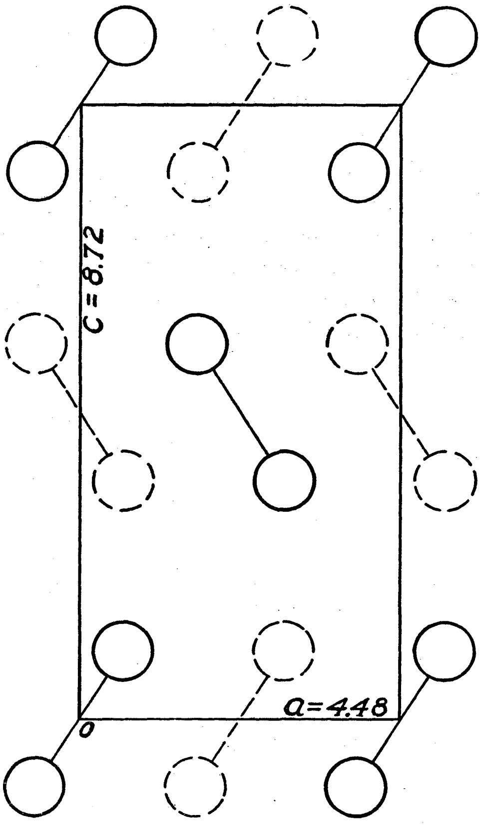

Fig. 2.—Structure of crystalline bromine projected upon the 010 plane. Full circles represent atoms in the plane of the paper, broken circles represent atoms above and below the plane of the paper by *b*/2. The Br_2 molecules are indicated by the connecting lines.

Summary

Oscillation patterns about the *c*-axis were made of a bromine crystal held at about −150°. The lattice is orthorhombic with axes: $a = 4.48$ Å., $b = 6.67$ Å., $c = 8.72$ Å. The 8 atoms are in the position 8*f* of the space group *Ccma* (V_h^{18}), with $x = 0.135$ and $z = 0.110$. The structure is isomorphous with that of iodine, and shows a definite Br_2 molecule with Br–Br distance of 2.27 ± 0.10 Å. The x-ray density at about −150° is 4.05.

CAMBRIDGE, MASS. RECEIVED OCTOBER 15, 1936

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(5) L. Pauling and M. Huggins, *Z. Krist.*, **87**, 205 (1934).

(6) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(7) Keesom and Taconis, *Physica*, **3**, 237 (1936).

[CONTRIBUTION NO. 570 FROM GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Photodecomposition of Ammonia

BY HENRY J. WELGE AND ARNOLD O. BECKMAN

Introduction

Although the photodecomposition of ammonia was one of the first photochemical reactions to be studied carefully and the initial investigation of Warburg[1] has been followed by many others, the nature of the reaction has remained in doubt. The results of the various investigations are summarized in Table I.

TABLE I

SUMMARY OF PREVIOUS INVESTIGATIONS

Photochemical unless otherwise noted

Date	Investigator	NH_3 pressure, mm.	Minimum products for H_2 detn., mm. × 10^3	H_2 yield, %	N_2H_2 yield	Quantum yield
1911	Warburg	45–900				0.25
1926	Kuhn[2]	5–900				.2 –0.5
1926	Dickinson and Mitchell[3]	0– 1	5	70 (sens.) 87 (dir.)		
1927	Bates and Taylor[4]		40	96 (dir.) 89 (sens.)	Amt. small	
1931	Koenig and Brings[5]	250			Small amt.	
1932	Gedye and Rideal[6]	44			0–57% of NH_3 decomp.	
1932	Wiig and Kistiakowsky[7]	0–760	15	75		.24
1934	Ogg, Leighton and Bergstrom[8]	1– 9	Large	75		.14
1935	Wiig[9]	0–900	20	75		.10– .33

Several investigators obtained as products only hydrogen and nitrogen in 3:1 molal ratio and a quantum yield of about 0.25 molecule of ammonia decomposed per quantum absorbed. Others obtained higher hydrogen to nitrogen ratios and still others obtained hydrazine in varying amounts.

The present investigation includes a study of the reaction products and determination of the quantum yields for both the direct photochemical decomposition and the mercury sensitized decomposition. Evidence is presented which makes possible a reconciliation of some of the apparently conflicting data of earlier investigations and which sheds new light on the nature of the decomposition. The results are of particular interest when the amount of decomposition is small; in some cases the partial pressure of the non-condensable products was as low as 10^{-4} mm. of mercury.

Materials and Apparatus

Commercial anhydrous ammonia, free from hydrazine and hydroxylamine, was drawn under vacuum into a storage bulb containing C. P. potassium hydroxide and was purified by repeatedly freezing in a liquid air trap and pumping off the non-condensable gases. Several samples of ammonia from different sources were used during the course of the investigation with completely concordant results.

Most of the apparatus employed has been described previously.[10,11] The vacuum system included mercury diffusion pump, McLeod gage, quartz fiber gage, a reaction cell of quartz (attached to the rest of the system through a quartz–Pyrex graded seal), a storage bulb for the ammonia, and several stopcocks and mercury cut-offs. The cut-offs were so placed that no stopcocks were included in that part of the system in which measurements were made.

The direct decomposition of ammonia was studied with the aid of radiation from a high-voltage condensed spark between water-cooled aluminum electrodes. Energy for the spark was supplied by a 13,000-volt, 10-kva. transformer with a 0.1-mf. condenser placed in parallel with the spark. The sensitized decomposition was produced by the 2537 Å. resonance radiation from a water-cooled quartz mercury arc. Radiation of wave length shorter than 2400 Å. was removed by an acetic acid filter.

In the quantum yield experiments monochromatic radiation, vacuum thermopiles and high-sensitivity galvanometers were used. The thermopiles had fused quartz windows attached with wax and were continuously evacuated by an oil diffusion pump. Monochromatic radiation was

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(1) Warburg, *Sitzber. preuss. Akad. Wiss.*, 746 (1911).

(2) Kuhn, *J. chim. phys.*, **23**, 521 (1926).

(3) Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

(4) Bates and Taylor, THIS JOURNAL, **49**, 2438 (1927).

(5) Koenig and Brings, *Z. physik. Chem.*, 541 (1931).

(6) Gedye and Rideal, *J. Chem. Soc.*, 1158 (1932).

(7) Wiig and Kistiakowsky, THIS JOURNAL, **54**, 1806 (1932).

(8) Ogg, Leighton and Bergstrom, *ibid.*, **56**, 318 (1934).

(9) Wiig, *ibid.*, **57**, 1559 (1935).

(10) Wenner and Beckman, *ibid.*, **54**, 2787 (1932).

(11) Myers and Beckman, *ibid.*, **57**, 89 (1935).

obtained by means of a quartz monochromator and was focused on the vane of one of the thermopiles, T_t (transmission). The fused quartz reaction cell, provided with plane windows, was inserted in this light path. The front window of the cell, attached at an angle of 45°, reflected a fraction of the incident radiation onto the vane of the second (reflection) thermopile, T_r. A recording device provided continuous records for both thermopiles.

Experimental Method

Since the decomposition products were very small in amount, it was essential to keep the system thoroughly outgassed. This was achieved by almost continuous evacuation during the investigation. The reaction system would retain for hours a vacuum better than 10^{-6} mm.

In experiments to determine the composition of the non-condensable products, a sample of purified ammonia was irradiated and the pressure and composition of the products not condensable in liquid air were determined by combined use of the McLeod and quartz fiber gages. These products were assumed to contain only hydrogen and nitrogen; it has been shown[12] that this method of analysis gives accurate results with such mixtures. The quartz fiber gage was calibrated frequently, using both nitrogen and hydrogen.

Quantum yields were measured by an absolute method. In each experiment the ratio of the transmission and reflection thermopile readings with the empty cell was first determined. The purified ammonia was then admitted and irradiated, a continuous photographic record being taken of both thermopile readings. Liquid air was applied and the pressure and composition of the non-condensable products determined. Calibrations of the quartz fiber gage were alternated with quantum yield runs. Blank experiments were also run, in some of which the shutter of the monochromator remained closed throughout the experiment; in others the shutter was opened as usual but the ammonia was kept frozen. The sensitivity of the transmission thermopile was measured frequently with the aid of standardized carbon lamps supplied by the Bureau of Standards. The transmission factors of the rear window of the cell and of the window of the transmission thermopile for the radiations used were determined experimentally.

Experimental Results

Products of the Photochemical Decomposition.—When the amount of ammonia decomposed was relatively large (*i. e.*, partial pressure of products greater than 0.05 mm.) the non-condensable products contained approximately 75% hydrogen and 25% nitrogen, in agreement with the results reported by several of the previous investigators (Table I). However, when the amount of decomposition was successively decreased, the percentage of hydrogen increased, approaching 100% in the limiting case. The data for the photochemical decomposition are represented by the circles in Fig. 1, in which the ordinates are the percentages of hydrogen in the non-condensable decomposition products and the abscissas are the total pressures of the non-condensable products as measured with the McLeod gage. The lowest pressure on which accurate analyses could be made was about 3×10^{-4} mm.

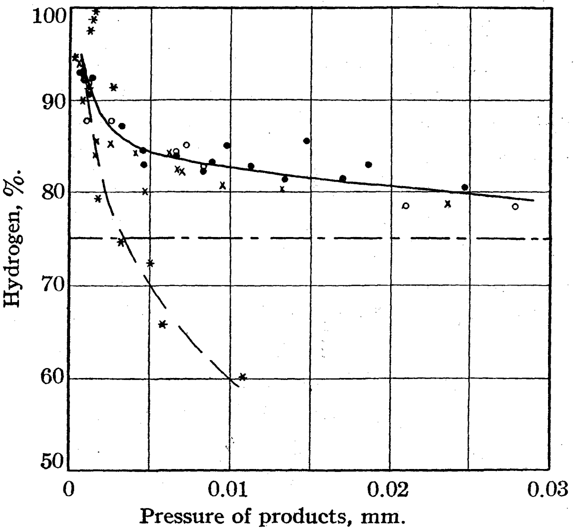

Fig. 1.—Composition of the non-condensable gases: ●, direct photochemical decomposition, 4 mm. NH_3; ○, direct photochemical decomposition, 20 mm. NH_3; $*$, mercury sensitized decomposition, 4 mm. NH_3, fresh cell; ×, mercury sensitized decomposition, 20 mm. NH_3.

To prove that the results could not be attributed to easily decomposed impurities in the ammonia, experiments were made not only with fresh samples of ammonia but also with the residual ammonia remaining from previous experiments, in which large amounts of decomposition had taken place and in which 75% hydrogen had been obtained. In all cases, the percentage of hydrogen was considerably greater than 75% for very small amounts of decomposition and decreased progressively toward 75% as the amount of decomposition was increased.

Percentages of hydrogen in excess of 75% indicate the formation of hydrazine during decomposition. Varying amounts of hydrazine in the decomposition products of ammonia have been reported by certain investigators who used a flow method. Thus Bates and Taylor[4] and Koenig and Brings[5] obtained small amounts of hydrazine, while Gedye and Rideal[6] reported hydrazine yields ranging from 0 to 57% of the amount stoichiometrically possible from the amount of ammonia decomposed. Other investigators obtained no evidence of hydrazine formation.

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(12) Beckman and Dickinson, THIS JOURNAL, **50**, 1870 (1928).

Hydrazine, if present, might be expected to condense with the undecomposed ammonia when liquid air is applied to the freezing-out trap. In several experiments the trap containing the condensed material was removed from the vacuum system and the contents dissolved in dilute acid. Tests with iodate, ammoniacal silver, and gold chloride failed to give a positive indication for hydrazine. Since the amount of hydrazine theoretically present (calculated from the pressure and composition of the non-condensable gases, assuming that the hydrazine is the only other product formed in the decomposition) is not greatly in excess of the minimum amount capable of detection (about 10^{-8} mol) by these methods, and since hydrazine is known to be strongly adsorbed on glass and quartz, it appeared probable that failure to detect hydrazine was due to the fact that most of the hydrazine remained in the reaction cell. Consequently, tests were made in which acidified, de-aerated water was added directly to the reaction cell and the aqueous liquid withdrawn and tested for hydrazine with ammoniacal silver nitrate. Positive indications for hydrazine were obtained in all cases. Control experiments made under identical conditions except that the ammonia was not irradiated gave no tests for hydrazine.

Quantum Yield for the Photochemical Decomposition.—The results of the quantum yield determinations for the direct decomposition of ammonia, using monochromatic radiation of 1990 Å., are given in Table II. In these experiments the amount of decomposition was always very small and the percentage of hydrogen in the non-condensable gases was large, averaging about 95%. Assuming that hydrazine, hydrogen and nitrogen are the only products, this means that 16 molecules of ammonia decompose to give hydrogen and hydrazine for every molecule that decomposes to hydrogen and nitrogen. The number of molecules of ammonia decomposed may be found by means of the stoichiometric relation

$$N_{\mathrm{NH_3}} = 6(f - 0.667)N\frac{pV}{RT} \tag{1}$$

where N is Avogadro's number, p is the total pressure of non-condensable gas and f is the mole fraction of hydrogen.

The number of quanta of 1990 Å. radiation absorbed may be calculated from the relation

$$N_{\mathrm{Q}} = \frac{(\beta D_{\mathrm{r}}S_{\mathrm{r}} - D_{\mathrm{t}}S_{\mathrm{t}})t}{\alpha_1\alpha_2hc/\lambda} \tag{2}$$

where β is the ratio of galvanometer deflections with the empty cell, D_{r} and D_{t} are the galvanometer deflections for the reflection and transmission thermopiles, S_{r} and S_{t} are the sensitivities of the transmission thermopile at deflections of D_{r} and D_{t}, *i. e.*, the number of ergs per second required to give unit deflection, t is the time of irradiation, α_1 and α_2 are the transmission factors for λ 1990 Å. of the rear window of the reaction cell and the window of the transmission thermopile, h is Planck's constant, c the velocity of light and λ is the wave length 1990 Å. The quantum yield is obtained by dividing $N_{\mathrm{NH_3}}$ by N_{Q}.

In the first four experiments listed in Table II the reaction cell was thoroughly outgassed by

TABLE II

QUANTUM YIELDS FOR THE PHOTOCHEMICAL DECOMPOSITION OF AMMONIA (λ = 1990 Å.)

Expt. no.	Pressure NH_3, mm.	Time, min.	Pressure products, mm. × 10^4	H_2 in products, %	Molecules NH_3 dec. × 10^{-14}	Quanta absorbed × 10^{-14}	Quantum yield
6[a]	5.0	33	3.5	95.2	33.8	47.0	0.72
10[a]	12.7	29.75	3.6	91.5	29.9	41.0	.73
5[a]	30.3	46	6.1	96.5	60.9	76.4	.80
9[a]	111.2	24	3.86	92.9	34.2	51.8	.66
							Av. .70
18	2.2	29.5	4.2	94.5	39.45	46.55	0.85
17	5.9	28	5.65	96.8	57.5	61.25	.94
13	6.0	29	6.37	96.8	64.75	68.37	.95
11	13.8	18	4.63	92.67	40.95	51.95	.79
15	14.3	29	8.2	95.5	80.15	85.78	.94
12	29.3	23	6.4	94.45	60.2	69.55	.87
16	30.0	18.5	5.0	95.6	49.03	54.55	.90
14	60.7	19.5	4.46	94.1	41.4	55.77	.74
19	128.2	29.5	8.7	90.5	70.2	81.9	.86
							Av. .87

[a] Fresh cell used in first four experiments, cell walls saturated with hydrogen atoms for remaining experiments.

TABLE III

QUANTUM YIELDS FOR THE SENSITIZED DECOMPOSITION OF AMMONIA (λ = 2537 Å.)

Expt. no.	Pressure NH_3, mm.	Time, min.	Pressure products, mm. × 10^4	H_2 in products, %	Molecules NH_3 dec. × 10^{-14}	Quanta absorbed × 10^{-14}	Quantum yield
26	0.25	26	0.32	(95.0)[a]	2.14	44.45	0.05
25	.60	21	.51	(95.0)[a]	3.4	34.85	.10
24	1.3	21	.64	(95.0)[a]	4.28	38.5	.112
19	1.4	23.65	.84	(95.0)[a]	7.55	48.2	.156
23	2.1	21	.78	(95.0)[a]	5.24	41.7	.125
18	4.9	21	1.01	(95.0)[a]	6.45	48.6	.133
28	8.3	21	1.15	(95.0)[a]	7.55	66.4	.114
29	8.3	39	0.88	(95.0)[a]	5.78	54.3	.105
17	14.3	16	.87	(95.0)[a]	5.58	43.73	.127
16	38.5	21	1.35	(95.0)[a]	8.7	80.0	.109
22	103.3	26	1.78	(95.0)[a]	11.77	109.5	.107
31a	3.1	150	7.45	94.7	68.7	445	.154
31b	3.1	212	10.6	96.7	105.3	628	.168
30a	8.5	100	4.56	84.7	34.55	359	.096
30b	8.5	145	7.5	93.0	64.2	520	.123
27a	20.6	100	3.88	90.0	30.0	360	.083
27b	20.6	240	9.57	95.0	90.3	865	.104
						Av. =	.12

[a] For these experiments the hydrogen in the non-condensable products was assumed to be 95%. For the remaining experiments the percentage of hydrogen was determined by analysis.

baking and evacuating prior to the experiment. Since it is known that hydrogen readily "cleans up" on fresh quartz surfaces,[13] it was felt that the observed quantum yields (av. = 0.70) might be low for that reason. Therefore, for the remainder of the experiments, prior to the admission of ammonia to the cell, hydrogen at a pressure of a few millimeters in the presence of mercury vapor was irradiated for several hours with intense mercury resonance radiation, followed by thorough evacuation. With such treatment of the cell, the observed quantum yields rose to an average value of 0.87. Blank experiments showed that irradiation of the empty treated cell produced negligible amounts of gas, proving that the increased quantum yield was not due to outgassing of adsorbed hydrogen. In Fig. 2 the quantum yields for the direct decomposition of ammonia are represented by the circles. The yields seem to approach unity as a limit and are not affected by changes in ammonia pressure nor the amount of products, when the latter is less than 10^{-3} mm.

Mercury Sensitized Decomposition.—The products of the sensitized decomposition were the same as in the direct decomposition. The percentage of hydrogen in the non-condensable products again varied from nearly 100% down to about 75% as the amount of decomposition increased, as shown in Fig. 1, where the crosses represent sensitized decompositions. It will be noticed that the same curve fits either type of decomposition, except when the ammonia pressure is low and a fresh cell is used. In this event, hydrogen is cleaned up on the walls to such an extent that its fraction in the gases drops considerably below 0.75 on continued irradiation with λ 2537 Å. When hydrogen alone is similarly irradiated in the cell, its pressure slowly falls off.

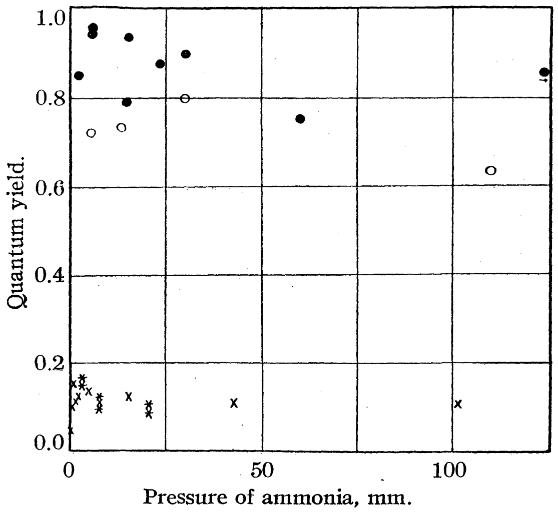

Fig. 2.—Quantum yield of the photodecomposition of ammonia: ○, direct decomposition, fresh cell; ●, direct decomposition, cell saturated with H atoms; *, sensitized decomposition; ×, sensitized decomposition, 95% H_2 assumed.

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(13) Cario and Franck, *Z. Physik*, **11**, 161 (1922).

The quantum yield of the sensitized decomposition was, however, much smaller than that of the direct decomposition, having an average value of 0.12, as shown in Table III, and in Fig. 2, where the crosses again represent sensitized decompositions. This value of the yield was independent of the amount of decomposition, if small, and of the ammonia pressure, except below 1 mm., where it fell rapidly to zero.

Discussion

The primary process in the photochemical decomposition of ammonia may be assumed to be a dissociation, since the absorption spectrum of ammonia is of the predissociation type,[14,15] involving the rupture of one of the hydrogen–nitrogen bonds.

$$NH_3 + h\nu \longrightarrow NH_2 + H$$

The most direct experimental evidence for this primary process is the work of Geib and Harteck,[16] who showed that the photochemical decomposition products of ammonia could effect the conversion of para to ortho hydrogen and therefore presumably contained hydrogen atoms.

In the lower limit of small amounts of decomposition, the products are substantially only hydrogen and hydrazine. The following mechanism accounts for their formation

$$\begin{aligned} NH_3 + h\nu &\longrightarrow NH_2 + H \\ H + H + M &\longrightarrow H_2 + M \\ NH_2 + NH_2 + M &\longrightarrow N_2H_4 + M \end{aligned}$$

This mechanism accounts satisfactorily for the additional experimental fact that the quantum yield is unity, independent of ammonia pressure. Other reaction steps assumed by previous investigators[4,7,8] are not needed. In particular, the reaction

$$H + NH_2 + M \longrightarrow NH_3 + M$$

leading to the re-formation of ammonia, does not play an important role, since the quantum yield is nearly unity.

The decomposition, with the exception of the primary process, probably proceeds heterogeneously on the walls of the reaction vessel at the low pressures of these experiments. Hydrogen atoms are known to be strongly adsorbed on glass[17] and are probably also adsorbed on quartz. The fact that no reducing substance was obtained in freezing-out traps may be taken as evidence that either NH_2 or N_2H_4 or both are adsorbed on the cell walls.

A little of the hydrazine will probably be decomposed by the hydrogen atoms, as shown by Dixon,[18] even when its amount is small. The decomposition of hydrazine in this way will give ammonia and some nitrogen, thus slightly reducing the hydrogen fraction below 100% and reducing the quantum yield below the value of unity. With larger amounts of products the effect is exaggerated, and the lower quantum yields obtained by previous investigators may be due in part to this effect. There is general agreement in recent investigations[7,9] that the non-condensable gaseous products contain 75% hydrogen and 25% nitrogen when relatively large amounts of products are obtained. These percentages also appear as the limiting values in the present experiments as the amount of decomposition successively increases. For small amounts of decomposition, however, the percentage of hydrogen is much greater, a fact which has a marked influence upon the calculation of the quantum yields. From equation 1 above, it is to be seen that for a given volume of non-condensable gas, the calculated number of ammonia molecules decomposed will be four times as large when the gas is 100% hydrogen as when it is 75% hydrogen. If the quantum yields given above in Table II had been computed on the assumption that the non-condensable gas consisted of 75% hydrogen and 25% nitrogen, the calculated quantum yields would have been reduced to approximately 0.25, in agreement with the results of others. Since the analyses showed that the non-condensable gas was substantially all hydrogen, the actual quantum yields are much larger, nearly unity.

The marked change in the composition of the products in the region of small amounts of decomposition illustrates a point which is often overlooked in photochemical investigations. Because of the difficulties which usually attend the analysis of the small amounts of products obtainable from quantum yield experiments, it is a common practice to get relatively large amounts of products for analysis, often radically changing the intensity of radiation, degree of monochromatization, concentration of the reactants, etc., from the conditions of the quantum yield experiments. Yet it is usually assumed that the reaction follows the

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(14) Leifson, *Astrophys. J.*, **63**, 73 (1926).

(15) Dixon, *Phys. Rev.*, **43**, 711 (1933).

(16) Geib and Harteck, *Z. physik. Chem.*, Bodenstein Festband, 849 (1931).

(17) Bonhoeffer, *ibid.*, **113**, 199 (1924).

(18) Dixon, THIS JOURNAL, **54**, 4262 (1932).

same course in both cases. The present experiments show that this assumption must be viewed with suspicion. The safe plan is to perform the experiments leading to a deduction of reaction mechanism under the same conditions as the quantum yield experiments, or better still to combine them in the same experiments.

The mercury-sensitized decomposition differs from the photochemical decomposition in the nature of the primary processes and by the fact that marked fluorescence was observed.[3]

$$\begin{aligned} Hg + h\nu_1 &\longrightarrow Hg' \\ Hg' + NH_3 &\longrightarrow NH_3' + Hg \\ NH_3' &\longrightarrow NH_3 + h\nu_2 \\ NH_3' &\longrightarrow NH_2 + H \end{aligned}$$

The low quantum yield for the photosensitized decomposition may be attributed to fluorescence and suggests that the quantum of λ 2537 Å. (approximately 112,000 cal. per mole) is barely sufficient to produce decomposition.

Summary

The photochemical and mercury photosensitized decompositions of ammonia have been investigated in the region of very small amounts of decomposition. In contrast to the results obtained with large amounts of decomposition, namely, a quantum yield of 0.25 and gaseous products consisting of 75% hydrogen and 25% nitrogen, with small amounts of decomposition the quantum yield approaches unity and the gaseous products approach pure hydrogen, in the case of the photochemical decomposition. For the photosensitized decomposition a quantum yield of 0.12 was obtained.

PASADENA, CALIF. RECEIVED OCTOBER 6, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Rearrangement of Acetylchloroaminobenzene in the Presence of Radioactive Hydrochloric Acid

BY A. R. OLSON, C. W. PORTER, F. A. LONG AND R. S. HALFORD

The mechanism of the Hofmann rearrangement of N-substituted aromatic amines has been under investigation, intermittently, over a period of sixty years. As early as 1881 Michael[1] advanced the theory that in the rearrangement of methylaniline hydrochloride into the hydrochloride of *p*-toluidine, the first step is a dissociation into methyl chloride and aniline. The methyl chloride is then supposed to act upon the aniline, substituting the methyl group for the para hydrogen atom. In 1920 Michael[2] reaffirmed this conclusion and referred to the dissociation mechanism as a "self-evident explanation."

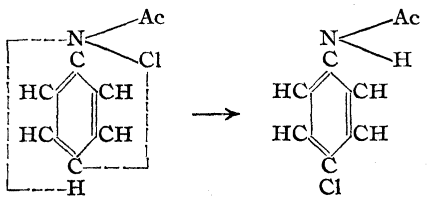
Orton and his colleagues[3] outlined a mechanism for the rearrangement of acetylchloroaminobenzene which has become almost universally accepted. They envisage the reaction as proceeding in three steps: (1) the hydrolysis of the chloroamine; (2) the production of chlorine from hydrochloric and hypochlorous acids; (3) the chlorination of acetanilide.

$$C_6H_5NClAc + H_2O \rightleftarrows C_6H_5NHAc + HClO \quad (1)$$

$$HClO + H^+ + Cl^- \rightleftarrows H_2O + Cl_2 \quad (2)$$

$$C_6H_5NHAc + Cl_2 \longrightarrow ClC_6H_4NHAc + H^+ + Cl^- \quad (3)$$

At the Richmond meeting of the American Chemical Society (1927) one of us presented the view that the arrangement is intramolecular.[4] It was postulated that a bond is formed between the chlorine atom and the para carbon atom while the chlorine is still attached to the nitrogen. Similarly it was assumed a bond is formed between the nitrogen atom and the para hydrogen atom in advance of any dissociation process. These weak bonds are represented by dotted lines in formula I. When molecules in state I become



I II

sufficiently activated the bonds represented by dotted lines become full valence bonds and the rearrangement is accomplished. In the Richmond

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[1] A. Michael, *Ber.*, **14**, 2105 (1881).

[2] A. Michael, THIS JOURNAL, **42**, 787 (1920).

[3] F. O. Chattaway and K. J. P. Orton, *Proc. Chem. Soc.*, **18**, 200 (1902); K. J. P. Orton and W. J. Jones, *Brit. Assn. Adv. Sci. Repts.*, 1910, p. 85; F. S. Kipping, *et. al.*, *Chem. News*, **108**, 155 (1913).

[4] C. W. Porter, paper read at the April meeting, 1927.

meeting this mechanism was referred to, derisively, as the "flip-flop theory."

The discovery of methods for producing artificial radioactivity has furnished a new tool for investigating problems of this type. Thus in this rearrangement, if we use ordinary acetylchloroaminobenzene and radioactive hydrochloric acid as a catalyst, we can determine the distribution of radioactivity among the products as the reaction progresses. This distribution will depend on the following factors: (1) the reaction mechanism or mechanisms; (2) the amount of exchange between radioactive chloride ion and chlorine (a) on the nitrogen of the chloroaminobenzene, (b) on the carbon of the chloroacetanilide and (c) of the molecular chlorine or hypochlorous acid in solution.

Of these factors 2b and 2c need no further investigation. Olson and Long[5] have shown that the exchange between chloride ion and chlorine on an aliphatic carbon is very slow. The exchange on an aromatic carbon is probably even slower and so it can be neglected in the present investigation. Also Long and Olson[6] have just shown that the equilibrium between chlorine and chloride ion is completely established before the chlorine can react with acetanilide. The remaining factors are considered in the present work.

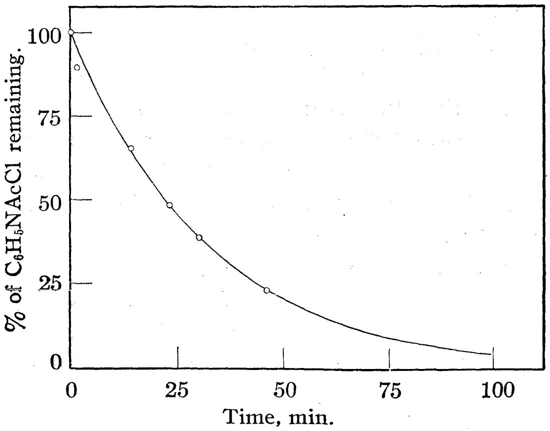

Fig. 1.—The circles are the experimental results for the chemical rate as taken from Table I. The solid line has been calculated from a unimolecular rate constant, k_1 = 0.0316 min.$^{-1}$.

Experimental

The acetylchloroaminobenzene was prepared by the method of Barnes and Porter.[7]

The radioactive chlorine was prepared in Professor E. O. Lawrence's radiation laboratory, by bombarding solid sodium chloride with deuterons.

The concentrations of the reagents and the temperature were chosen so that the half-life of the reaction was somewhat shorter than the half-life of the radioactive chlorine. The solvent was aqueous alcohol (20% alcohol by volume).

In making a run, the acetylchloroaminobenzene was dissolved in the aqueous alcohol solution to which enough sulfuric acid had been added to make it 1 *N* with respect to hydrogen ion. The radioactive sodium chloride was dissolved separately in a predetermined volume of the same solvent, so that after a portion of the solution had been used for the initial radioactive analysis, the remaining portion, when mixed with the chloroamine, would produce a solution 0.04 molar with respect to both acetylchloroaminobenzene and radioactive sodium chloride. The solutions were brought to the temperature of the thermostat before mixing and the time of mixing was taken as the zero time for the reaction.

At times shown in Table I, 5-cc. samples were withdrawn and analyzed in the usual manner by adding excess potassium iodide solution and titrating the liberated iodine with standard thiosulfate. The results are given in Table I and plotted in Fig. 1. The solid line in this figure has been calculated using a unimolecular rate constant, k_1 = 0.0316.

TABLE I

DATA FOR CHEMICAL RATE

Time, min.	Thio used, cc.	% C_6H_5NAcCl unreacted
0	3.90	100
1.5	3.50	89.8
14	2.55	65.4
23	1.90	48.7
30	1.50	38.5
46	0.90	23.0

In addition to following the rate of rearrangement in the usual chemical way, we determined the rate of change with time of the radioactivity of the chloride ion in solution. This change was due not only to the natural radioactive decay but also to the fact that some radioactive chloride ions were used in the reaction and were replaced by non-radioactive chloride ions. At regular intervals 100-cc. samples were withdrawn from the reaction vessel, silver nitrate solution was added and the silver chloride was filtered off, washed and dried. A weighed amount of this silver chloride was then dissolved in a known volume of ammonium hydroxide and the radioactivity of the chloride ion was determined by the method outlined by Olson, Libby, Long and Halford.[8]

In addition to these measurements, two determinations of a different type were made. In the first of these the radioactivity of the rearranged product, *p*-chloroacetanilide, was obtained. This was done by taking a somewhat larger sample than usual, destroying the chloroamine with iodide ion, reducing the liberated iodine with thiosulfate, then extracting the rearranged product with benzene. After evaporating the benzene, the chloroacetanilide was fused with potassium hydroxide, dissolved in water and

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[5] A. R. Olson and F. A. Long, THIS JOURNAL, **56**, 1294 (1934).

[6] F. A. Long and A. R. Olson, *ibid.*, **58**, 2214 (1936).

[7] C. D. Barnes and C. W. Porter, *ibid.*, **52**, 1721 (1930).

[8] A. R. Olson, W. F. Libby, F. A. Long and R. S. Halford, *ibid.*, **58**, 1313 (1936).

acidified with nitric acid. Excess silver nitrate was then added, the silver chloride filtered off, dried and examined for radioctivity in the usual manner. Two sources of inaccuracy entered into this determination. First, the silver chloride was quite dark, indicating the presence of some silver sulfide. Second, the amount of silver chloride obtained from this experiment was only one-fifth as much as we otherwise used for a radioactive determination.

The second experiment was devised to determine the rate with which radioactive chlorine replaces the non-radioactive chlorine on the nitrogen of the acetylchloroaminobenzene. After the reaction was about one-fourth over, a sample of the reaction mixture was removed and sufficient sodium carbonate was added to make the solution somewhat alkaline. This was done to convert any slight amount of chlorine into hypochlorite and chloride ions. The chloroamine and chloroanilide were then extracted with benzene. This benzene extract was shaken thoroughly with an aqueous solution of sodium sulfite which reduced the chloroamine to chloride ion and acetanilide. The aqueous solution was acidified, the chloride precipitated as silver chloride and its radioactivity determined.

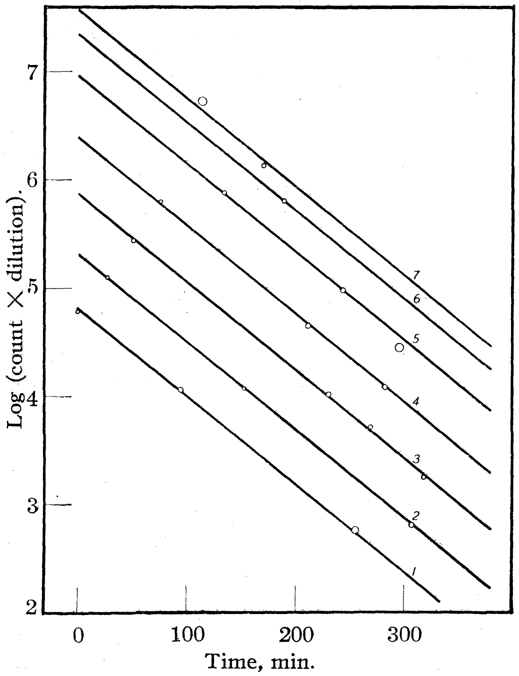


Fig. 2.—The numbers of the curves refer to the correspondingly numbered samples in Table II. The curves have been displaced upward by 0.6 unit from the preceding curve with the exception of Curve 6 which has been displaced twice this amount.

In Fig. 2 we have plotted the time of counting against the logarithm of the product of the net count times the dilution for all these silver chloride samples. In every case the slope of the line corresponds to the known half-life of radioactive chlorine. If we call the radioactivity of the control sample 100%, then, from the intercepts of these lines on the $t = 0$ axis, we can calculate immediately the percentages of radioactivity in each of these samples as compared with the control. The results of these calculations are given in Table II, and the data for the chloride ion in solution have been plotted in Fig. 3.

TABLE II

No. of corresp. curve in Fig. 2	Source of AgCl	Time, min.	% radioactivity compared to control sample
1	Solution	0	100
2	Solution	6.67	79.2
3	Solution	20	72.7
4	Solution	44	60.2
5	Solution	81.2	55.7
6	Chloroacetanilide	30	40.5
7	Chloroamine	11.16	4.09

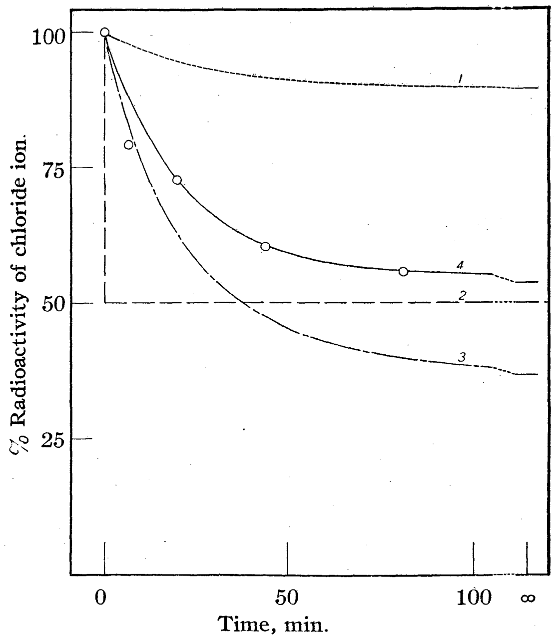


Fig. 3.—Graphic representation of the results for various mechanisms. Curve 1 is for intramolecular rearrangement with exchange on the nitrogen. Curves 2 and 3 give the upper and lower limits for the chlorine intermediate path. Curve 4 is for the two mechanisms proceeding simultaneously. The circles are the experimental results as shown in Table II.

With the datum given in Table II it is possible to calculate the specific rate of the exchange reaction

$$C_6H_5NAcCl + {}^*Cl^- \xrightarrow{k_2} C_6H_5NAcCl^* + Cl^-$$

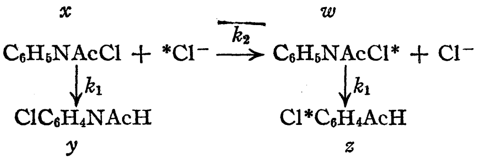
with an accuracy sufficient for our purpose, by assuming that the concentration of radioactive chloride ion is, over this short time interval, constant and equal to its initial value. Table II shows that approximately 4% of the chlorine of the acetylchloroaminobenzene is radioactive after 11.16 minutes. This corresponds to a specific rate constant for this reaction of $k_2 = 0.094$ mole^{-1} min.$^{-1}$.

In addition to the data given above several preliminary runs were made. The data for these runs are not included here, for, while the results are in accord with this run, they are not sufficiently accurate to merit inclusion.

Detailed Consideration of Possible Mechanisms

(1) Intramolecular rearrangement without exchange on the nitrogen of the chloroamine: This mechanism alone cannot possibly account for the experimental facts since, then, there would be no decrease of the radioactivity of the chloride ion in solution as the reaction progressed.

(2) Intramolecular rearrangement, allowing for exchange on the nitrogen: Schematically this mechanism can be represented by



$$\begin{array}{ccc} x & & w \\ C_6H_5NAcCl + {}^*Cl^- & \xrightarrow{k_2} & C_6H_5NAcCl^* + Cl^- \\ \downarrow k_1 & & \downarrow k_1 \\ ClC_6H_4NAcH & & Cl^*C_6H_4AcH \\ y & & z \end{array}$$

The specific rate of interchange of chlorine on the nitrogen of the chloroamine is given by k_2 and the specific rate of the rearrangement is given by k_1.

To obtain the rate expression for this mechanism, let x, y, w and z be the concentrations of C_6H_5NAcCl, ClC_6H_4NAcH, $C_6H_5NAcCl^*$ and $Cl^*C_6H_4AcH$, respectively, at time, t. In addition, let a be the initial concentration of C_6H_5NAcCl and b be the initial concentration of radioactive chloride ion.

We can therefore write

$$\begin{aligned} dx/dt &= -k_1x - k_2(b - w - z)x \\ dw/dt &= k_2(b - w - z)x - k_1w \\ dy/dt &= +k_1x \\ dz/dt &= +k_1w \end{aligned}$$

Since the hydrogen ion and the total chloride ion concentrations do not change during a run (except very slowly due to side reactions) we have included the magnitude of these factors in k_1, the chemically determined rate constant. The equations then represent the fact that under these conditions the chemical rate is unimolecular, depending only on $x + w$, the total concentration of chloroamine. The rate at which chloroamine is converted into the radioactive variety depends not only on the concentration of the inactive chloroamine, but also upon $b - w - z$, the concentration of the radioactive chloride ion, since this, as distinguished from b, the total chloride ion concentration, is a function of the time.

This set of equations can be solved conveniently by a series of approximations. In the first approximation we set the radioactive chloride ion concentration, $^*Cl^-$, equal to b. Integration with this assumption gives

$$\begin{aligned} x &= ae^{-(k_1 + k_2b)t} \\ w &= a[e^{-k_1t} - e^{-(k_1 + k_2b)t}] \\ z &= a\left[\frac{k_2b}{k_1 + k_2b} + \left(1 - \frac{k_2b}{k_1 + k_2b}\right) e^{-(k_1 + k_2b)t} - e^{-k_1t}\right] \\ y &= a - (x + w + z) \end{aligned}$$

Making use of the values $k_1 = 0.0316$ and $k_2b = 0.00376$, as given in earlier paragraphs, we can calculate the concentrations of radioactive chloride ion which should be present at any time t according to this mechanism. This we have done. The dotted line, labeled 1, in Fig. 3 shows the results of these calculations. The very large discrepancy between the calculated and observed percentages cannot be accounted for by the approximation which we have introduced in order to simplify the calculations, for k_2b would need to be almost ten times as large as the value found, in order to obtain an agreement between the observed and calculated values. It is obvious, therefore, that this mechanism by itself cannot account for the data observed under these experimental conditions.

(3) The reaction proceeds through the intermediate formation of chlorine: (a) The concentration of chlorine is large. All of the chemical evidence is against this assumption. However, it may not be amiss to point out that if all the chloroamine reacted to give chlorine before any of the final product were formed, then the radioactivity of the chloride ion in solution would drop to 50% of its original value and thereafter remain constant. The assumption of a large concentration of chlorine is equivalent mathematically, so far as the distribution of radioactivity in the products is concerned, to assuming that the equilibrium

$$C_6H_5NAcCl + H^+ Cl^- \rightleftarrows Cl_2 + C_6H_5NacH$$

is established rapidly. Therefore any mechanism which depends upon such a *rapid* reversible reaction must be wrong.

(b) The concentration of chlorine is small. In order to get the limiting value under this assumption we shall assume that the concentration of chlorine is infinitesimal and that no exchange on the nitrogen occurs. We can represent the mechanism as

$$C_6H_5NAcCl + H^+ + \begin{bmatrix} Cl^- \\ {}^*Cl^- \end{bmatrix} \longrightarrow C_6H_5NAcH + \begin{bmatrix} {}^*Cl_2 \\ Cl_2 \end{bmatrix} \qquad (1)$$

$$C_6H_5NAcH + \begin{bmatrix} {}^*Cl_2 \\ Cl_2 \end{bmatrix} \begin{array}{l} \nearrow {}^*ClC_6H_4NAcH \\ \searrow ClC_6H_4NAcH \end{array} + H^+ + \begin{bmatrix} {}^*Cl^- \\ Cl^- \end{bmatrix} \qquad (2)$$

where $\begin{bmatrix} {}^*Cl_2 \\ Cl_2 \end{bmatrix}$ includes all the varieties of chlorine molecules. We do not wish to commit ourselves to any particular mechanism by which molecular chlorine may be formed from the chloroamine, but wish to assume merely that molecular chlorine is an intermediate.

Since the concentration of chlorine remains small, the total rate of production of the chloroanilide must be equal to the rate of disappearance of chloroamine, and therefore equal to the chemical rate.

Designating, as before, the concentrations at time t, of C_6H_5NAcCl, ClC_6H_4NAcH and $^*Cl$-C_6H_4NAcH as x, y and z, respectively, we obtain

$$-\mathrm{d}x/\mathrm{d}t = +k_1bx = \mathrm{d}y/\mathrm{d}t + \mathrm{d}z/\mathrm{d}t$$

where, for convenience, we have replaced k_1 of a former section by k_1b. The ratio $(\mathrm{d}z/\mathrm{d}t)/(\mathrm{d}y/\mathrm{d}t)$ is equal to the ratio of the probability that a chlorine atom in molecular chlorine is radioactive, to the probability that it is inactive. Since we have shown that there is a very rapid interchange between chloride ion and chlorine, this ratio of probabilities is merely the ratio of the concentrations of radioactive chloride ion to inactive chloride ion, which in turn is $(b-z)/z$.

Our rate equations are then

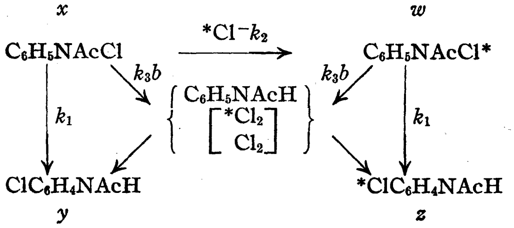
$$\begin{aligned} \mathrm{d}x/\mathrm{d}t &= -k_1bx \\ \mathrm{d}z/\mathrm{d}t &= +k_1(b - z)x \\ \mathrm{d}y/\mathrm{d}t &= +k_1zx \end{aligned}$$

The integrated expressions are

$$\begin{aligned} x &= ae^{-k_1bt} \\ b - z &= be^{-(1 - e^{-k_1bt})} = (^*Cl^-) \\ y &= a - x - z \end{aligned}$$

Curve 3 in Fig. 3 represents the values for the percentages of radioactive chloride ion in solution calculated under this assumption. Curve 2 is a plot of the percentages of radioactive chloride ion under the assumptions of paragraph (a) or the equivalent assumption that the exchange on the nitrogen is very fast. Any assumption with respect to the concentration of chlorine or with respect to the speed of the exchange on the nitrogen, but which retains the chlorine intermediate as the sole path of the reaction, must give a curve which lies intermediate between curve 3 and curve 2. Since our experimental curve lies outside of these limits, we can conclude that the reaction cannot go solely by a chlorine intermediate. It is thus evident that no single mechanism so far proposed is sufficient to explain the experimental facts which we have observed.

(4) Intramolecular rearrangement and the chlorine intermediate mechanism acting simultaneously: We can represent such a combination of these two mechanisms schematically as



As before, since chlorine does not accumulate in the solution, the chemical rate of disappearance of the chloroamine, $-(\mathrm{d}x/\mathrm{d}t + \mathrm{d}w/\mathrm{d}t)$, must be equal to the rate at which chloroacetanilide is formed by all paths, *i. e.*, $\mathrm{d}y/\mathrm{d}t + \mathrm{d}z/\mathrm{d}t$. According to this mechanism it also will be equal to $(k_1 + k_3b)(x + w)$. If we set $\mathrm{d}y/\mathrm{d}t = \mathrm{d}y'/\mathrm{d}t + \mathrm{d}y''/\mathrm{d}t$ and $\mathrm{d}z/\mathrm{d}t = \mathrm{d}z'/\mathrm{d}t + \mathrm{d}z''/\mathrm{d}t$ where $\mathrm{d}y''/\mathrm{d}t$ and $\mathrm{d}z''/\mathrm{d}t$ are the contributions of the chlorine intermediate mechanism to the rates, we see that $(\mathrm{d}z''/\mathrm{d}t)/(\mathrm{d}y''/\mathrm{d}t)$ must as before be equal to $(^*Cl^-)/(Cl^-)$ which now becomes $(b - w - z)/(w + z)$.

The differential equations, with the same symbols as used originally, are

$$\begin{aligned} \mathrm{d}x/\mathrm{d}t &= -k_1x - k_2x(b - w - z) - k_3bx \\ \mathrm{d}w/\mathrm{d}t &= +k_2x(b - w - z) - k_1w - k_3bw \\ \mathrm{d}z/\mathrm{d}t &= +k_1w + k_3(x + w)(b - w - z) \\ \mathrm{d}y/\mathrm{d}t &= +k_1x + k_3(x + w)(w + z) \end{aligned}$$

Assuming that the concentration of radioactive chloride ion is constant and equal to the initial value, the following approximate expressions for x and w, as functions of time, are obtained.

$$\begin{aligned} x &= ae^{-(k_1 + k_2b + k_3b)t} \\ w &= a[e^{-(k_1 + k_3b)t} - e^{-(k_1 + k_2b + k_3b)t}] \end{aligned}$$

Substituting these expressions in the equation for $\mathrm{d}z/\mathrm{d}t$, we get an expression to integrate which contains an exponential to an exponential. Expanding one exponential by a series and integrating, we finally obtain

$$z = ae^{+(k_3a/m)e^{-mt}}\Big[(1 - e^{-mt}) - \frac{k_3a}{m}(1 - e^{-2mt}) + \frac{k_3^2a^2}{2m^2}(1 - e^{-3mt}) - \frac{k_3^3a^3}{6m^3}(1 - e^{-4mt}) + \dots - \frac{k_1}{m + n}(1 - e^{-(m+n)t}) + \frac{k_3a}{2m + n}\left(1 + \frac{k_1}{m}\right)(1 - e^{-(2m+n)t}) - \frac{k_3^2a^2}{m(3m + n)}\left(1 + \frac{k_1}{2m}\right)(1 - e^{-(3m+n)t}) + \dots\Big]$$

where $m = k_1 + k_3b$ and $n = k_2b$. The specific chemical rate is given by $k_1 + k_3b$. k_2 has been evaluated from the experiment on the exchange of the chlorine on the nitrogen of the chloroamine.

The fraction of chloride ion in solution which is radioactive is given by $[b-(w + z)]/b$. This obviously depends upon the values chosen for k_1 and k_3. If we choose $k_1 = 0.0136$ and $k_3b = 0.0180$ we get curve 4 in Fig. 3 which agrees well with the experimental data. The values of the rate constants chosen above correspond to 43% of the acetylchloroaminobenzene rearranging *intramolecularly* and 57% disappearing through the *chlorine intermediate* path. It is quite likely that changes in the experimental conditions would change not only the actual values of these three rate constants but also the relative amounts going by the two paths.

By calculating, according to the combined mechanisms of the preceding paragraph, $z/(y + z)$ for $t = 30$ minutes we obtain the value, 48.2%. The experimental value of this quantity, taken from Table II, is 40.5%. Considering the inaccuracies of this particular determination we feel that the check is sufficiently close.

In all of this work we must not overlook the fact that we are placing a heavy burden on the single determination of k_2. However, calculations show that a 100% change in the value of this rate constant will not affect our conclusions materially.

Summary

The rearrangement of ordinary acetylchloroaminobenzene has been induced by the action of radioactive hydrochloric acid.

The time rates of change of the percentages of radioactivity in the products have been measured. The rate with which the chlorine on the nitrogen of acetylchloroaminobenzene interchanges with the chloride ion in solution also has been measured.

For these measurements it has been shown that under the conditions of this experiment the rearrangement of acetylchloroaminobenzene does not proceed exclusively either by an intramolecular rearrangement or by a chlorine intermediate.

A combination of these two mechanisms, with 43% of the reaction going by direct rearrangement, and 57% through a chlorine intermediate, will explain all our results.

BERKELEY, CALIF. RECEIVED AUGUST 24, 1936

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, OHIO STATE UNIVERSITY]

Vapor Pressures of Saturated Solutions

BY ALFRED E. HIRSCHLER

Roehl[1] has pointed out the interesting fact that when all the scanty available data on vapor pressures of saturated aqueous salt solutions are plotted as log P against $1/T$, straight lines are obtained which are all parallel to the water curve. He was unable to offer an explanation for this "unexpected" result.

While this fact does seem somewhat surprising at first sight, it is the purpose of this paper to show that a closer scrutiny reveals that this is just what would be expected from the magnitudes of the heat effects involved.

The change in fugacity of water from a continuously saturated solution of a solid solute as the temperature rises is given by the equation[2a]

$$\mathrm{d}\ln f_1/\mathrm{d}T = (H_1^* - \overline{H}_1)/RT^2 + N_2(H_2' - \overline{H}_2)/N_1RT^2 \quad (1)$$

where f_1 is the fugacity of water from the solution, H_1^* the molal heat content of attenuated water vapor, H_2' the molal heat content of the solid salt, $\overline{H}_1$, N_1 and $\overline{H}_2$, N_2 the partial molal heat contents and mole fractions of water and solute, respectively. In this equation and those to follow, constant pressure is assumed. We may choose pure liquid water, and an infinitely dilute

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[1] Roehl, THIS JOURNAL, **58**, 1291 (1936).

(2) (a) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Co., New York, 1923, p. 220; (b) p. 222; (c) p. 201; (d) p. 92; (e) p. 477.

aqueous solution as standard states for solvent and solute, respectively, and represent the corresponding molal heat contents by H_1^0 and H_2^0. We then have

$$\begin{aligned} \mathrm{d}\ln f_1/\mathrm{d}T &= [(H_1^* - H_1^0) - (\overline{H}_1 - H_1^0)]/RT^2 + \\ &\qquad N_2[(H_2' - H_2^0) - (\overline{H}_2 - H_2^0)]/N_1RT^2 \\ &= (\Delta H_\mathrm{i} - \overline{L}_1)/RT^2 + N_2(L_2' - \overline{L}_2)/N_1RT^2 \end{aligned}$$

where ΔH_i is the molal heat of vaporization of water into a vacuum (the so-called ideal heat of vaporization), and $\overline{L}_1$, $\overline{L}_2$ and L_2' are the relative heat contents of the substances involved. Rearranging slightly

$$\begin{aligned} \mathrm{d}\ln f_1/\mathrm{d}T &= \Delta H_\mathrm{i}/RT^2 - (N_1\overline{L}_1 + N_2\overline{L}_2 - N_2L_2')/N_1RT^2 \\ &= \Delta H_\mathrm{i}/RT^2 - (L - N_2L_2')/N_1RT^2 \qquad (2) \end{aligned}$$

where L is the relative heat content of one mole of the solution.

Now, $L - N_2L_2'$ is the total or integral heat of solution involved in the formation of one mole of the saturated solution. The mole fraction is numerically equal to the number of moles of each substance taken. Using sodium chloride as an example, we may write

$$N_2\ \mathrm{NaCl(s)} + N_1\mathrm{H_2O(l)} = 1 \text{ mole saturated solution}$$

The integral heat of solution is the value of $\Delta H_\mathrm{s} = \Delta L$ for this process, where the symbol ΔH_s represents the heat absorbed in the formation of one mole of the saturated solution from its components.

$$\Delta H_\mathrm{s} = \Delta L = L - N_2L' - N_1L_1 = L - N_2L$$

since L_1 for the liquid water is zero by choice of standard state.

Hence

$$\mathrm{d}\ln f_1/\mathrm{d}T = (\Delta H_\mathrm{i} - \Delta H_\mathrm{s}/N_1)/RT^2 \qquad (3)$$

The corresponding equation for pure water is[2c]

$$\mathrm{d}\ln f_1/\mathrm{d}T = \Delta H_\mathrm{i}/RT^2 \qquad (4)$$

These equations are exact. For practical purposes they may be modified slightly. Assuming water vapor to be a perfect gas, we can replace the fugacity by the vapor pressure, and the latter by the total pressure P if the solute is not appreciably volatile. At the same time, to be consistent, we may replace the ideal heat of vaporization by that ordinarily determined.[3] Then

$$\mathrm{d}\ln P/\mathrm{d}T = (\Delta H - \Delta H_\mathrm{s}/N_1)/RT^2 \qquad (5)$$
$$\mathrm{d}\ln P/\mathrm{d}T = \Delta H/RT^2 \qquad (6)$$

If we plot log P against $1/T$ for equations (5) and (6), the plot in each case should be a straight line of slope $-(\Delta H - \Delta H_\mathrm{s}/N_1)/2.303R$ in the case of equation (5) and of slope $-\Delta H/2.303R$ for equation (6).

It is now obvious that if the term $\Delta H_\mathrm{s}/N_1$ is small compared to ΔH, the vapor pressure curves of saturated solution and pure solvent will be nearly parallel, the more nearly so the smaller the integral heat of solution. For a solution of a non-volatile solid which forms a perfect solution the two curves should be exactly parallel, as the heat of solution is then zero.[2b]

For most aqueous salt solutions, N_1 is not far from unity, so that the magnitude of ΔH_s practically determines the size of the correction factor, the solubility having small effect. Further, the heat effect in forming one mole of solution must always involve less than 18 g. of water. Since most heats of solution, expressed in terms of 1000 g. of water, are much smaller than the heat of vaporization of water, it can be seen that $\Delta H_\mathrm{s}/N_1$ usually will be quite small compared to ΔH.

This conclusion may be illustrated by a specific example. The necessary heat quantities for sodium chloride, one of the cases cited by Roehl, have been determined.[2d] The saturated solution is 6.12 m at 25° $\overline{L}_1 = 11.5$ cal., $\overline{L}_2 = -702$ cal., $L' = -1019$ cal., $N_1 = 0.9007$ and $N_2 = 0.0993$.

$$\Delta H_\mathrm{s} = N_1\overline{L}_1 + N_2\overline{L}_2 - N_2L' = 42.6 \text{ cal.}$$
$$\Delta H_\mathrm{s}/N_1 = 47.3 \text{ cal.}$$

We may take the molal heat of vaporization of water at 25° as 10,450 cal.[2e] The difference in slope of the vapor pressure curves for pure water and for saturated solution at 25° should thus only differ by 47.3/10,450, or 0.45%, which is less than the usual experimental error.

In the foregoing discussion it has been assumed that ΔH and ΔH_s are independent of temperature. This is only true as a first approximation. ΔH at 100° is 9730 cal.[2e] While exact data on ΔH_s are lacking, it is known that in general solutions become more ideal as the temperature is raised, so that we would expect ΔH_s to decrease also. The percentage deviation of the slopes of the vapor pressure curves might well remain sensibly constant up to the boiling point of the solution.

Sodium chloride may be taken as typical of a strong electrolyte in aqueous solution. The heats of solution of many electrolytes will be found to be of the same order of magnitude. However, a heat of solution eleven times that of sodium chloride will give rise to a difference in slope of only 5%. We may thus state as a working rule that vapor pressures of saturated aqueous salt solutions plotted as log P *vs.* $1/T$ will be parallel

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(3) Since pressure has such a small effect on vapor pressures, we may apply the equation to a liquid under a variable vapor pressure.

to the curve for pure water. In the absence of data a determination of the vapor pressure of the saturated solution at any one temperature will enable the entire curve to be drawn with a good degree of approximation.

It may be remarked that equations (5) and (6) apply equally well to the case of non-aqueous solutions, with the same assumptions, when the corresponding heat quantities are used. We may again predict a fairly close parallelism between the log P–$1/T$ curves for pure solvent and saturated solution. For a given value of ΔH_s, we would expect the deviation in slope for a non-aqueous solution to be much greater than for an aqueous solution. The heat of vaporization of water is abnormally high, and the solubility of electrolytes (or other solutes) expressed in terms of mole fractions are lower in water than in most other liquids. Consequently, for non-aqueous solutions, $\Delta H_s/N_1$ would be larger, and at the same time ΔH smaller, than for water. On the other hand, it must be pointed out that deviations of solutions from ideality are as a rule much less in other liquids than in water, particularly in the case of organic liquids, where many approximately ideal solutions are known. Therefore, for a great many solutions of organic substances, ΔH_s will be very small or zero, and for them the slopes of the vapor pressure curves will be sensibly parallel.

Finally, the assumptions under which equation (1) was derived make it possible to apply it to the case where a liquid is the saturating phase, provided only that its composition does not change with temperature. Owing to the phenomenon of mutual solubility, this will not ordinarily be true. Nevertheless, if the change in composition is not great, we may expect an approximate parallelism between the log P–$1/T$ curves if the "solute" is non-volatile; and between the log p_1–$1/T$ curves for the instance of an appreciably volatile solute.

Summary

1. An explanation is offered for the parallelism of the log P–$1/T$ curves for some saturated aqueous solutions and pure water.

2. An equation is developed from which it is predicted that this phenomenon will be true in general for saturated solutions, both aqueous and non-aqueous.

3. It is suggested that in the absence of data, a knowledge of the vapor pressure of a saturated solution at one temperature will make it possible to obtain the entire curve to a good degree of approximation.

BLUFFTON, OHIO RECEIVED AUGUST 31, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF MERCK & CO., INC.]

The Acetyl Derivatives of Gluconic and Xylonic Acids

BY RANDOLPH T. MAJOR AND ELMER W. COOK

The only record in the literature of an acetylated sugar acid is that described by Upson and Bartz. These investigators prepared 2,3,4,6-tetraacetyl-*d*-gluconic acid monohydrate by the acetylation of δ-*d*-gluconolactone.[1] This reaction has been repeated in this Laboratory. Tetraacetyl-*d*-gluconic acid monohydrate with practically the same melting point reported by the previous workers was obtained but the optical activity found was different. Since the previous investigators did not report the solvent used for the measurement of the optical activity it seems probable that a different solvent was used in this Laboratory than the one used by Upson and Bartz. Tetraacetyl-*d*-gluconic acid monohydrate was also prepared by the oxidation of tetraacetyl-*d*-glucose.

Pentaacetyl-*d*-gluconic acid has been prepared by two different processes. The first was by the oxidation of aldehydo-*d*-glucose pentaacetate.[2] In the course of attempts to improve the methods of obtaining aldehydo-*d*-glucose pentaacetate, it was found that *d*-glucose tetraacetate gave the ring form of tetraacetyl-*d*-glucose semicarbazone with semicarbazide. This had been prepared previously by Wolfrom, Georges and Soltzberg by acetylation of *d*-glucose semicarbazone.[2b]

The second method of preparing pentaacetyl-*d*-gluconic acid was by further acetylation of

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[1] Upson and Bartz, THIS JOURNAL, **53**, 4226 (1931).

[2] (a) Wolfrom, *ibid.*, **51**, 2190 (1929); (b) Wolfrom, Georges and Soltzberg, *ibid.*, **56**, 1795 (1934).

tetraacetyl-*d*-gluconic acid. All attempts to acetylate *d*-gluconic acid directly by means of acetic anhydride with either zinc chloride or pyridine gave a gummy mixture.

Ethyl pentaacetyl-*d*-gluconate was prepared by esterification of the corresponding acid. This ester had been prepared previously by Volpert by acetylation of ethyl *d*-gluconate.[3] Pentaacetyl-*d*-gluconic phenylhydrazide was synthesized by acetylating gluconic phenylhydrazide.

The tetraacetylxylonic acids have been synthesized by the oxidation of the corresponding aldehydoxylose tetraacetates. Aldehydo-*d*-xylose tetraacetate was prepared first by Wolfrom, Newlin and Stahly.[4] A more satisfactory method of obtaining this compound, as well as its levo and racemic isomers, was found to be by acetylation of xylose triacetate semicarbazone followed by treatment with nitrous acid[2b] (p. 1794). In the acetylation of xylose semicarbazone the principal product obtained was a xylose semicarbazone tetraacetate with a ring structure.

Experimental

2,3,4,6-Tetraacetylgluconic Acid Monohydrate

Acetylation of δ-Gluconolactone.—Fused zinc chloride (20 g.) was dissolved in 250 cc. of acetic anhydride and the solution cooled to 0°. δ-Gluconolactone (50 g.) was added with stirring and the mixture kept at 0° for thirty minutes. Thereafter the mixture was allowed to come to room temperature. With occasional shaking all of the lactone soon dissolved. After standing for twenty-four hours the solution was poured into 1000 cc. of ice water. The mixture was stirred for one and one-half hours when tetraacetylgluconic acid monohydrate separated; yield 80%; m. p. 114–115°.[5]

Oxidation of Tetraacetylglucose.—Tetraacetylglucose[6] (5 g.) was dissolved in 125 cc. of hot water in a flask and the solution quickly cooled to room temperature. Potassium bicarbonate (4.4 g.) was added and allowed to dissolve; this was followed by the addition of 1.5 g. of bromine. The flask was stoppered and shaken, the stopper being removed occasionally to relieve the pressure from the carbon dioxide. As soon as the bromine had reacted, additional bromine (0.9 g.) was introduced to complete the reaction. The oxidation was complete in about forty minutes. The solution was cooled to 0° and 23 cc. of 1.93 normal hydrochloric acid was added. Upon standing tetraacetylgluconic acid monohydrate separated; yield 0.7 g. An additional quantity was recovered from the mother liquors by extraction with chloroform; m. p. 114–115°; $[\alpha]^{20}_D$ −5° (alcohol; *c*, 2).

Anal. Calcd. for $C_{14}H_{22}O_{12}$: C, 43.96; H, 5.80. Found; C, 44.10; H, 5.97.

Pentaacetylgluconic Acid

***d*-Glucose Semicarbazone Tetraacetate.**—Glucose tetraacetate (0.5 g.) was dissolved in 5 cc. of warm water and the solution cooled quickly to room temperature. Semicarbazide hydrochloride (0.16 g. or 1 mol) and potassium acetate (0.22 g. or 1.6 mol) were added and the mixture shaken until dissolved. Soon glucose semicarbazone tetraacetate separated as an oil which on standing for two to three days crystallized. The product was recrystallized from water. Thus crystallized the hydrated compound sintered at 118–120° and melted around 163°. When dried at 110° the melting point became 171°; $[\alpha]^{20}_D$ −53° (alcohol; *c*, 2); $[\alpha]^{20}_D$ −6.5° (alcohol-free chloroform, *c*, 2).[7]

Anal. Calcd. for $C_{15}H_{23}O_{10}N_3$: C, 44.45; H, 5.72; N, 10.37. Found: C, 44.63; H, 5.98; N, 10.30.

Oxidation of Pentaacetylaldehydoglucose.—Pentaacetylaldehydo-*d*-glucose was oxidized with bromine by the same method previously described for the oxidation of tetraacetyl-*d*-glucose. The pentaacetylgluconic acid monohydrate obtained was recrystallized from water; m. p. 72–73°; $[\alpha]^{20}_D$ +7.5° (alcohol-free chloroform; *c*, 2); yield 64%.

Anal. Calcd. for $C_{16}H_{24}O_{13}$: C, 45.26; H, 5.69. Found: C, 45.42; H, 5.80. An acetyl determination showed five acetyl groups.

Acetylation of Tetraacetylgluconic Acid.—Tetraacetyl-*d*-gluconic acid monohydrate (50 g.) was dissolved in 188 cc. of acetic anhydride (ice-bath) containing 18 g. of zinc chloride in solution. After standing in the ice-bath for thirty minutes the solution was allowed to come to room temperature and remain at this temperature for twenty-four hours. The solution was then poured into 1000 cc. of ice water and thoroughly stirred. Pentaacetylgluconic acid crystallized after about one hour and an additional amount was recovered from the mother liquor by extraction with chloroform. The crude product thus obtained from the acetylation melted at 93–95° but on standing the melting point changed, finally becoming as low as 55°. By recrystallizing from water the monohydrate of melting point 72–73° was obtained. A mixed melting point with a specimen obtained as described in the preceding paragraph showed no depression; yield 90%.

Anhydrous Pentaacetylgluconic Acid.—Pentaacetylgluconic acid monohydrate (50 g.) recrystallized from absolute alcohol was dissolved in 500 cc. of hot toluene. About 100 cc. of the toluene was distilled on an oil-bath. Upon cooling anhydrous pentaacetylgluconic acid separated. The product was filtered and washed successively with toluene and petroleum ether; m. p. 110–111°; $[\alpha]^{20}_D$ +11.5° (alcohol-free chloroform; *c*, 2). Upon standing in the air for several days the anhydrous acid did not take up water of crystallization as its melting point remained unchanged.

Anal. Calcd. for $C_{16}H_{22}O_{12}$: C, 47.27; H, 5.46. Found: C, 47.30; H, 5.53.

Ethyl Pentaacetylgluconate.—Pentaacetyl-*d*-gluconic acid (10 g.) was dissolved in 30 cc. of absolute alcohol con-

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[3] Volpert, *Ber.*, **19**, 2622 (1886).

[4] Wolfrom, Newlin and Stahly, THIS JOURNAL, **53**, 4382 (1931).

[5] Upson and Bartz[1] give 114–117° as the melting point of tetraacetylgluconic acid monohydrate.

[6] Fischer, *Ber.*, **45**, 914 (1912).

[7] Wolfrom, Georges and Soltzberg[2b] give 171–172° as the melting point and $[\alpha]^{25}_D$ −9° (chloroform, *c*, 3.8) as the optical rotation of *d*-glucose semicarbazone tetraacetate.

taining 2% hydrogen chloride and the solution warmed at 60° for four minutes. Upon cooling and stirring a solid crystallized. It was filtered and washed with a little alcohol; m. p. 103–104°; $[\alpha]^{20}D$ +20.5° (alcohol-free chloroform, *c*, 2).[8] Ethyl pentaacetylgluconate was also prepared by acetylating ethyl gluconate in the usual manner with either pyridine or fused zinc chloride. For analysis a sample fused and dried at 120° was allowed to cool and solidify *in vacuo* over sulfuric acid.

Anal. Calcd. for $C_{12}H_{26}O_{12}$: C, 49.75; H, 6.04. Found: C, 49.84; H, 6.19.

Pentaacetylgluconicphenylhydrazide.—Gluconicphenylhydrazide (10 g.) was added to 50 cc. of acetic anhydride containing 4 g. of zinc chloride (fused) in solution. The mixture was kept cold during the first thirty minutes and then was allowed to stand for twenty-four hours at room temperature. A gum formed when the acetylation mixture was poured into ice water. The mixture was extracted with chloroform and the chloroform extract washed with sodium bicarbonate in ice water and finally with water. The extract was evaporated *in vacuo*, when the gummy residue slowly started to crystallize. It was recrystallized from alcohol by the addition of ether accompanied by cooling; yield of pentaacetylgluconic phenylhydrazide, 90%; m. p. 152–154°; $[\alpha]^{20}D$ +28° (alcohol, *c*, 2).

Anal. Calcd. for $C_{22}H_{28}O_{11}N_2$: C, 53.20; H, 5.69; N, 5.64. Found: C, 53.14; H, 5.65; N, 5.65.

***d*-Xylose Semicarbazone Tetraacetate.**—Finely powdered *d*-xylose semicarbazone (26 g.) was stirred into 180 cc. of pyridine and 120 cc. of acetic anhydride at 60–70° for six hours. At the end of this time practically all the xylose semicarbazone had dissolved. After the solution had stood at room temperature for one to two days 10 g. of crystalline material separated. The acetylation mixture was poured into ice water and after standing for one hour was extracted with chloroform. The extract was washed successively with cold dilute sulfuric acid, sodium bicarbonate and ice water. After it had been dried over calcium chloride the extract was evaporated *in vacuo* and the residue crystallized from absolute alcohol. The product (3 g.) was the same as that separated from the acetylation mixture. It was recrystallized from absolute alcohol; m. p. 232–233°; $[\alpha]^{20}D$ +21° (methanol, *c*, 1). Treatment in aqueous solution with nitrous acid did not produce aldehydo-*d*-xylose tetraacetate.

Anal. Calcd. for $C_{14}H_{21}O_9N_3$: C, 44.78; H, 5.64; N, 11.20. Found: C, 45.03; H, 5.70; N, 11.37.

However, the mother liquors from the tetraacetate, m. p. 232–233°, gave a sirup which on treatment with dilute nitrous acid yielded aldehydo-*d*-xylose tetraacetate.

Aldehydo-*l*-xylose Tetraacetate.—*l*-Xylose triacetate (51 g.)[9] was added to a warm alcoholic solution containing a 10% excess of semicarbazide. After warming for fifteen to twenty minutes the solution was evaporated *in vacuo* to a gum. The gum was dissolved in 86 cc. of pyridine and treated with 57 cc. of acetic anhydride accompanied by cooling. After the solution had stood for twenty-four hours at room temperature it was poured into ice water. The mixture was allowed to stand for an hour and then extracted with chloroform. The extract was washed successively with cold dilute sulfuric acid, sodium bicarbonate and water. After it had been dried over calcium chloride the extract was evaporated *in vacuo* to a gum. The gum was refluxed for twenty minutes, in a solution of 6.5 g. of oxalic acid in 250 cc. of methanol. The gum which was obtained by evaporation *in vacuo* was dissolved in 800 cc. of water; 75 g. of sodium nitrite in 200 cc. of water was added. Accompanied by slow stirring and cooling to 15–20°, 180 cc. of 6 normal hydrochloric acid was added gradually. This was followed by portionwise addition of 60 g. of sodium nitrite and gradual addition of 120 cc. of 6 normal hydrochloric acid. Again 60 g. of sodium nitrite was added and 120 cc. of 6 normal hydrochloric acid. Finally 60 g. of sodium nitrite was added and the solution stirred vigorously with norite. The mixture was filtered and the filtrate extracted with chloroform. After the extract had been dried over calcium chloride it was evaporated *in vacuo*. Aldehydo-*l*-xylose tetraacetate soon crystallized out of the resulting gum and with the addition of dry ether was filtered. It was recrystallized from dry ether; yield 33%; m. p. 90–91°; $[\alpha]^{20}D$ +22.5° (alcohol-free chloroform, *c*, 2).[10] Aldehydo-*d,l*-xylose tetraacetate made by mixing equal quantities of the *d* and *l* forms melted at 85–86°.

Anal. Calcd. for $C_{13}H_{18}O_9$: C, 49.03; H, 5.70. Found: C, 49.09; H, 5.53.

Tetraacetylxylonic Acid.—Aldehydoxylose tetraacetate (18.7 g.) was dissolved in 400 cc. of warm water at 50° in a flask and the solution quickly cooled to room temperature. Bromine (10.5 g.) was added followed by 9.5 g. of calcium carbonate. The mixture was stirred occasionally and after two hours the oxidation was nearly complete. The mixture was extracted with chloroform to remove any unreacted aldehydoxylose tetraacetate. It was then made acid with 104 cc. of 1.9 normal hydrochloric acid and extracted with chloroform. The extract was dried over calcium chloride and evaporated *in vacuo* to a gum. Petroleum ether was added and upon stirring tetraacetylxylonic acid crystallized. It was recrystallized from benzene; yield 90%.

Tetraacetyl-*d*-xylonic acid melted at 86–88°; $[\alpha]^{20}D$ +5° (alcohol, *c*, 2); $[\alpha]^{20}D$ −2° (alcohol-free chloroform, *c*, 2).

Anal. Calcd. for $C_{13}H_{18}O_{10}$: C, 46.69; H, 5.43. Found: C, 46.46; H, 5.52.

Tetraacetyl-*l*-xylonic acid melted at 86–88°; $[\alpha]^{20}D$ −4.5° (alcohol, *c*, 2).

Tetraacetyl-*d,l*-xylonic acid melted at 134–135°; $[\alpha]^{20}D$ 0° (alcohol, *c*, 2).

Anal. Calcd. for $C_{13}H_{18}O_{10}$: C, 46.69; H, 5.43. Found: C, 46.77; H, 5.39.

A mixture of equal quantities of tetraacetyl-*d*-xylonic acid and tetraacetyl-*l*-xylonic acid crystallized out of toluene also melted at 134–135°.

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[8] Volpert[3] gave 103.5° as the melting point of ethyl pentaacetylgluconate.

[9] Prepared by the method described by Hudson and Dale, THIS JOURNAL, **40**, 999 (1918), for the preparation of *d*-xylose triacetate.

[10] Wolfrom, Newlin and Stahly[4] give 87–89° as the melting point and $[\alpha]^{26}D$ −15.9° in chloroform as the optical rotation of aldehydo-*d*-xylose tetraacetate.

Summary

1. Tetraacetyl-*d*-gluconic acid has been prepared by the oxidation of tetraacetyl-*d*-glucose with bromine.

2. Pentaacetyl-*d*-gluconic acid was obtained by the oxidation of aldehydo-*d*-glucose pentaacetate and by acetylation of tetraacetyl-*d*-gluconic acid.

3. Ethyl pentaacetyl-*d*-gluconate and pentaacetyl-*d*-gluconic phenylhydrazide were prepared.

4. The ring form of *d*-xylose semicarbazone tetraacetate was isolated.

5. Aldehydoxylose tetraacetates have been prepared by the treatment of the corresponding semicarbazones with nitrous acid.

6. Tetraacetylxylonic acids have been obtained by the oxidation of aldehydoxylose tetraacetates.

RAHWAY, N. J. RECEIVED SEPTEMBER 17, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF MERCK & CO., INC.]

Preparation and Properties of Pentaacetyl-2-keto-*d*-glucoheptonic Acid

BY RANDOLPH T. MAJOR AND ELMER W. COOK

The 2-keto-sugar acids have acquired in recent years considerable interest due to the fact that the enol forms of these acids have been shown to be vitamin C and its homologs.[1]

A new method of preparing the acetyl derivatives of these acids has become possible since the recent synthesis of the fully acetylated sugar acids.[2]

The acetyl sugar acid was converted into its acid chloride with phosphorus pentachloride; it is noteworthy that thionyl chloride was not a satisfactory agent for the purpose. The chloride was converted into the corresponding cyanide by means of silver cyanide. This was hydrolyzed in turn to the corresponding acid. This acid could be esterified readily.

The series of reactions described above has been carried through to completion starting with pentaacetyl-*d*-gluconic acid and through, except for the last step, with tetraacetyl-*d,l*-xylonic acid.

Attempts are being made to hydrolyze the acetyl groups and enolize the keto group of pentaacetyl-2-ketoglucoheptonic acid and its ester to give a homolog of vitamin C.

Experimental

Acetylated Sugar Acid Chloride.—The dry fully acetylated sugar acid was added with cooling to a suspension of one molecular equivalent of phosphorus pentachloride in ten times its weight of dry ether. The reaction was soon complete as shown by disappearance of the phosphorus pentachloride.

Pentaacetyl-*d*-gluconyl Chloride.—After the solution had stood at room temperature for two or three hours the ether was evaporated *in vacuo*. Dry xylene was then added. This and the phosphorus oxychloride formed in the reaction were removed by evaporation at 45 to 50° *in vacuo*. The addition of xylene followed by evaporation *in vacuo* was repeated twice. The residual gum was dissolved in dry ether. Upon evaporation in a slight vacuum beautiful white crystals separated; m. p. 68–70°; yield, 88%; $[\alpha]^{20}_D$ +2° (alcohol-free chloroform, *c*, 2).

Anal. Calcd. for $C_{16}H_{21}O_{11}Cl$: C, 45.22; H, 4.99; Cl, 8.35. Found: C, 45.60; H, 4.90; Cl, 8.27.

With water the acid chloride gave pentaacetyl-*d*-gluconic acid monohydrate, m. p. 72–73°.[2]

Tetraacetyl-*d,l*-xylonyl Chloride.—White crystals appeared soon after solution of the phosphorus pentachloride. The precipitate was recrystallized from dry ether; m. p. 90–92°; yield, 71%; $[\alpha]^{20}_D$ 0° (alcohol-free chloroform, *c*, 2).

Anal. Calcd. for $C_{13}H_{17}O_9Cl$: C, 44.26; H, 4.86; Cl, 10.08. Found: C, 44.25, 44.33; H, 4.80, 5.03; Cl, 10.18, 10.32.

Ethyl Ester of Acetylated Sugar Acids.—When a solution of an acetylated sugar acid chloride in absolute alcohol was evaporated *in vacuo* a crystalline residue was left which was washed with cold water and recrystallized from absolute alcohol.

Ethyl pentaacetyl-*d*-gluconate melted at 103–104°.[3]

Ethyl tetraacetyl-*d,l*-xylonate melted at 70–72°; $[\alpha]^{20}_D$ 0° (alcohol, *c*, 0.06).

Anal. Calcd. for $C_{15}H_{22}O_{10}$: C, 49.70; H, 6.12. Found: C, 49.53; H, 6.13.

Pentaacetyl-*d*-gluconamide.—Dry ammonia was bubbled through a solution of pentaacetyl-*d*-gluconic acid chloride in dry ether. The white precipitate which formed was washed with water to remove ammonium chloride. The pentaacetyl-*d*-gluconamide which remained melted at 183–184°.[4]

Tetraacetyl-*d,l*-xylonamide.—This compound was prepared in the same way as pentaacetyl-*d*-gluconamide except that it did not precipitate from the ether with the

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(1) Hirst, *Chemistry and Industry*, 221 (1933); Haworth, *ibid.*, 482 (1933).

(2) Major and Cook, THIS JOURNAL, **58**, 2474 (1936).

(3) Volpert, *Ber.*, **19**, 2622 (1886), gives 103.5° as the melting point of ethyl pentaacetyl-*d*-gluconate.

(4) Zemplén and Kiss, *Ber.*, **60**, 170 (1927), give 183.5–184° as the melting point of pentaacetyl-*d*-gluconamide.

ammonium chloride but could be recovered from the ether filtrate by evaporation. It was recrystallized from benzene; m. p. 130–132°; $[\alpha]^{20}\text{D}$ 0° (alcohol-free chloroform, *c*, 0.05).

Anal. Calcd. for $C_{13}H_{19}O_9N$: C, 46.83; H, 5.75; N, 4.20. Found: C, 46.82; H, 5.76; N, 4.11.

Pentaacetyl - 2 - keto - *d* - glucoheptonitrile.—Pentaacetylgluconyl chloride (10 g.) was heated for one hour with 4.7 g. of silver cyanide in a closed tube at 120 to 125°. The fused contents were shaken frequently to ensure good contact of the acid chloride with the silver cyanide. After cooling the gummy material was extracted thoroughly with anhydrous ether and filtered from the silver salts. Petroleum ether was added carefully to precipitate a part of the product as a dark colored sirup, thereby removing most of the color. Then an excess of petroleum ether was added with cooling. A gum was precipitated along with some crystalline product. The supernatant liquor was poured off and on evaporation yielded crystalline pentaacetyl-2-keto-*d*-glucoheptonitrile. The gum was dissolved in a small quantity of absolute alcohol and upon standing in the ice box for twenty-four hours yielded a quantity of pentaacetyl-2-keto-glucoheptonitrile. The product was purified by recrystallizing it from absolute alcohol; yield 34%; m. p. 116°; $[\alpha]^{20}\text{D}$ +7° (alcohol-free chloroform, *c*, 2). When this compound was heated in water with either dilute acid or base, hydrogen cyanide was evolved.

Anal. Calcd. for $C_{17}H_{21}O_{11}N$: C, 49.14; H, 5.10; N, 3.37. Found: C, 49.32; H, 5.24; N, 3.16.

Tetraacetyl-2-keto-*d,l*-gulononitrile.—This nitrile was prepared from tetraacetyl-*d,l*-xylonyl chloride in the same way as pentaacetyl-2-keto-*d*-glucoheptonitrile except that the filtrate obtained after the addition of sufficient petroleum ether to the ether extract to produce slight turbidity was treated with another larger portion of petroleum ether which precipitated a gum. Trituration of this gum with absolute alcohol yielded a solid precipitate. It was recrystallized from alcohol; m. p. 125–126°.

Anal. Calcd. for $C_{14}H_{17}O_9N$: N, 4.08. Found: N, 3.83.

Pentaacetyl-2-keto-*d*-glucoheptonic Acid.—Pentaacetyl-2-keto-*d*-glucoheptonitrile (7.55 g.) was dissolved in 20 cc. of pure dioxane. To this 13.1 cc. of 1.39 normal hydrogen chloride in dioxane was added. The solution was cooled and 0.33 cc. of water added. After this had stood in the ice box for twenty-four hours an additional 0.33 cc. of water was added. The solution was allowed to stand for another twenty-four hours, by which time ammonium chloride had precipitated. Ether was added and the ammonium chloride filtered. The filtrate was evaporated *in vacuo* to a gum. The gum was dissolved in ether and evaporation *in vacuo* repeated. The gum that remained crystallized upon scratching; m. p. 136–138°. After recrystallization from water the product melted at 160–161°; $[\alpha]^{20}\text{D}$ 0° (alcohol, *c*, 2); yield 40%. A solution of the keto acid in water was acid to congo red paper. It was extremely soluble in alcohol, ether, chloroform and acetone.

Anal. Calcd. for $C_{17}H_{22}O_{13}$: C, 46.98; H, 5.11. Found: C, 46.98; H, 5.05.

Ethyl Pentaacetyl-2-keto-*d*-glucoheptonate.—A solution of 1 g. of pentaacetyl-2-keto-*d*-glucoheptonic acid in 10 cc. of absolute alcohol containing 2% hydrogen chloride was warmed at 55–60° for five minutes. The solution was cooled quickly to nearly room temperature and then allowed to crystallize; yield, 60%; m. p. 97–98°; $[\alpha]^{20}\text{D}$ 0° (alcohol, *c*, 2).

Anal. Calcd. for $C_{19}H_{26}O_{13}$: C, 49.33; H, 5.67. Found: C, 49.19, 49.38; H, 5.91, 5.67.

Methyl Tetraacetyl-2-keto-*d*-gluconate.—One gram of methyl 2-keto-*d*-gluconate[5] was added to 5 cc. of acetic anhydride containing 0.4 g. of zinc chloride at 0°. As soon as solution was complete (about thirty minutes) the mixture was allowed to come to room temperature and remain there for twenty-four hours. It was then poured into 25 cc. of ice water; a white solid separated which was recrystallized from absolute alcohol; m. p. 168–169°; yield, 61%; $[\alpha]^{20}\text{D}$ −133° (alcohol-free chloroform, *c*, 2).[6]

Anal. Calcd. for $C_{15}H_{20}O_{11}$: C, 47.90; H, 5.36. Found: C, 47.79; H, 5.30.

Summary

1. Pentaacetyl-*d*-gluconyl chloride and tetraacetyl-*d,l*-xylonyl chloride have been prepared from the corresponding acids.

2. Ethyl pentaacetyl-*d*-gluconate and ethyl tetraacetyl-*d,l*-xylonate have been prepared from the corresponding acid chlorides.

3. Pentaacetyl-*d*-gluconamide and tetraacetyl-*d,l*-xylonamide have been prepared from the corresponding acid chlorides.

4. Pentaacetyl - 2 - keto - *d* - glucoheptonitrile and tetraacetyl-2-keto-*d,l*-gulononitrile have been prepared from the corresponding chlorides.

5. Pentaacetyl-2-keto-*d*-glucoheptonic acid has been synthesized by hydrolysis of the corresponding nitrile.

6. Ethyl pentaacetyl-2-keto-*d*-glucoheptonate has been prepared by esterification of the corresponding acid.

7. Methyl tetraacetyl-2-keto-*d*-gluconate has been prepared by acetylation of methyl 2-keto-*d*-gluconate.

RAHWAY, N. J. RECEIVED SEPTEMBER 17, 1936

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(5) Ohle and Wolter, *Ber.*, **63B**, 843 (1930).

(6) Ohle and Wolter[5] reported that the methyl tetraacetyl-2-keto-*d*-gluconate they obtained was an oil; $[\alpha]^{18}\text{D}$ −38.8° (chloroform, *c*, 2.552). Since this was formed in pyridine it is possible that this was an acetyl derivative of an enol form of methyl 2-keto-*d*-gluconate.

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, LOYOLA UNIVERSITY SCHOOL OF MEDICINE]

New Derivatives of *l*-Allonic and *l*-Altronic Acid. I[1]

BY FRED L. HUMOLLER, W. F. MCMANUS AND W. C. AUSTIN[2]

In a previous communication[3] from this Laboratory we announced the preparation of a crystalline lactone of *l*-allonic acid as well as the calcium salt of *l*-altronic acid and their conversion into crystalline *l*-allose and *l*-altrose, respectively. At that time lack of material prevented us from making a more detailed study of *l*-allonic and *l*-altronic acids and their derivatives. The present study was undertaken in order to determine in greater detail the physical constants of the two acids and their derivatives in general, and the rotational behavior of the *l*-allonolactone, previously reported, in particular.

The allonic and altronic acids used in this study were prepared from *l*-ribose by methods already published.[3,4] The *l*-allonic acid can be isolated in the form of the crystalline lactone previously reported, if the aqueous solution of the acid is evaporated and the resulting sirup heated on the steam-bath for several hours. This lactone has an initial specific rotation of +7.2°, which becomes constant in twenty-four days at +3.6°. The melting point of this compound is at 129–130°.

When, however, a freshly prepared aqueous solution of the free acid is concentrated rapidly under reduced pressure and the resulting sirup taken up in absolute ethanol without being exposed to a temperature higher than 50°, a crystalline substance is obtained having a composition corresponding to the formula $C_6H_{10}O_6$. It is therefore a lactone of *l*-allonic acid. In contradistinction to the previously reported lactone it shows an initial specific rotation of −54.8°. A further distinction from the known lactone is its behavior toward dilute solutions of bases; for, whereas the former cannot be titrated in ice-water solution using phenolphthalein as indicator, the new lactone can be titrated practically quantitatively under these conditions. When freshly dissolved in water both lactones are neutral to litmus. Rehorst[5] has found a similar differential instability toward dilute solutions of bases among the δ- and γ-lactones that he studied.

Further evidence that this new lactone belongs to the δ-series and that the lactone previously reported belongs to the γ-series is furnished by the rate of mutarotation of these two substances as shown in Fig. 1. The relatively rapid change in rotation of the new lactone as compared with the small and slow change of the previously reported lactone indicates that they belong to the δ- and γ-series of lactones, respectively.[6] Obviously further direct evidence would be highly desirable before definitely ascribing a certain ring structure to these lactones, but the instability of the strongly mutarotating lactone would make direct methylation studies of doubtful value. Therefore until evidence to the contrary is brought forth we shall call the new, strongly mutarotating lactone the δ-lactone of *l*-allonic acid and the previously reported lactone the γ-lactone of *l*-allonic acid.

The ease with which the ring can shift in the case of the δ-lactone is shown by its peculiar behavior during the determination of its melting point. If a sample of this lactone is heated slowly (increasing the temperature about 1° per minute), it melts at 129–130°, that is, at the same temperature at which the γ-lactone melts. If, however, the temperature is raised more rapidly it will melt unsharply at 140–144°. An investigation revealed that slowly heating the δ-lactone to its melting point (130°) was sufficient to change it into the γ-form. This observation explains why we were unable to observe a depression of the melting point of a mixture of the two lactones.

The mutarotation of free *l*-allonic acid is of interest in several respects. Its initial rotation of +11° is less levo-rotatory than that of either of its lactones, hence it follows Hudson's lactone rule as modified for lactones of small rotation.[7] The allonolactones were considered to be the only

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[1] These studies, a portion of which was reported on the program of the meeting of the American Chemical Society in Pittsburgh, Sept. 7, 1936, were in part abstracted from a dissertation submitted by Mr. McManus to the Graduate School of Loyola University in partial fulfilment of the requirements for the degree of Master of Science.

[2] Dr. W. C. Austin, whose untimely death occurred in November, 1935, participated in the initial phases of this problem.

[3] Austin and Humoller, THIS JOURNAL, **56**, 1153 (1934).

[4] Austin and Humoller, *ibid.*, **56**, 1152 (1934).

[5] Rehorst, *Ber.*, **63**, 2279 (1930).

[6] Haworth, "The Constitution of Sugars," E. Arnold & Co., London, 1929, pp. 23–24.

[7] Hudson, "Relation between Rotatory Power and Structure in the Sugar Group," Scientific Papers of the Bureau of Standards, No. 533, Government Printing Office, 1926, p. 288.

doubtful exception among the aldonic acid lactones cited, although Hudson already had predicted at that time that allonic acid would show a rotation in agreement with his theory. The peculiar type of mutarotation of *l*-allonic acid as shown in Fig. 1 strongly indicates that an aqueous solution of the acid changes upon standing in part into the δ-lactone and this in turn changes into the more stable γ-lactone.

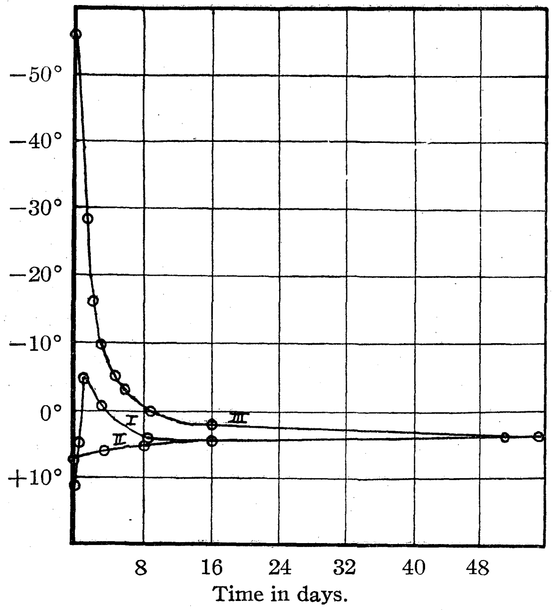

Fig. 1.—The mutarotation of *l*-allonic acid and its lactones: curve I, *l*-allonic acid; curve II, γ-*l*-allonolactone; curve III, δ-*l*-allonolactone.

Attempts to prepare a crystalline lactone of *l*-altronic acid according to the method generally employed to prepare the stable form of lactones were not successful. However, when a freshly prepared aqueous solution of the acid is concentrated rapidly under reduced pressure without exposing the acid to elevated temperature a crystalline substance is obtained. An analysis of the substance for C and H indicates that this compound is not a lactone but the free *l*-altronic acid. This conclusion is confirmed by the finding that this substance is acid to congo red and can be titrated like any organic acid.

Recently Posternak[8] pointed out in a very brief announcement that the allomucic acid prepared by E. Fischer[9] by heating mucic acid in aqueous pyridine is actually a mixture of equal parts of *d*- and *l*-talomucic acid. Posternak did not report, however, the preparation of allomucic acid. Therefore it was thought desirable to prepare allomucic acid from allonolactone and compare it with the substance obtained by the pyridine rearrangement of mucic acid. Allomucic acid prepared by the oxidation of *l*-allonolactone with nitric acid melts at 187.5° with decomposition and charring, and it crystallizes in rectangular prisms, whereas the substance prepared by Fischer's method from mucic acid melts at 166–171° with decomposition but no charring. A mixture of the two substances melts at 173°. Obviously both substances are optically inactive. The findings of Posternak together with our results seem to show that Fischer was mistaken in assuming that in the pyridine rearrangement of mucic acid both of the hydroxyl groups adjacent to the carbonyl groups are inverted. At present work is in progress to prepare derivatives of allomucic acid.

Experimental

Preparation of δ-*l*-Allonolactone.—A concentrated solution of the lactone in hot water was treated with a slight excess of sodium hydroxide. The solution was then chilled in ice water and an amount of sulfuric acid equivalent to that of the base was added. The solution was poured immediately into 10 volumes of absolute ethanol. After filtering off the precipitated sodium sulfate, the filtrate was concentrated rapidly under reduced pressure to a thin sirup. The sirup was taken up in four volumes of absolute ethanol and clarified. The filtrate was again concentrated under reduced pressure. During this second evaporation the lactone usually crystallizes out spontaneously. After crystallization was complete the crystals were filtered off and washed with alcohol and then with ether. The mother liquors yielded further crops on concentration. Recrystallization of the lactone from absolute ethanol did not change its physical constants. These together with analytical data are given in Table I.

Conversion of the δ-Lactone into the γ-Lactone.—A sample of 0.2028 g. of the δ-lactone having a specific rotation $[\alpha]^{20-25}\text{D}$ −46.9° was heated slowly in a small flask to 130°. The lactone melted at this temperature. However, it failed to crystallize on cooling. The material was dissolved in water and the solution made up to 25 cc. After clarification to remove a slight amount of color, it was found that the solution now had a specific rotation of $[\alpha]^{20-25}\text{D}$ +3.7°.

Preparation of the Phenylhydrazide of *l*-Allonic Acid.[10]—The phenylhydrazide of *l*-allonic acid was prepared from the δ-lactone by the usual method. Its specific rotation and melting point are given in Table I. They are identical with those of a sample of the phenylhydrazide prepared from the γ-lactone. A mixture of the two did not show any depression of the melting point.

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[8] Posternak, *Naturwissenschaften*, **23**, 287 (1935).

[9] Fischer, *Ber.*, **24**, 2136 (1891).

[10] The melting point of this compound given by Austin and Humoller[3] was an unfortunate error, and we take this opportunity to correct it here.

TABLE I

ANALYSES AND PHYSICAL CONSTANTS OF NEW SUBSTANCES

Substance	M. p., °C.	$[\alpha]^{20-25}_D$ in water Init.	Final	Formula	Analyses, % Calcd. C	H	Found C	H
δ-*l*-Allonolactone	140–144	−54.8°	+3.66°	$C_6H_{10}O_6$	40.4	5.7	40.9	5.9
l-Altronic acid	110	−8.1°		$C_6H_{12}O_7$	36.7	6.2	37.3	6.5
Allomucic acid	187.5	Inactive		$C_6H_{10}O_8$	34.3	4.8	34.2	5.1
l-Allonic acid phenylhydrazide	142–145	−23.6°						
l-Altronic acid phenylhydrazide	151–152	+18.4°						

Preparation of *l*-Altronic Acid.—A solution of 17 g. of calcium *l*-altronate in 400 cc. of hot water was treated with sufficient oxalic acid to remove the calcium quantitatively. The filtrate from the calcium oxalate was concentrated under reduced pressure to a thin sirup. The sirup was poured into ten volumes of absolute alcohol. A small amount of insoluble material was filtered off. Upon concentration under reduced pressure the filtrate yielded 10 g. of crystalline material by spontaneous crystallization. *l*-Altronic acid was recrystallized from absolute ethanol to constant melting point. The physical constants and the analysis are given in Table I.

Preparation of the Phenylhydrazide of *l*-Altronic Acid.—*l*-Altronic acid readily formed a phenylhydrazide when treated with phenylhydrazine in the usual manner. The substance was recrystallized from hot absolute ethanol to constant melting point of 151–152°. It has a tendency to separate out from a hot alcohol solution in jelly-like masses which upon standing assume crystalline form.

Rearrangement of Mucic Acid in Aqueous Pyridine.—The reaction was carried out in general according to the procedure of Fischer.[9] If the reaction mixture was allowed to come into contact with the metal of the pressure vessel during the heating period extensive destruction took place. If the reaction mixture was kept in a glass vessel during the heating, a yield of about 12% of a substance showing all the properties described by Fischer was obtained. This racemic talomucic acid was recrystallized from hot water for the melting point determination. It is interesting to note that racemic talomucic acid resembles allomucic acid much more in solubility than it does *d*- or *l*-talomucic acid.

Preparation of Allomucic Acid.—A solution of 1 g. of γ-*l*-allonolactone in 50 cc. of nitric acid of sp. gr. 1.15 was heated on the steam-bath. When the evolution of brown fumes of oxides of nitrogen became too vigorous, the reaction was controlled by removing the reaction mixture from the steam-bath and cooling. The solution was evaporated in this manner to about half its volume. It was then diluted to about 50 cc. and concentrated to a few cc. under reduced pressure. This process of diluting and concentrating was repeated once more. During the second concentration allomucic acid began to crystallize in the distilling flask. After crystallization had gone to completion, the crystals were filtered off and washed thoroughly with water. About 0.6 g. of allomucic acid was thus obtained. The acid was recrystallized by dissolving it in hot water, concentrating the solution under reduced pressure and then cooling it for several days. The melting point and analysis of allomucic acid are given in Table I. Allomucic acid is quite insoluble in cold water but is much more soluble in hot water probably due to lactone formation, for after it has been thus dissolved it takes many days before it begins to crystallize again, even after concentrating the solution. For rotational studies 0.3461 g. of allomucic acid was dissolved in 10 cc. of a sodium hydroxide solution. No significant rotation could be observed.

All melting points cited in this paper are uncorrected for stem exposure. The authors wish to express their gratitude to Mr. D. Peterson of the Department of Biochemistry, The University of Chicago, for carrying out the micro carbon and hydrogen determinations cited in this paper.

Summary

1. A new crystalline lactone of *l*-allonic acid has been prepared and some of its physical constants determined. From its behavior toward dilute alkali and from its rate of mutarotation it has been concluded that this substance is the δ-lactone and that the previously prepared lactone is the γ-lactone of *l*-allonic acid.

2. Methods for converting one lactone into the other have been presented.

3. *l*-Altronic acid has been prepared and some of its physical constants recorded.

4. The phenylhydrazides of *l*-allonic and of *l*-altronic acids have been prepared and their melting point and specific rotation recorded. Their rotations show that these two substances follow the phenyl-hydrazide rule of rotation.[7]

5. Allomucic acid has been prepared. From a comparison of its properties with those of the substance obtained by the pyridine rearrangement of mucic acid it has been concluded that the two are not identical.

CHICAGO, ILL. RECEIVED OCTOBER 5, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

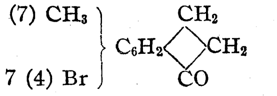
An Improved Method for the Synthetic Preparation of Methylcholanthrene

BY LOUIS F. FIESER AND ARNOLD M. SELIGMAN

Numerous requests for supplies of methylcholanthrene and inquiries concerning the two methods of preparation developed in this Laboratory have caused us for some time to give attention to the problem of producing the hydrocarbon in quantity sufficient to meet the wide-spread demand for material required for various forms of biological experimentation. The preparation from cholic acid[1] affords a fairly simple and rapid method of obtaining a few grams of the carcinogenic hydrocarbon, but the purification of the material obtained in this way is somewhat troublesome, the yield amounts to less than 4 g. from 100 g. of the bile acid, and the process becomes cumbersome when working on a large scale. The synthetic method[2] affords a better yield (11%, over-all) and a more easily purified product, but the process as originally described had the disadvantage of being rather lengthy, involving eight separate steps.

As the synthesis seemed to offer more possibility for improvement than the degradative method, a search was made for a shorter route to the required intermediates. In the initial stages of the original process, *p*-bromotoluene was converted into 4-bromo-7-methylhydrindene through a mixture of hydrindones (I) obtained through the following sequence of reactions

$$p\text{-}CH_3C_6H_4Br \longrightarrow CH_3C_6H_3(Br)CH_2Cl \longrightarrow CH_3C_6H_3(Br)CH_2CH(COOR)_2 \xrightarrow{\text{(2 steps)}} CH_3C_6H_3(Br)CH_2CH_2COOH \longrightarrow$$



$$\left.\begin{array}{r}4\ (7)\ CH_3\\ 7\ (4)\ Br\end{array}\right\} C_6H_2\langle CH_2 - CH_2 - CO\rangle \quad \text{I}$$

As an alternate route to the ketone mixture I we investigated the hydrindone synthesis of Mayer and Müller,[3] but all attempts to cyclize the chloro ketone mixture (II) obtained from *p*-bromotoluene and β-chloropropionyl chloride were unsuccessful. No trace of either of the two previously described[2] (crystalline) methylbromohydrindones (I) was observed and the only substance isolated as a solid is an isomer of these compounds and probably is a vinyl ketone (III).[4]

$$\underset{\text{II}}{CH_3C_6H_3(Br)COCH_2CH_2Cl} \longrightarrow \underset{\text{III}}{CH_3C_6H_3(Br)COCH{=}CH_2}$$

This unfavorable result was rather surprising, for Mayer and Müller report that the corresponding chloro ketone from *p*-chlorotoluene can be cyclized readily. On trying the latter reaction for comparison, the results were so generally satisfactory that it seemed worth while to investigate the use of a chlorohydrindene in place of a bromo compound in the methylcholanthrene synthesis, and eventually a very convenient process was evolved.

The Friedel and Crafts reaction with β-chloropropionyl chloride can be conducted easily with as much as one-half kilogram of *p*-chlorotoluene in one lot and the cyclization of the crude chloro ketone mixture (oil) likewise proceeds well on a large scale. A purified mixture of the hydrindones IV and V was obtained in over-all yield of 61%. Although Mayer and Müller report the isolation of only one isomer (m. p. 128°), two compounds actually are formed and a fairly sharp separation can be accomplished by fractional distillation in vacuum. Dr. W. F. Bruce has kindly informed us that he has synthesized both isomers by another method and established the fact that the higher melting compound of Mayer and Müller is 4-methyl-7-chlorohydrindone-1 (IV), while the isomer is 7-methyl-4-chlorohydrindone (V). On this basis, and from the results of our fractionation, it appears that in the original Friedel and Crafts reaction substitution ortho to the methyl group predominates in the ratio of about 2:1. The course of the reaction seems to be quite similar to that observed by Wahl[5] in a careful study of the chlorination of *p*-chlorotoluene (58% substitution ortho to the methyl group). It is interesting that in the Blanc reaction with

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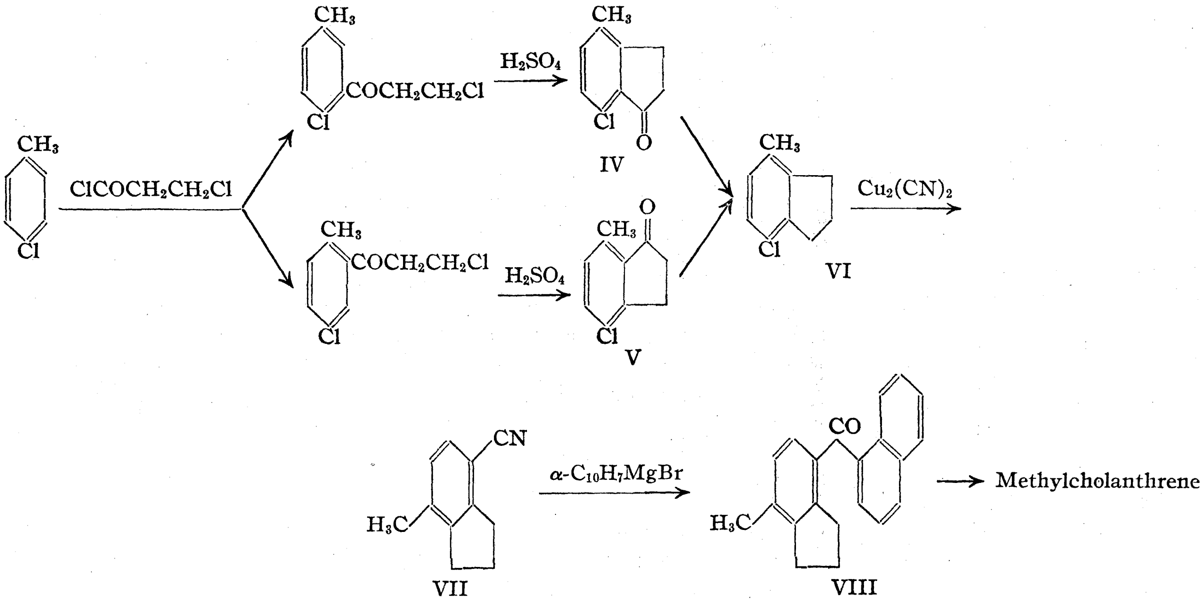
[1] Fieser and Newman, THIS JOURNAL, **57**, 961 (1935). Difficulty may be experienced in effecting the hydrogenation of dehydrocholic acid unless this material is reasonably free from impurities. An adequate purification of the crude oxidation product of cholic acid consists in precipitation of the acid from a solution in dilute alkali and crystallization from acetone. Four 40-g. lots of the purified acid have been hydrogenated in succession with one 3-g. charge of catalyst.

[2] Fieser and Seligman, *ibid.*, **57**, 228, 942 (1935).

[3] Mayer and Müller, *Ber.*, **60**, 2278 (1927).

[4] This substance, m. p. 129–132° (from alcohol), was obtained in small amounts by heating crude II with concentrated sulfuric acid at 100° for one-half hour (found: C, 53.61; H, 4.35), the bulk of the product being an oil. Steam distillation of II gave a viscous oil which polymerized on standing (probably a mixture of the vinyl ketones III) and which could not be cyclized with sulfuric acid or aluminum chloride.

[5] Wahl, *Compt. rend.*, **202**, 2161 (1936).



p-bromotoluene the situation is reversed, substitution occurring chiefly adjacent to the bromine atom in the ratio 1.8:1.[2]

For the purpose of the present synthesis a separation (or distillation) is not required, and 4-chloro-7-methylhydrindene (VI) was obtained in 95% yield from the mixture of hydrindones. For the preparation of the ketone VIII the chloro compound VI was first converted into the nitrile VII by the Rosenmund–von Braun method. Fairly satisfactory results were obtained using cuprous cyanide without a solvent[6] at 265°, but a better procedure was encountered by Dr. E. B. Hershberg in the course of work on a related problem and applied by him to the present reaction. Using pyridine as solvent, as suggested in the patent literature,[7] the reaction took place at a lower temperature (220–230°) and the nitrile was obtained (pure) in 78% yield. The condensation of the nitrile with α-naphthylmagnesium bromide proceeded very smoothly and the ketimine was obtained as a crystalline yellow hydrochloride. This was hydrolyzed in the presence of toluene, and on vacuum distillation the ketone VIII was obtained in a satisfactory condition in 89% yield, based on the nitrile. The yield of the ketone is about twice as great as that obtained from 7-methyl-4-bromohydrindene and α-naphthoyl chloride,[2] and the yield in two steps from the chloro compound (69%) is better than in the single step previously employed.

No difficulty was experienced in conducting the pyrolysis of the ketone VIII on a large scale. The bulk of the methylcholanthrene was obtained in a very pure condition after one or two crystallizations of the crude distillate and the remainder was purified as the picrate, the total yield being 49%. In working with large quantities of material it was observed that the hydrocarbon invariably is accompanied by an oily substance. This was collected from the mother liquors and purified by removing traces of methylcholanthrene by its preferential reaction with sulfuric acid. The resulting pale yellow oil, b. p. 221–226° (4 mm.), had the composition of a tetrahydro derivative of methylcholanthrene, but, as it proved to be quite resistant to dehydrogenation with selenium, such a structure is unlikely. The hydrocarbon, which unfortunately yielded no picrate, more probably is 4-methyl-7-(1-naphthylmethyl)-hydrindene, formed by the reduction of the carbonyl group of the starting material (VIII). That some form of reduction process occurs during the pyrolysis is clear from the composition of the hydrocarbon, and it is interesting that products both of reduction and of oxidation[8] (anthrones) have been observed as by-products in the Elbs reaction, suggesting a process of disproportionation as a side reaction.

Each of the six steps of the new synthesis can be carried out rapidly and on a reasonably large scale, and the over-all yield (20%) is quite satis-

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[6] Von Braun and Manz, *Ann.*, **488**, 111 (1931).

[7] Ger. Pat. 271,790 (1914), 293,094 (1916).

[8] Morgan and Coulson, *J. Chem. Soc.*, 2551 (1929); Fieser and Peters, This Journal, **54**, 3742 (1932).

factory. Using ordinary equipment, 75 g. of methylcholanthrene can be prepared conveniently from 176 g. of *p*-chlorotoluene, and the first three reactions can be conducted easily with amounts three times as great. The β-chloropropionic acid required as starting material can be prepared readily from trimethylene chlorohydrin in 79% yield by a modification of the usual method[9] for which we are indebted to Professor E. H. Huntress and Dr. E. B. Hershberg. Also included in the experimental part is a procedure developed by Dr. M. S. Newman for the preparation of methylcholanthrene-choleic acid,[10] a compound of interest for biological experimentation in the form of the water-soluble sodium salt.

The modifications reported in this paper widen somewhat the scope of the general synthesis, and various further applications are at present under investigation. We are indebted to Drs. Hershberg and Newman for the contributions noted, and to Mr. Phillip A. Shaffer, Jr., for able assistance in conducting the experiments.

Experimental Part[11]

β-Chloropropionyl Chloride.—Following the procedure recommended by Huntress and Hershberg, 250 g. of trimethylene chlorohydrin was added gradually from a dropping funnel to 775 cc. of concentrated nitric acid (sp. gr. 1.42) contained in a 3-liter long-necked flask provided with a mechanical stirrer and a thermometer suspended in the liquid, and cooled in an ice-bath (hood). The temperature of the reaction mixture was carefully controlled to 25–30° throughout the addition, which required about three hours. Stirring was continued for a short time, and after standing overnight the mixture was heated for one-half hour on the steam to complete the reaction. The solution was combined with that from a second oxidation of the same amount of material and the nitric acid was removed by distillation up to about 100° at 25 mm. The β-chloropropionic acid then distilled at 115° (25 mm.), or 120° (30 mm.); yield 445–465 g. (78–81%).

The acid prepared in this way (465 g.) was refluxed with 800 g. of purified thionyl chloride (all-glass apparatus) for three hours and the excess thionyl chloride was removed by careful fractionation from a modified Claisen flask at the pressure of the water pump. The β-chloropropionyl chloride then distilled at 53° (23 mm.) or 87° (95 mm.); yield 525 g. (96%).

Friedel and Crafts Reaction.—A 5-liter three-necked flask provided with a mercury-sealed Hershberg wire-stirrer[12] and a calcium chloride tube was charged with 525 g. of β-chloropropionyl chloride, 525 g. of *p*-chlorotoluene and 2100 cc. of carbon bisulfide, and 1050 g. of aluminum chloride was added to the stirred solution in 100-g. portions over a period of three hours. Stirring was then continued at room temperature for ten hours, by which time the greater part of the aluminum chloride had been converted into a liquid complex. To complete the reaction the mixture was warmed to 40–45° and stirred for two hours without further heating. It was then cooled thoroughly by stirring in an ice-bath and the liquid was decanted into dry flasks and then poured cautiously through a funnel into a stirred mixture of ice and concentrated hydrochloric acid, using in all 12 liters of ice and 1.5 liters of acid distributed among several beakers. The residue in the reaction flask, containing aluminum chloride, was decomposed separately with ice and acid. The aqueous liquor was separated in portions and washed once with ether. The carbon bisulfide layer was extracted once with water, combined with the ethereal extract and, without drying, evaporated at the pressure of the water pump. The residual red-brown oil containing a mixture of the two β-chloropropionyl derivatives and weighing about 910 g. (theoretical, 897 g.) was used at once or else stored in the ice box.

Cyclization.—Approximately one-half of the above oil (910 g.) was added from a separatory funnel with efficient stirring (wire stirrer) to 2600 cc. of concentrated sulfuric acid contained in a 5-liter flask and preheated to 105° (hood). The addition was completed in thirty minutes, and the solution was kept at 105–110° with stirring for twenty-five minutes longer. The mixture was then carefully cooled by applying wet towels, then water, then ice, while stirring, and after reaching a temperature of 25° (twenty minutes) it was poured onto about 12 liters of cracked ice and the volume was made up to about 16 liters with water. The reaction product separated as a crystalline, tan precipitate, and this was collected on a large Büchner funnel and washed thoroughly with water. The washing removed a considerable amount of very dark tar (which is reprecipitated by the dilute acid in the filtrate) and left a light tan, granular product. This was combined with the material obtained in the same manner from the second half of the chloro ketone mixture and the product without being dried was dissolved in boiling alcohol, using a considerable excess of the solvent. For clarification the dark solution was filtered by suction through a 2-cm. pad of Norite, changing the pad frequently, as required. After a second filtration the solution was light yellow, and after suitable concentration and cooling there was deposited a first crop of nearly colorless crystals (390 g.). A second crop was obtained after clarification and concentration of the solution, and finally the remainder was precipitated with water. The total yield of light colored hydrindone mixture suitable for the next step was 460 g. (61%).

In another experiment the crude, tan hydrindone mixture from 490 g. of *p*-chlorotoluene was taken up while wet in benzene and the solution was washed with aqueous sodium chloride solution, dried and after removing the solvent the product was distilled at reduced pressure from a modified Claisen flask. There was obtained in the first fraction, b. p. 152–157° (8 mm.), 213 g. of colorless solid melting at 75–79° and consisting very largely of **7-methyl-4-chlorohydrindone-1** (V). Recrystallized several

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[9] "Organic Syntheses," Coll. Vol. I, 1932, p. 162.

[10] Fieser and Newman, THIS JOURNAL, **57**, 1602 (1935).

[11] All melting points are corrected. Analyses by Mrs. G. M. Wellwood.

[12] Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

times from alcohol, a sample of the substance formed long needles, m. p. 82–82.4°.

Anal. Calcd. for $C_{10}H_9OCl$: C, 66.47; H, 5.03. Found: C, 66.31; H, 5.10.

The second fraction distilled largely at 172–180° (8 mm.), and the colorless distillate weighed 112 g. and melted at 110–120°. Crystallization from alcohol afforded pure **4-methyl-7-chlorohydrindone-1**(IV), which formed leaf-like prisms melting at 128° as recorded by Mayer and Müller.[3] The substance is considerably less soluble than the isomer. As the total yield in this experiment was low (46%), and as a considerable residue remained from the distillation, it is probable that much material was lost during the prolonged process of fractionation, possibly through biindone formation under the influence of impurities in the crude material. For this reason the approximate ratio of the isomers V and IV (66:34) in the total distillate may be only a rough indication of the course of the original substitution. In an earlier small-scale experiment in which the distillation was carried out more rapidly without attention to the separation of isomers, the yield from 140 g. of *p*-chlorotoluene was 59%. Purification of the crude hydrindone mixture by rapid distillation thus appears to be satisfactory when handling small quantities, but in large-scale operation it is safer to crystallize the material.

4-Methyl-7-chlorohydrindene (VI).—For the Clemmensen reduction the 460-g. batch of mixed hydrindones described above was divided into three portions, each of which was dissolved in 750 cc. of alcohol. The solutions were kept hot on the steam-bath and in the course of four to five hours each solution was added in portions through a reflux condenser to a gently boiling mixture prepared by shaking 1600 g. of granulated zinc with a warm solution of 80 g. of mercuric chloride, decanting, washing once with water, and adding 500 cc. of water, 200 cc. of alcohol and 1100 cc. of concentrated hydrochloric acid. After the addition the mixtures were kept boiling for ten hours, during which time 900 cc. of concentrated hydrochloric acid was added in portions to each flask. After standing overnight to cool, the aqueous liquors were decanted, diluted with water to twice the original volume and extracted twice with ether. The greater part of the reaction product was recovered from the zinc residues by thorough extraction with ether, taking care to break up any lumps of metal. The various ethereal extracts were combined, the solvent was removed by distillation and the residual oil was steam distilled from a solution of sodium hydroxide. The colorless oil in the distillate, together with that extracted from the aqueous layer with ether, was dried and distilled, the yield of colorless, mobile liquid, b. p. 132–133° (25 mm.), being 403 g. (95%).

Anal. Calcd. for $C_{10}H_{11}Cl$: C, 72.09; H, 6.66. Found: C, 71.76; H, 6.98.

4-Methyl-7-cyanohydrindene (VII).—In the most satisfactory experiment (by E. B. H.) 27.8 g. of thoroughly dry, powdered cuprous cyanide was poured into a 30-mm. Pyrex bomb tube constricted near the top, and 49.3 g. of 4-methyl-7-chlorohydrindene was added. After shaking vigorously to wet all of the powder, 40 cc. of dry pyridine was added, taking care not to mix the layers. The tube was then sealed and given a few quick shakes to mix the contents. A pyridine–cuprous cyanide complex forms with much evolution of heat and the mixture sets to a solid mass. On being heated in a furnace to 220–230° this dissolves to a clear, dark brown solution. After twenty hours at this temperature the tube was cooled and opened and, after adding 20–30 cc. of pyridine, warmed over a flame until the solid had dissolved. The hot solution was poured into a separatory funnel containing water and the mixture was extracted with ether. The filtered ethereal extract was washed with concentrated ammonia solution to remove copper salts, then with water, and finally with dilute hydrochloric acid. The ethereal solution was filtered to remove some precipitated solid, washed with saturated salt solution, filtered and evaporated. The residue on distillation gave 36.2 g. (78%) of distillate, b. p. 162–164° (21 mm.), which solidified at once to a colorless solid. This material was suitable for use in the Grignard reaction.

When no solvent was employed (A. M. S.), the best results were obtained by heating 80 g. of 4-methyl-7-chlorohydrindene and 41 g. of dry cuprous cyanide at 265° for eighteen hours. Before the tube was sealed it was evacuated several times to mix the reagents, and after the first ten hours of heating the tube was removed and shaken well. It was found convenient to isolate the reaction product by vacuum distillation (2 mm.) directly from the bomb-tube, and for this purpose an end section of the tube was drawn down to a diameter of 6 mm. and bent upward so that it subsequently could be cleaned easily and sealed to a delivery tube leading to a bulb receiver. The reaction product, together with some starting material, distilled readily in a colorless condition and was accompanied by only a small amount of inorganic sublimate (56 g.). The material was collected and dried in ether and on fractionation there were obtained 7.5 g. of starting material and 46.5 g. of nitrile (3° range); yield 68%, based on the chloro compound actually consumed. At the above temperature the conversion invariably was incomplete, and at higher temperatures considerable material was destroyed. The collection of the product by distillation from the bomb tube seemed to give yields just as good as the very tedious process of extraction with benzene.

4-Methyl-7-cyanohydrindene crystallizes well from petroleum ether, and a dilute solution deposits large, flat, rectagonal prisms with a characteristic design resembling the section of an hourglass. The pure substance melts at 72.9–73.2°.

Anal. Calcd. for $C_{11}H_{11}N$: C, 84.01; H, 7.06. Found: C, 83.80; H, 7.21.

The corresponding **amide** was obtained by refluxing the nitrile with concentrated hydrochloric acid. It formed colorless needles from alcohol, m. p. 176–177.4°.

Anal. Calcd. for $C_{11}H_{13}ON$: C, 75.40; H, 7.48. Found: C, 75.35; H, 6.85.

Hydrolysis of the amide with alkali gave **4-methylhydrindene-7-carboxylic acid;** irregular prisms from alcohol, m. p. 227–229°.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 74.82; H, 6.87.

4-Methyl-7-(α-naphthoyl)-hydrindene (VIII).[2]—To the Grignard reagent prepared from 195 g. of α-bromonaphthalene, 37 g. of magnesium and 800 cc. of dry ether, 100 cc. of dry benzene was added and about half of the ether was removed by distillation. A solution of 120 g. of 4-methyl-7-cyanohydrindene in 650 cc. of benzene was then added rapidly with stirring, the heat of the reaction bringing the mixture nearly to the boiling point. After refluxing overnight, the mixture was poured onto 1 kg. of ice and 500 cc. of concentrated hydrochloric acid, when the ketimine hydrochloride separated as fine yellow crystals. The organic solvents were removed with steam and, after cooling, the yellow solid was collected on a Büchner funnel and transferred to a 5-liter flask. To effect hydrolysis 1 liter of water, 500 cc. of concentrated hydrochloric acid, 500 cc. of glacial acetic acid, and 600 cc. of toluene were added and the mixture was refluxed until the ketimine hydrochloride had completely disappeared (three hours). The acetic acid was found to facilitate the hydrolysis, while the toluene dissolves the ketone as it is formed and also floats the solid material and prevents bumping. The aqueous layer was extracted once with ether and the combined ether–toluene solution was washed with water and submitted to steam distillation from a mixture with dilute alkali. After removal of the solvent the distillation was continued in order to eliminate some naphthalene. The residual oil was dried in ether and distilled at 2 mm., b. p. 211–214°, the yield of light yellow, viscous oil being 194 g. (89%). On one occasion, after evaporating the bulk of the ether prior to the distillation of the crude ketone, the material crystallized to a hard solid on standing for a day or so. After this product had been distilled it remained as a glass when kept for over a week. The analytical sample from the earlier work[2] began to crystallize after about twenty months.

Methylcholanthrene.—The pyrolysis of 168.5 g. of the ketone was conducted in three lots and the products were combined for purification. In a 100-cc. flask with a sealed-on receiving bulb a portion of the ketone was warmed over a free flame and then placed in a preheated nitrate bath and heated at 405–410°, uncorr., for forty minutes. A nitrogen atmosphere is unnecessary. Since the true temperature of the bath was not determined, it may be noted that the pyrolysis temperature is sharply defined by brisk bubbling which is hardly noticeable at a temperature 5° lower. The water and hydrocarbon cleavage products collecting in the receiver amounted to 6 g. in a typical 56.5-g. run. At the end of the period of heating the flask was removed from the bath and cooled somewhat with a blast of air. A capillary was inserted, the receiver was rinsed with acetone and the hydrocarbon was distilled at 2–3 mm. pressure. It is convenient to distill the material rather rapidly and to remove traces of entrained tar in a second distillation. There was a fair amount of tarry residue in the first distillation, and the first few drops of the distillate failed to solidify.

The redistilled material from the three pyrolyses consisted of a bright yellow solid weighing 113.3 g. This was dissolved in 400 cc. of benzene, and after cooling slightly 1 liter of ether was added. The bulk of the methylcholanthrene separated in a nearly pure condition as fine yellow needles (72 g.). This was dissolved in 500 cc. of benzene and 300 cc. of ether was added; on cooling, the hydrocarbon separated as beautiful yellow needles of high purity, m. p. 178.5–179.5°; yield 63 g. The mother liquor from this crystallization was concentrated and treated with 12 g. of picric acid, affording 12.5 g. of methylcholanthrene picrate, m. p. 176–177°. The original mother liquor was evaporated and the residual oil was submitted to pyrolysis at 405–410°, uncorr., for thirty-five minutes, but no appreciable amount of water was formed. Vacuum distillation gave an oil which solidified only partially, and on warming this with 100 cc. of ether and cooling, there was obtained in all 14.6 g. of solid, consisting of quite impure methylcholanthrene. Treated with picric acid in benzene solution, this yielded, after suitable recrystallization, 14.5 g. of satisfactory methylcholanthrene picrate, m. p. 178–179°. The total yield of the hydrocarbon, collected as such or as the picrate, amounted to 77.1 g. (49%).

The ethereal mother liquor remaining after the removal of the impure methylcholanthrene left on evaporation 26 g. of a somewhat dark oil which set to a glass on cooling. Only traces of picrate could be obtained from this material, and in earlier experiments it had been found that heating the oil with selenium resulted in no noticeable increase in the quantity of methylcholanthrene still present. To remove this hydrocarbon completely a solution of the oil in about 150 cc. of tetrachloroethane was shaken mechanically with 3-cc. portions of concentrated sulfuric acid, each time decanting the solution as well as possible and washing the acid residue with fresh solvent. The acid liquor at first was colored a dull reddish-black, but after repeating the process a few times it acquired a clear, brilliant, crimson color similar to that given by pure methylcholanthrene under the same conditions. After about ten extractions the material was recovered for inspection and distilled. The product (11 g.) was then treated as before until fresh acid acquired only a light red color (about ten extractions). The decanted solution was then filtered twice through Norite on a sintered glass funnel to remove traces of acid and the nearly colorless filtrate was subjected to steam distillation. The residual oil was dried in ether over calcium chloride and twice distilled in vacuum. The pale yellow distillate (7.4 g.) formed a glass. No picrate could be obtained from the material in either alcohol or benzene. After two careful fractionations the main portion of the oil (5.2 g.) distilled at 221–226° (4 mm.). The analysis is that of 4-methyl-7-(1-naphthylmethyl)-hydrindene.

Anal. Calcd. for $C_{21}H_{20}$: C, 92.60; H, 7.41. Found: C, 92.71; H, 7.34.

A sample of the oil was treated in glacial acetic acid with sufficient dichromate for conversion to the ketone VIII, but the recovered product gave no methylcholanthrene on pyrolysis and resembled the starting material. The oily hydrocarbon is attacked only slowly on being heated with dilute nitric acid; after oxidation finally had been accomplished the clear solution was evaporated and the residue sublimed. Phthalic anhydride was identified in the first sublimate and there was then obtained a substance which crystallized from benzene as colorless prisms which became opaque on drying and melted at 189–191° (found: C, 54.27; H, 1.33).

Methylcholanthrene-choleic Acid.—Conditions have not been found under which the choleic acid crystallizes directly from a solution of the components, and the following process has been employed. Fifteen grams of commercial desoxycholic acid is dissolved in 200 cc. of absolute alcohol, the solution is filtered, 0.4 g. of methylcholanthrene is added, and the mixture is refluxed for a few minutes in order to bring the hydrocarbon into solution. On standing undisturbed overnight the solution deposits a few large clusters of long, fine, rather pale yellow needles of pure methylcholanthrene. This material is collected, and the filtrate is concentrated to a volume of about 125 cc. and allowed to stand overnight without disturbance. Methylcholanthrene-choleic acid separates at this point as small clusters of fine, colorless needles amounting to 0.7–2.1 g. The melting point usually is 196.5–197°, sometimes 197.5–198°. There is some drawing together of the particles a few degrees lower, and some darkening at the melting point. From 0.1 to 0.2 g. of methylcholanthrene, depending on the size of the first crop of the choleic acid, is dissolved in the mother liquor and on slow cooling a further crop of the choleic acid is obtained. This procedure can be repeated about four times, keeping the volume about 125 cc. If the solution darkens, it is clarified with Norite.

Summary

By a modification of the synthetic method previously described, methylcholanthrene can be prepared rapidly and on a large scale using *p*-chlorotoluene, β-chloropropionyl chloride, and α-bromonaphthalene as the starting materials. The over-all yield in the six-step process is 20%.

CONVERSE MEMORIAL LABORATORY
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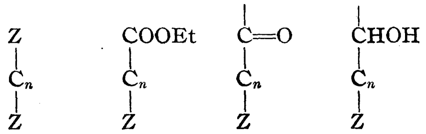
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Synthesis of Pyrrolidines, Piperidines and Hexahydroazepines[1,2]

BY JOSEPH H. PADEN AND HOMER ADKINS

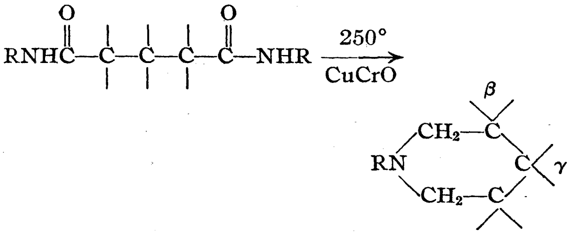
Compounds of the types



$Z{-}C_n{-}Z \qquad \mathrm{COOEt}{-}C_n{-}Z \qquad \mathrm{C{=}O}{-}C_n{-}Z \qquad \mathrm{CHOH}{-}C_n{-}Z$

where *n* is 2, 3 or 4 and Z is $-CN$, $-CONH_2$, $-CONHR$, $-\overset{|}{\underset{|}{C}}-NH_2$, $-\overset{|}{\underset{|}{C}}-NHR$, $-\overset{|}{\underset{|}{C}}-NO$, $-\overset{|}{\underset{|}{C}}-NO_2$, $-\overset{|}{C}{=}NOH$ or $-\overset{|}{C}{=}N-N{=}$ presumably may be converted into cyclic amines by catalytic hydrogenation. The present paper is concerned primarily with the synthesis of such amines from diamides of succinic, glutaric and adipic acids. Attention has been also given to the hydrogenation of imides to cyclic amides over nickel or to cyclic amines over copper–chromium oxide. In addition a new process for the preparation of cyclic amines by the alkylation of amines with glycols has been developed.

Piperidines from Glutaramides.—The eight substituted piperidines prepared by ring closure from glutaramides as indicated in Table I have substituents on the nitrogen and (or) in the gamma position.



Presumably piperidines bearing substituents in the beta position could be prepared similarly, while it is obviously impossible to prepare alpha substituted piperidines from glutaramides. Among the piperidines prepared, the group on the nitrogen was *n*-amyl, benzyl or phenethyl, while the substituents on the central carbon were methyl, dimethyl or phenyl. The yield of piperidines was not much modified by the character of the substituent, being approximately 70%, which was also the yield of piperidine obtained from glutaramide itself. The lowest yield (62%) of a piperidine was due to incomplete hydrogenation and becomes the highest (81%) if allowance is made for the recovered amide.

The other products of reaction, isolated in the yields given in Table I, can be accounted for by cleavage at the nitrogen to carbon bond in the amide or the piperidine. The effect of structure upon the extent of this type of reaction will be considered in a subsequent section.

Three dipentamethylene glutaramides of the type

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(1) Azepine is the seven-membered ring containing one nitrogen atom and three double bonds. Hexahydroazepine was suggested by Dr. Austin M. Patterson in preference to the synonymous terms hexamethyleneimine or homopiperidine.

(2) The Wisconsin Alumni Research Foundation allotted funds for a research assistantship held by J. H. P.

TABLE I

HYDROGENATION OF AMIDES OVER COPPER–CHROMIUM OXIDE

The reactions were carried out at 250–260° under 200–400 atm. of hydrogen using 700–800 cc. of dioxane per mole of diamide.

GLUTARAMIDES

Glutaramide (substituents)	Moles	Catalyst, g.	Time, hrs.	Yield of products, %
Unsubstituted[3]	0.068	4	2	70 Piperidine
Di-N-phenethyl	.18	11	1.5	77 1-Phenethylpiperidine[4] 19 Piperidine 25 Phenethylamine 15 Diphenethylamine 8 Ethylbenzene
Di-N-phenethyl-β-methyl	.10	6	3	70 1-Phenethyl-4-methylpiperidine 11 4-Methylpiperidine[5] 23 Phenethylamine 19 Diphenethylamine 5 Unchanged amide
Di-N-phenethyl-β-phenyl	.084	5	2.5	70 1-Phenethyl-4-phenylpiperidine 3 4-Phenylpiperidine[6] 8 Phenethylamine 7 Diphenethylamine
Di-N-*n*-amyl	.13	9	3	74 1-*n*-Amylpiperidine[7,8] 37 Di-*n*-amylamine 9 *n*-Amylamine Trace of piperidine
Di-N-*n*-amyl-β-methyl	.114	6	2	62 1-*n*-Amyl-4-methylpiperidine 18 Di-*n*-amylamine 24 Unchanged amide
Di-N-*n*-amyl-β-phenyl	.10	6	2.25	72 1-*n*-Amyl-4-phenylpiperidine 7 4-Phenylpiperidine[6] 32 Di-*n*-amylamine
Di-N-*n*-amyl-β,β-dimethyl	.115	6	4.6	69 1-*n*-Amyl-4,4-dimethylpiperidine 23 Di-*n*-amylamine 9 Unchanged amide
Di-N-benzyl-β-phenyl	.065	5	2	65 1-Benzyl-4-phenylpiperidine 16 4-Phenylpiperidine[6] 30 Benzylamine 20 Dibenzylamine
Di-N-pentamethylene	.18	9	1.5	46 1,5-Di-N-piperidinopentane[9] 30 5-(N-Piperidino)-pentanol-1[10] 20 Piperidine
Di-N-pentamethylene-β-methyl	.118	6	5	71 1,5-Di-N-piperidino-3-methylpentane
Di-N-pentamethylene-β,β-dimethyl	.11	6	5.5	45 1,5-Di-N-piperidino-3,3-dimethylpentane
MISCELLANEOUS AMIDES				
Di-N-*n*-amyl adipamide	0.36	18	4	34 1-*n*-Amylhexahydroazepine 41 Di-*n*-amylamine
1-β-Cyclohexylethylpyrrolidone-2	.067	3	1	96 1-β-Cyclohexylethylpyrrolidine
1-*n*-Amylpyrrolidone-2	.04	3	1	87 1-*n*-Amylpyrrolidine[11]
1-β-Cyclohexylethyl-4-methylpiperidone-2	.057	3	1	89 1-β-Cyclohexylethyl-4-methylpiperidine

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(3) Pinner, *Ber.*, **23**, 2943 (1890).

(4) Pollard and Robinson, *J. Chem. Soc.*, 2770 (1927).

(5) Ladenburg, *Ann.*, **247**, 69 (1888).

(6) Bally, *Ber.*, **20**, 2590 (1887); Schlinck, *ibid.*, **32**, 952 (1899).

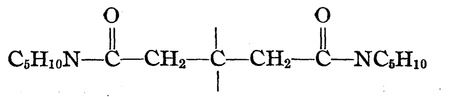
(7) Robinson and Robinson, *J. Chem. Soc.*, **123**, 542 (1923).

(8) Coffman, THIS JOURNAL, **57**, 1978 (1935).

(9) Von Braun, Kühn and Goll, *Ber.*, **59**, 2337 (1926).

(10) Adkins, Kuick, Farlow and Wojcik, THIS JOURNAL, **56**, 2425 (1934).

(11) Wojcik and Adkins, *ibid.*, **56**, 2419 (1934).

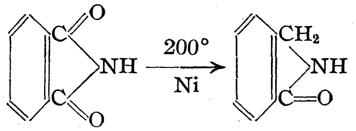


$$C_5H_{10}N-\overset{O}{\overset{\|}{C}}-CH_2-\underset{|}{\overset{|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-NC_5H_{10}$$

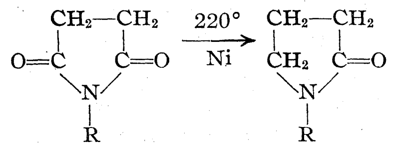
did not undergo ring closure but gave open chain diamines of the type $C_5H_{10}N(CH_2)_2(\underset{|}{\overset{|}{C}}CH_2)_2$-$NC_5H_{10}$, *i. e.*, substituted cadaverines. Di-N-pentamethyleneglutaramide also gave a 30% yield of an amino alcohol, $C_5H_{10}N(CH_2)_4CH_2OH$.

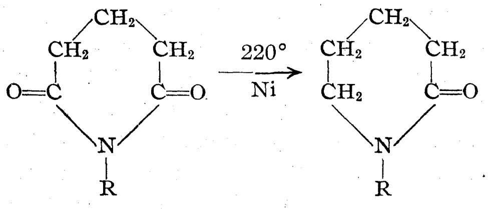
A Hexahydroazepine from an Adipamide.—The yield of 1-*n*-amylhexahydroazepine from di-*n*-amyl adipamide was half as large as that of the piperidines from the glutaramides. The formation of a hexahydroazepine was overlooked in earlier experiments[11] since it has approximately the same boiling point as di-*n*-amylamine which is also produced in the hydrogenation.

Pyrrolidones and Piperidones from Imides.—Cramer[12] observed that phthalimide was converted to phthalimidine by treatment with a nickel catalyst in methylcyclohexane solution at 200° under 200–250 atm. of hydrogen.



Attempts to obtain a similar reaction with succinimide or succinamide were not successful. It has now been found that succin- and glutaramides which bear an alkyl group on the nitrogen atom may be converted successfully at 200–220° over nickel to 2-pyrrolidones and 2-piperidones, respectively.

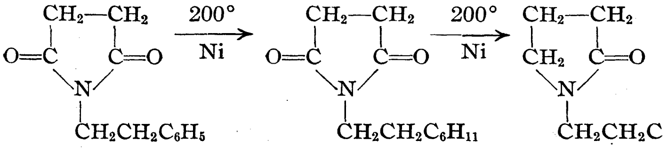




This behavior is similar to that observed in the pyrrole series where the presence of a group on the nitrogen atom greatly facilitates hydrogenation. The resulting pyrrolidones and piperidones are cyclic amides which do not react further under the conditions of the experiments.

As is indicated in Table II three imides were investigated and the yields of products were 46–79%. The reactions were rather slow at 200–220° and would probably have been much more rapid at a higher temperature, but dioxane is the only available solvent which is satisfactory for this type of reaction and it may not be used with Raney nickel above about 220°. The reaction with N-*n*-amylsuccinimide was incomplete after two applications of catalyst. The low yield reported is due to the difficulty of separating the pyrrolidone from the imide. The yields of products from N-phenethylimides were quite satisfactory and no difficulty was encountered in purifying them by fractionation since their boiling points differed much more from that of the starting material than was the case with 1-*n*-amylpyrrolidone-2.

The first reaction in the hydrogenation of the two N-phenethylimides was the saturation of the benzene ring which occurs very rapidly at 200°. It was found possible to isolate 1-β-cyclohexylethylsuccinimide (II) in a yield of 93% when the hydrogenation of N-phenethylsuccinimide (I) was interrupted after twenty minutes. Longer treatment resulted in the removal of one carbonyl oxygen and in the formation of 1-β-cyclohexylethylpyrrolidone-2 (III).



I II III

These reactions are examples of two selective hydrogenations. First, the hydrogenation of a phenyl group in the presence of an imido carbonyl group which is labile to hydrogen under the conditions of the reaction. This is possible because of the difference in rate of reaction. Secondly, we have the hydrogenolysis of an imido carbonyl group while the amido carbonyl remains unchanged.

In the hydrogenation of N-phenethyl-β-methylglutarimide (IV) no attempt was made to isolate the N-cyclohexylethylimide. The reaction was allowed to proceed to completion and the product was 1-β-cyclohexylethyl-4-methylpiperidone-2 (V).

Piperidines from Glutarimides.—In a glutarimide (VI) the ring system of the piperidine

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(12) Cramer and Adkins, THIS JOURNAL, **52**, 4354 (1930).

TABLE II

HYDROGENATION OF IMIDES OVER RANEY NICKEL

The reactions occurred at 200–220° under 200–400 atm. of hydrogen using 50–80 cc. of dioxane per tenth mole of imide.

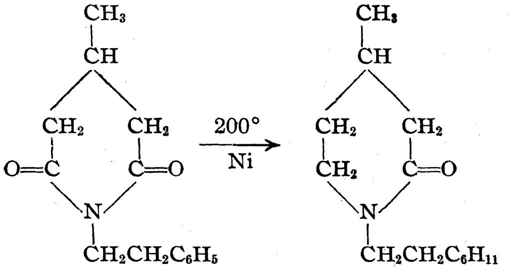
Imide	Moles	Catalyst, g.	Time, hrs.	Yield of products, %
N-Phenethylsuccinimide	0.1	4	0.3	93 N-β-Cyclohexylethylsuccinimide
N-β-Cyclohexylethylsuccinimide	.12	12	5	79 1-β-Cyclohexylethylpyrrolidone-2
N-*n*-Amylsuccinimide	.15	7	9	46 1-*n*-Amylpyrrolidone-2
N-Phenethyl-β-methylglutarimide	.11	7	10	74 1-β-Cyclohexylethyl-4-methylpiperidone-2

TABLE III

HYDROGENATION OF GLUTARAMIDES OVER COPPER–CHROMIUM OXIDE

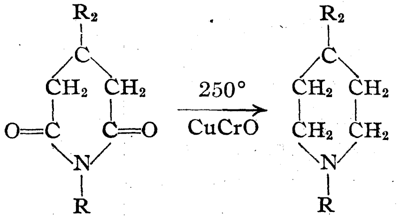
The reactions were carried out at 250–260° under 200–400 atm. of hydrogen using 700–800 cc. of dioxane per mole of imide.

Glutarimide (substituents)	Moles	Catalyst, g.	Time, hrs.	Yield of products, %
β-Methyl[13]	0.118	6	1.5	46 4-Methylpiperidine[14]
β-Phenyl[15]	.118	6	1.5	55 4-Phenylpiperidine[16]
N-Benzyl-β-phenyl	.110	6	3	42 1-Benzyl-4-phenylpiperidine
				32 4-Phenylpiperidine
N-*n*-Amyl-β,β-dimethyl	.148	8	3.5	67 1-*n*-Amyl-4,4-dimethylpiperidine
				7 4,4-Dimethylpiperidine[17]
				11 Unchanged imide
N-Phenethyl-β,β-dimethyl	.130	7	1.5	55 1-Phenethyl-4,4-dimethylpiperidine
				16 4,4-Dimethylpiperidine
				7 Unchanged imide
N-Benzyl-β,β-dimethyl	.081	4	7	32 1-Benzyl-4,4-dimethylpiperidine
				31 4,4-Dimethylpiperidine



IV V

(VII) is already present, and it might be expected that the yields of piperidine would be somewhat greater than in the case of the amides, due to the lessening of any side reactions which might precede ring closure.



VI VII

Inspection of Table III, however, shows that this is not the case. The yields of the corresponding piperidines from N-benzyl-β-phenyl-, N-*n*-amyl-β,β-dimethyl- and N-phenethyl-β,β-dimethylglutarimide were of the order of 70–75% of ring compounds. The cleavage of the phenethyl and benzyl groups from the nitrogen atom giving the piperidines free from substituents in the 1-position is quite noticeable in these compounds. An attempt to remove the benzyl group to a larger extent was made with N-benzyl-β,β-dimethylglutarimide by running the reaction for a longer time. That much of it was removed is shown by the low yield of 1-benzyl-4,4-dimethyl-piperidine.

The hydrogenation of β-methyl- and β-phenylglutarimides was not very satisfactory. Since the simple amides of glutaric acids are quite insoluble substances and so are difficult to purify by crystallization, it was hoped that the easily purified imides would furnish a convenient method for preparing the piperidines which are unsubstituted in the 1-position. The yields of 4-methyl- and 4-phenylpiperidines from these substances were rather low, however. In both cases the catalyst was found to be red after the reaction was over, indicating that it had been deactivated. This might be due to the hydrolysis of the imide by the

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(13) Sircar, *J. Chem. Soc.*, 600 (1927).

(14) Ladenburg, *Ann.*, **247**, 69 (1888).

(15) Vorländer, *ibid.*, **320**, 86 (1902).

(16) Bally, *Ber.*, **20**, 2590 (1887).

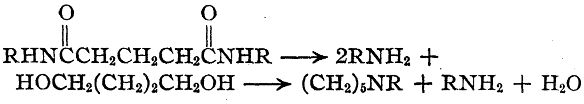
(17) Komppa, *Ann. acad. sci. Fennicae*, A, 3 (1911); *cf. C. A.*, **7**, 1359 (1913).

water formed in the reaction, the resulting acid and ammonia deactivating the catalyst. Residues of high boiling material were left after the product had been distilled, amounting to 33% of the starting material in the case of β-methylglutarimide, and 24% with β-phenylglutarimide.

Since the amides of β,β-dimethylglutaric acid are difficult to obtain, and the imides may be prepared in satisfactory yields in most cases (see Table V), the hydrogenation of the imides seems to be the best method of preparing N-alkylated derivatives of 4,4-dimethylpiperidine.

Pyrrolidines and Piperidines from Pyrrolidones and Piperidones.—Three cyclic amides, 1-β-cyclohexylethyl-pyrrolidone-2, 1-*n*-amyl-pyrrolidone-2 and 1-β-cyclohexylethyl-4-methylpiperidine-2, were almost quantitatively converted over copper chromium oxide to pyrrolidines and a piperidine (Table I).

Pyrrolidines, Piperidines and a Hexahydroazepine from Glycols and Amines.—Speculation as to the course of the reaction involved in the formation of piperidines from glutaramides led to the development of another useful method for obtaining piperidines. As indicated in a later section, it seemed possible that the cyclic amines were formed from glycols and amines produced by the hydrogenolysis of the carbon to nitrogen bond in the amides



$$\mathrm{RHN}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2CH_2CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NHR} \longrightarrow 2\mathrm{RNH_2} +$$

$$\mathrm{HOCH_2(CH_2)_2CH_2OH} \longrightarrow \mathrm{(CH_2)_5NR} + \mathrm{RNH_2} + \mathrm{H_2O}$$

Since 1,5-glycols may be prepared readily by the hydrogenation of glutaric esters, it was decided to ascertain whether glycols would react with amines to give piperidines. The reactions were carried out under the same conditions as were used for hydrogenation of amides. The results of four such reactions are summarized in Table IV. It is seen that pentanediol-1,5 and its 3-methyl and 3-phenyl derivatives react with *n*-amyl-, benzyl- or phenethylamine to give yields of 70–75% of piperidines. This is the same order of magnitude as the yields obtained from amides or imides (Tables I and II).

The preparation of piperidines from glycols and amines is a rather more convenient method than by the hydrogenation of amides: first, because glycols are in general more easily purified and handled than amides, and second, because only one mole of amine is necessary for this reaction, whereas four moles of amine are necessary to prepare a glutaramide from the corresponding ester.

Pyrrolidines may be prepared in a similar manner. The data in Table IV shows that butanediol-1,4 reacted with phenethyl- and benzylamine to give yields of 71 and 76% of the corresponding pyrrolidines. These yields are similar to those previously obtained by the hydrogenation of N-phenethylsuccinimide and N-*n*-amylsuccinimide.

It was thought that the reaction of glycols and amines might occur under milder conditions than were necessary for the hydrogenation of amides. Consequently, phenethylamine and butanediol-1,4

TABLE IV

REACTION OF GLYCOLS WITH AMINES

Equimolecular amounts of glycol and amine were heated at 250° for one hour under 200–400 atm. of hydrogen, using 600–800 cc. of dioxane and 30–60 g. of CuCrO per mole.

Amine	Glycol	Moles	Yield of products, %
Phenethyl	Pentanediol-1,5	0.25[a]	76 1-Phenethylpiperidine 15 Phenethylamine
Benzyl	Pentanediol-1,5	.4	71 1-Benzylpiperidine
Benzyl	3-Methylpentanediol-1,5	.2	68 1-Benzyl-*d*-methylpiperidine 5.5 4-Methylpiperidine
n-Amyl	3-Phenylpentanediol-1,5	.1	73 1-*n*-Amyl-4-phenylpiperidine 3 4-Phenylpiperidine 14 Di-*n*-amylamine
Benzyl	Butanediol-1,4	.2	76 1-Benzylpyrrolidine 4 Benzylamine
Phenethyl	Butanediol-1,4	.15[b]	71 1-Phenethylpyrrolidine
Phenethyl	Butanediol-1,4	.15[c]	35 4-(N-Phenethylamino)-butanol-1 19 1-Phenethylpyrrolidine 43 Unchanged amine and glycol
Benzyl	Hexanediol-1,6	.22[d]	23 1-Benzylhexahydroazepine

[a] A 25% excess of amine was used, but this is disadvantageous. [b] Time of reaction was three and one-half hours. [c] 200° for half an hour. [d] One and one-half hours.

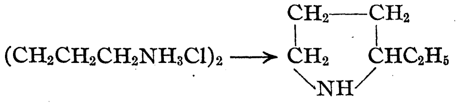
were heated at 200° for one-half hour, but the reaction was not complete. A yield of only 19% of 1-phenethylpyrrolidine was obtained, and 43% of the amine and glycol were recovered. A 35% yield of the amino alcohol formed by reaction at only one end of the glycol, was also obtained: $C_6H_5CH_2CH_2NHCH_2CH_2CH_2CH_2OH$. No more experiments along this line were carried out, but it is quite possible that by modifying the conditions, higher yields of amino alcohols of this type might be obtained.

It was of interest to determine whether or not hexanediol-1,6 would react with an amine to give a hexahydroazepine in the same manner as pentanediol-1,5 gives piperidines. It was found that benzylamine and hexanediol-1,6 reacted (Table IV) to give a 25% yield of 1-benzylhexahydroazepine. The structure of this substance was proved by removal of the benzyl group by treatment with copper–chromium oxide at 275°.

$$(CH_2)_6NCH_2C_6H_5 \xrightarrow[\text{CuCrO}]{H_2} (CH_2)_6NH + C_6H_5CH_3$$

The hexahydroazepine formed was characterized by the preparation of three derivatives which corresponded with those reported in the literature.

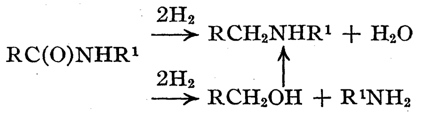
When a reaction should lead to a ring containing more than six atoms, rearrangements frequently occur resulting in the formation of five- or six-membered rings containing the extra atoms in a side chain. Thus Müller and Feld[18] found that on thermal decomposition 1,6-diaminohexane dihydrochloride gave 2-ethylpyrrolidine instead of hexahydroazepine.



Also, a rearrangement to give a 2,3 or 4-methylpiperidine might be possible. All of these possibilities are ruled out by the derivatives of the hexahydroazepine mentioned above. The structure of the 1-amylhexahydroazepine might be assumed to be proved through analogy with the 1-benzyl derivative. It was found to differ in properties from 1-*n*-amyl-4-methylpiperidine which was formed from the corresponding glutaramide. A sample of 1-amyl-2-methylpiperidine was prepared by alkylating 2-methylpiperidine with *n*-amyl alcohol and this was different from the 1-amylhexahydroazepine.

As was mentioned above the same yields of piperidines were obtained whether the glutaramide or an amine and a glycol were used. In the formation of the seven-membered ring, however, a substantially higher yield was obtained from the amide than from the amine and glycol.

Mechanism of Conversion of Amides to Cyclic Amines.—The conversion of an amide to an amine of the same carbon content may proceed either through hydrogenolysis of the oxygen to carbon bond in the amide or through hydrogenolysis of the carbon to nitrogen bond followed by interaction of the alcohol and amine so formed.



$$\begin{tikzcd}[column sep=small] & RCH_2NHR^1 + H_2O \\ RC(O)NHR^1 \arrow[ur, "2H_2"] \arrow[dr, "2H_2"'] & \\ & RCH_2OH + R^1NH_2 \arrow[u] \end{tikzcd}$$

There are no experimental observations available which definitely rule out one of these mechanisms as contrasted with the other. In support of the two-step process may be cited these facts. (1) Alcohols of the type RCH_2OH and amines of the type R^1NH_2 have been obtained as the result of the hydrogenation of amides. (2) Alcohols or glycols and amines react under the conditions used for the hydrogenation of amides to give amines in yields similar to those obtained directly from the amides. (3) Benzoylpiperidine is cleaved completely to toluene, piperidine and water far more rapidly than benzylpiperidine undergoes hydrogenolysis. This indicated that the primary cleavage in benzoylpiperidine is at the carbon to nitrogen rather than at the carbon to oxygen linkage. Against the two-step process may be cited the fact that ammonia does not react with glycols (at 250° over copper–chromium oxide in dioxane) to give good yields of the corresponding amines.

Since the hydrogenolysis of carbon to nitrogen bonds takes place under the same conditions as those effective for the breaking of carbon to oxygen bonds, it seems reasonable to assume that both types of reaction occur. Further studies in the reaction of alcohols and amines and of hydrogen with amides must be made before a definite conclusion can be drawn as to the relative importance of the two types of reactions.

Insofar as the formation of cyclic amines from open chain amides is concerned, it appears that hydrogenation precedes ring closure. There are two pieces of evidence which indicate that N-substituted glutaramides are not converted to imides. In the first place, di-N-*n*-amylglutar-

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(18) Müller and Feld, *Monatsh.*, **58**, 12 (1931).

TABLE V

PREPARATION OF GLUTARAMIDES AND IMIDES FROM ESTERS

The ester (0.1 to 0.3 mole) was heated with amine (0.4 to 1.2 moles) under 100–150 atm. of hydrogen.

Diethyl glutarate (substituents)	Amine	Temp., °C.	Time, hrs.	Yield of products, % Amide	Imide
Unsubstituted	Ammonia	175	4	96[a]	..
Unsubstituted	Phenethyl	250	9	83[b]	..
Unsubstituted	*n*-Amyl	250	3	94[c]	..
Unsubstituted	Piperidine	250	10	81[f]	..
β-Methyl	Phenethyl	250	3	94[b]	..
β-Methyl	*n*-Amyl	200	3	93[d]	..
β-Methyl	Piperidine	200	4	93[f]	..
β-Methyl	Benzyl	200	5	42[b]	..
β-Phenyl	Phenethyl	180	4	93[b]	..
β-Phenyl	*n*-Amyl	200	3	87[e]	..
β-Phenyl	Piperidine	200	4	86[f]	..
β-Phenyl	Benzyl	200	5	85[b]	..
β,β-Dimethyl	Phenethyl	250	5	..	71[f,b]
β,β-Dimethyl	*n*-Amyl	250	7	35[f]	61[f]
β,β-Dimethyl	*n*-Amyl	250	1	36[f]	61[f]
β,β-Dimethyl	Piperidine	250	7	86[f]	..
β,β-Dimethyl	Benzyl	200	2.5	..	39[f,g]
β,β-Dimethyl	Benzyl	250	9	53[f]	44[f,g]

[a] This product was washed with ethyl acetate, acetone and ether. [b] Recrystallized from 95% ethyl alcohol. [c] Recrystallized from 95% ethyl alcohol to which two volumes of acetone was added. [d] Recrystallized from acetone. [e] Recrystallized from 95% ethyl alcohol to which two volumes of ether was added. [f] The product was fractionated. [g] Recrystallized from a small amount of methyl alcohol.

amide was recovered unchanged after heating at 200° for eight hours, so apparently heat does not cause the formation of imides from glutaramides. Secondly, when one mole of diethyl-β,β-dimethylglutarate was heated with four moles of *n*-amylamine in a bomb at 250° (Table V), the same yields of imide and amide were obtained after heating either for one or for seven hours. Similar results were obtained with the same ester and benzylamine. Evidently none of the amide cyclicized during the extra hours of heating, and it would seem that the two products were probably formed by different reactions.

There appears to be no experimental observation that definitely answers the question as to whether the ring closure involves an aminoamide, an hydroxyamide, a diamine or a glycol and an amine. All of these reactions may occur under the conditions used for the conversion of amides to cyclic amines.

Hydrogenolysis of N-Substituted Piperidines.—The preparation of *pure* primary glutaramides is difficult. The N-monosubstituted glutaramides are readily prepared in high purity. Moreover, primary glutaramides are not as readily hydrogenated as are the substituted amides. Thus it is better to use N-substituted amides even though a piperidine is desired which contains no substituent on the nitrogen. This necessitates using an amine such as benzyl or phenethyl in which the carbon to nitrogen bond has been rendered liable toward hydrogenolysis by the presence of a phenyl group. The tendency of such amides and amines to undergo cleavage is shown in Table I by the formation of 19% piperidine along with 77% 1-phenethylpiperidine, 11% 4-methylpiperidine along with 70% 1-phenethyl-4-methylpiperidine and 16% 4-phenylpiperidine along with 65% 1-benzyl-4-phenylpiperidine.

Data are given in Table VII which indicate the conditions necessary for the cleavage of the amines. A comparison of these data with those in

TABLE VI

PREPARATION OF IMIDES FROM ACIDS

One mole of acid was heated with one mole of amine at 250° under 100–150 atm. of hydrogen using 350–400 cc. of dioxane per mole of acid.

Acid	Amine	Time, hrs.	Yield of products, % Amide	Imide
β-Phenylglutaric	Benzyl	7		62[a,b]
Glutaric	*n*-Amyl	6.5	14[c]	42[a]
β-Methylglutaric anhydride	Phenethyl	4	10[d]	58[d]
Succinic	Phenethyl	5.5		89[b]

[a] This product was fractionated. [b] Recrystallized from 95% ethyl alcohol. [c] Recrystallized from a mixture of equal volumes of 95% ethyl alcohol and acetone. [d] These products were partially separated by fractional crystallization from methyl alcohol. The yields given here are of the pure substances (see Experimental Part).

TABLE VII

HYDROGENOLYSIS OF 1-PHENETHYL- AND 1-BENZYLPIPERIDINES

Forty cc. of dioxane was used as the solvent in each experiment

Piperidine	Moles	Catalyst, g.	Time, hrs.	Temp., °C.	Yields, % Piperidine	Yields, % Unchanged material
1-Phenethyl	0.104	4CuCrO	4.3	250	18	68
1-Phenethyl	.104	4Ni	4	165	7	87
1-Benzyl	.118	4CuCrO	6	250	36	54
1-Benzyl	.149	7Ni	7	170	43	49

Table I would indicate that hydrogenolysis occurred more rapidly with the amides than with the piperidines.

Experimental Part

The reaction products from the hydrogenations were in general centrifuged and fractionated through a Widmer column. Low boiling basic compounds carried over in the dioxane fraction were recovered as hydrochlorides which were recrystallized from ethanol and ether. The various amines were characterized by their neutral equivalents and in most cases by the formation of solid derivatives. The hydrochlorides of all the piperidines and pyrrolidines except 4-phenylpiperidine were prepared. The properties and analyses of those substances which apparently have not been previously reported are given in Table VIII.

In a number of cases where separation could not be effected by fractionation, it was necessary to purify tertiary amines through the use of benzenesulfonyl chloride. In the case of 1-phenethyl-4-phenylpiperidine it was necessary to distil the amine away from the sulfonamide since the hydrochloride of the amine is insoluble in water. In a few cases the yield of secondary amine reported in the tables is based upon the yield of its benzenesulfonamide isolated. 4-Phenylpiperidine was separated from dibenzylamine by cooling the mixture in ice and salt.

The **1-benzyl-4-phenylpiperidine** from **di-N-benzyl-β-phenylglutaramide** gave the correct neutral equivalent of 251 and the hydrochloride gave the correct chlorine analysis, but it was contaminated with some substance apparently of the same molecular weight. The hydrochloride melted at 198–201° and the melting point was lowered by recrystallization. This substance when prepared by hydrogenating N-benzyl-β-phenylglutarimide gave a hydrochloride melting at 210–211°. The 1-benzyl-4-phenylpiperidine was purified by treatment of 8.8 g. with 3.0 g. of $C_6H_5SO_2Cl$ and 20 cc. of 10% sodium hydroxide solution. The benzenesulfonamide of the impurity was a red oil which was insoluble in ether, dilute hydrochloric acid and dilute sodium hydroxide. It was carried through the separation procedure (with appreciable mechanical loss, due to its insolubility) until the piperidine was in solution in dilute hydrochloric acid. At this point, it formed a lower insoluble layer which was separated. It did not crystallize. This treatment gave 7.6 g. of the pure piperidine which corresponded to a yield of 10.6 g. (0.042 mole) in the original fraction of 12.2 g. from 0.065 mole of amide. The yield was thus 65% of the theoretical. The hydrochloride now melted at 211–212°.

The principal fraction from the hydrogenation of di-N-*n*-amyladipamide distilled at 80–88° (9 mm.) and weighed 53.5 g. This was divided for purposes of preliminary investigation into two fractions: (1) 37.3 g., b. p. 80–88° (9 mm.), and (2) 16.2 g., b. p. 88° (9 mm.). Both fractions gave the pure phenyl isocyanate derivative of diamylamine, m. p. and mixed m. p. 78–79°. By titration, it was found that fraction (1) was 36% **1-*n*-amylhexahydroazepine** and 64% diamylamine. Fraction (2) was found to contain 89% of the hexahydroazepine and 11% of diamylamine. These figures indicated that 28.0 g., or 46%, of the hexahydroazepine, and 25.5 g., 45%, of diamylamine were formed in the reaction.

To separate these two substances 50.4 g. of fractions (1) and (2) were combined and treated gradually with 55.0 of benzenesulfonyl chloride and 185 cc. of 10% sodium hydroxide solution. On working up the reaction mixture in the usual manner, there was obtained 19.0 g. of 1-*n*-amylhexahydroazepine b. p. 94–95° (13 mm.). This corresponded to 21.0 g. in the original fraction or 34% of the theoretical. Forty-three and nine-tenths grams of the benzenesulfonamide of diamylamine was obtained which is 41% of the theoretical. That the 1-*n*-amylhexahydroazepine is not identical with either 1-amyl-2- or -4-methylpiperidine is shown by the difference in the refractive indices and the wide divergence in the melting points of the hydrochlorides (see Table VIII). The picrate of 1-*n*-amylhexahydroazepine melts at 109–110° (corr.).

The 25% excess of phenethylamine used in the preparation of 1-phenethylpiperidine[19] from amine and glycol was detrimental since the yield was not increased, and the excess amine contaminated the product.

The fraction from the reaction of **3-phenylpentanediol-1,5** and *n*-amylamine boiling at 133–137° at 2 mm. was found to contain 3% of **4-phenylpiperidine** and 73% of **1-*n*-amyl-4-phenylpiperidine.** Two grams of this fraction was treated with enough benzenesulfonyl chloride to react completely if all the fraction was 4-phenylpiperidine. After reaction was complete, the material was dissolved in ether and the unreacted tertiary amine extracted with dilute hydrochloric acid. The ether solution was dried and the ether evaporated, leaving 0.12 g. of the benzenesulfonamide of 4-phenylpiperidine, m. p. and mixed m. p. 108–109°, after one recrystallization. This amount corre-

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[19] Pollard and Robinson, *J. Chem. Soc.*, 2770 (1927).

TABLE VIII

ANALYTICAL DATA

Glutaramides

Glutaramide (substituents)	Formula	B. p. or m. p.,[a] °C.	n^{25}D	Nitrogen, % Calcd.	Nitrogen, % Found	Hydrochloride M. p., °C.	Hydrochloride Analysis for chlorine Calcd.	Hydrochloride Analysis for chlorine Found
Di-N-phenethyl	$C_{21}H_{26}O_2N_2$	M 158.5–159.5		8.28	8.29			
Di-N-*n*-amyl	$C_{15}H_{39}O_2N_2$	M 147–148		10.37	10.43			
Di-N-pentamethylene	$C_{15}H_{26}O_2N_2$	B 193–197 (1 mm.) M 53–54		10.53	10.69			
Di-N-phenethyl-β-methyl	$C_{22}H_{28}O_2N_2$	M 190–191.5		7.95	7.82			
Di-N-*n*-amyl-β-methyl	$C_{16}H_{32}O_2N_2$	M 149–150		9.85	9.70			
Di-N-benzyl-β-methyl	$C_{20}H_{24}O_2N_2$	M 194–195		8.64	8.52			
Di-N-pentamethylone-β-methyl	$C_{16}H_{28}O_2N_2$	B 188–190 (1 mm.)	1.5122	9.99	10.00			
Di-N-phenethyl-β-phenyl	$C_{27}H_{30}O_2N_2$	M 177.5–178		6.76	6.63			
Di-N-*n*-amyl-β-phenyl	$C_{21}H_{34}O_2N_2$	M 166–167		8.09	8.07			
Di-N-benzyl-β-phenyl	$C_{25}H_{26}O_2N_2$	M 159.5–160.5		7.25	7.10			
Di-N-pentamethylene-β-phenyl	$C_{21}H_{30}O_2N_2$	B 240–248 (1 mm.)		8.18	8.02			
Di-N-*n*-amyl-β,β-dimethyl	$C_{17}H_{34}O_2N_2$	B 210–212 (2 mm.) M 39–41		9.38	9.55			
Di-N-pentamethylene-β,β-dimethyl	$C_{17}H_{30}O_2N_2$	B 183–187 (1 mm.)	1.5083	9.52	9.36			
Glutarimides (substituents)								
N-Phenethyl-β,β-dimethyl	$C_{15}H_{19}O_2N$	M 80.5–81.5		5.71	5.81			
N-*n*-Amyl-β,β-dimethyl	$C_{12}H_{21}O_2N$	B 115–116 (2 mm.)	1.4638	6.63	6.56			
N-Benzyl-β,β-dimethyl	$C_{14}H_{17}O_2N$	B 148–151 (2 mm.) M 63–64		6.06	6.25			
N-Benzyl-β-phenyl	$C_{16}H_{17}O_2N$	M 98–99		5.00	4.95			
N-Phenethyl-β-methyl	$C_{14}H_{17}O_2N$	M 98–100		6.06	6.20			
N-*n*-Amyl	$C_{10}H_{17}O_2N$	B 105–106 (1 mm.)	1.4754	7.64	7.58			
Piperidines (substituents)								
1-*n*-Amyl[7]	$C_{10}H_{21}N$	B 76–76.5 (13 mm.)	1.4616[8]			223–224		
1-Phenethyl[4b]	$C_{13}H_{19}N$	B 127–128 (10 mm.)				232–233	15.72	15.57
4-Methyl[5]	$C_6H_{13}N$					186–189.5	26.15	26.22
1-*n*-Amyl-2-methyl	$C_{11}H_{23}N$	B 92–93 (16 mm.)	1.4500	8.27	8.09	166.5–167.5	17.24	17.18
1-Phenethyl-4-methyl	$C_{14}H_{21}N$	B 141–142 (12 mm.)	1.5114	6.89	7.02	254–256	14.79	14.55
1-β-Cyclohexylethyl-4-methyl	$C_{14}H_{27}N$	B 135.5–137 (12 mm.)	1.4735	6.69	6.55	277–278	14.43	14.39
1-Benzyl-4-methyl	$C_{13}H_{19}N$	B 128–129 (14 mm.)	1.5126	7.40	7.36	166.5–168	15.72	15.46
1-*n*-Amyl-4-methyl	$C_{11}H_{23}N$	B 83–84 (10 mm.)	1.4443	8.27	8.36	239–241	17.24	17.16
1-Amyl-4,4-dimethyl	$C_{12}H_{25}N$	B 96–97 (12 mm.)	1.4445	7.64	7.80	302	16.16	16.17
1-Phenethyl-4,4-dimethyl	$C_{15}H_{23}N$	B 149–150 (12 mm.)	1.5074	6.45	6.63	252	14.00	13.85
1-Benzyl-4,4-dimethyl	$C_{14}H_{21}N$	B 114–115 (5 mm.)	1.4822	6.89	6.91	335–336	14.80	14.75
1-*n*-Amyl-4-phenyl	$C_{61}H_{25}N$	B 129–130 (1 mm.)	1.5113	6.06	5.88	245–246	13.28	13.18
1-Phenethyl-4-phenyl	$C_{19}H_{23}N$	B 170–174 (2 mm.) M 74–75		5.28	5.18	270–271	11.75	11.63
1-Benzyl-4-phenyl	$C_{18}H_{21}N$	B 157–159 (1 mm.)	1.5585	5.57	5.42	212–213	12.34	12.30
Pyrrolidines (substituents)								
1-β-Cyclohexylethyl	$C_{12}H_{23}N$	B 116–117 (12 mm.)	1.4748	7.75	7.62	224–225	16.29	16.20
1-Benzyl[6]	$C_{11}H_{15}N$	B 98–100 (10 mm.)				153.5–154.5	17.95	18.08
Hexahydroazepines (substituents)								
1-*n*-Amyl[c]	$C_{11}H_{23}N$	B 94–95 (13 mm.)	1.4551	8.27	8.20	217–218	17.24	17.40
1-Benzyl	$C_{13}H_{19}N$	B 130–132 (12 mm.)	1.5243	7.40	7.57	158.5–159.5	15.71	15.63

TABLE VIII (*Concluded*)

Pentanes (substituents)	Formula	B. p. or m. p.,[a] °C.	n^{25}D	Nitrogen, % Calcd.	Nitrogen, % Found	Hydrochloride M. p., °C.	Hydrochloride Analysis for chlorine Calcd.	Hydrochloride Analysis for chlorine Found
1,5-Di-N-piperidino[9d]	$C_{15}H_{30}N_2$	B 130–131 (2 mm.)				252–253	22.83	22.79
1,5-Di-N-piperidino-3-methyl	$C_{16}H_{32}N_2$	B 123–125 (1 mm.)	1.4810	11.10	11.02	246–248	21.82	21.77
1,5-Di-N-piperidino-3,3-dimethyl	$C_{17}H_{34}N_2$	B 133–134 (1 mm.)	1.4839	10.52	10.48	314–316	20.90	20.77
Miscellaneous compounds								
N-β-Cyclohexylethylsuccinimide	$C_{12}H_{19}O_2N$	B 145–148 (2 mm.) M 53–54		6.70	6.78			
1-β-Cyclohexylethylpyrrolidone-2	$C_{12}H_{21}ON$	B 136–138 (2.5 mm.)	1.4907	7.18	7.29			
1-*n*-Amylpyrrolidone-2	$C_9H_{17}ON$	B 87–88.5 (1 mm.)	1.4619	9.03	9.18			
1-β-Cyclohexylethyl-4-methylpiperidone-2	$C_{14}H_{25}ON$	B 146–149 (2 mm.)	1.4872	6.27	6.17			
4-(N-Phenethylamino)-butanol-1	$C_{12}H_{19}ON$	B 176–178 (9 mm.)	1.5243	7.25	7.30	127–128	15.45	15.33
4-(N-Phenethylamino)-butyl benzoate	$C_{19}H_{23}O_2N$					153–155	10.31	10.73
4-Phenylpiperidine-benzenesulfonamide	$C_{17}H_{19}O_2NS$	M 108–109		4.65	4.79			

[a] All melting points below 250° are corrected. [b] The picrate melted at 147–148°. Pollard and Robinson[19] gave 144–145°. [c] The picrate melted at 109–110°. [d] Melting point of the picrate, 188–189°; von Braun, Kühn and Goll[9] gave 185°.

sponds to 0.064 g. of 4-phenylpiperidine in 2.00 g. of the mixture, or 3.2%.

The following fractions were obtained from the reaction of **phenethylamine** and **butanediol-1,4** at 200°:

	B. p., °C.	M.	G.	Product
1	79– 81	9	7.8	43% Phenethylamine
2	110–119	9	10.6	1-Phenethylpyrrolidine + butanediol-1,4
3	175–179	9	10.1	35% 4-(N-Phenethylamino)-butanol-1

Fraction 2 was extracted three times with ether (15-cc. portions), the glycol being mostly insoluble. This ether solution of **1-phenethylpyrrolidine** was dried over sodium sulfate and filtered. Into the ether solution a stream of dry hydrogen chloride was passed. A liquid layer separated which solidified in an ice-bath. It was filtered and recrystallized, m. p. and mixed m. p. 159–170°.[11] The yield was 4.3 g. or 14%. This amount of hydrochloride corresponds to 3.8 g. of the free amine so that fraction (2) contained, by difference, 10.8 − 3.6 = 7.2 g. of butanediol-1,4, which would be 55% of the starting amount. Since, however, 35 + 14 = 49% of the glycol is accounted for in the two amines, it is evident that this makes a total of 104% of butanediol. The discrepancy is probably due to incomplete recovery of 1-phenethylpyrrolidine from fraction (2). Assuming that an amount of diol corresponding to the phenethylamine (43%) was unreacted, we obtain a yield of 23% for 1-phenethylpyrrolidine. The average of 14 and 23% is reported as the yield of the pyrrolidine in the table. The hydrochloride of the benzoate of 4-(N-phenethylamino)-butanol-1 was prepared by heating 1.0 g. of the amino alcohol with 1.0 g. of benzoyl chloride at 175° for 1 hour.[20] On cooling, the product was recrystallized from absolute alcohol and ether.

The main fraction from the reaction of **benzylamine** with **hexanediol-1,6** distilled at 119–133° (9 mm.) and weighed 12.5 g. Twelve grams of this fraction was treated with 20.0 g. of benzoyl chloride and 100 cc. of 10% sodium hydroxide and shaken for thirty minutes. It was then warmed on the steam-bath for half an hour to hydrolyze all the benzoyl chloride. On cooling, the alkaline solution was extracted three times with ether, and the unreacted amine extracted from the ether with 5% hydrochloric acid. This solution was made alkaline, the insoluble layer separated and the aqueous layer extracted three times with ether. The ethereal solution of the amine was dried, the ether distilled and the residue fractionated under reduced pressure. Eight and two-tenths grams of **1-benzylhexahydroazepine** was obtained, b. p. 131–134° (13 mm.). This corresponded to 8.55 g. in the original fraction, or a yield of 23% of the theoretical. On refractionation, this substance distilled at 130–132° (12 mm.).

To prove the structure of this substance, the benzyl group was removed by treatment with copper–chromium oxide at 275° for six and one-half hours. Five and three-tenths grams of the material in 9.7 cc. of dioxane was hydrogenated in a small bomb designed for quantitative hydrogenations. One and four-tenths moles of hydrogen per mole of compound instead of the calculated value of 1.0 was absorbed. This excess of hydrogen was undoubtedly due to reaction of the dioxane with hydrogen, which proved to be very detrimental in this case.

After all the material was distilled which would come over at atmospheric pressure (with the oil-bath at 20°), there remained 5.1 g. of high boiling residue, of which 2.0 g. distilled between 130 and 217° at 2 mm. The residue was even higher boiling. This material was probably formed by alkylation of the hydroxyl groups, formed in the reaction of dioxane with hydrogen, with the amino group in the hexahydroazepine formed.

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(20) McElvain, THIS JOURNAL, **48**, 2182 (1926).

However, when dry hydrogen chloride was passed into the dioxane fraction and the solvent removed under reduced pressure, 0.25 g., 6.6% of **hexahydroazepine** hydrochloride remained. After two recrystallizations it melted at 229–231° (corr.). Müller and Sauerwald give the melting point of this substance as 236° (corr.). Von Braun and Goll give the melting point as 222° while Wallach gives 221–224°. This substance could not be either 2-, 3- or 4-methylpiperidine hydrochloride because samples of the 2- and 4-derivatives were available for comparison and 3-methylpiperidine hydrochloride melts at 171–172°. Also, it apparently is not 2-ethylpyrrolidine hydrochloride because this substance is described as a hygroscopic solid which melts below 100°.

The *p*-toluenesulfonamide melted at 75° in agreement with the value of 75° reported in the literature by Ziegler,[21] and the chloroplatinate melted at 199° (corr.). Müller and Sauerwald[22] gave the melting point at 197° (corr.).

A sample of 2-ethylpyrrolidine was prepared in this Laboratory by Mr. James Rainey, by the hydrogenation of 2-acetylpyrrole. The picrate of this substance melted at 85–86° and the chloroplatinate at 190–191°. Both of these melting points agree with those reported by Müller and Wachs.[23] The chloroplatinate apparently was pure since the melting point was not raised by further recrystallization. The melting point was not depressed by mixing with the chloroplatinate of hexahydroazepine, however. The mixed melting point was 193°.

Preparation of Amides and Imides

In making simple amides, the ester was treated with gaseous ammonia in a bomb at 250° (Table V). The ammonia was introduced into a bomb as a liquid. The ester was placed in a test-tube in a bomb, and the latter was cooled in an ice–calcium chloride bath for about three hours. Then liquid ammonia was run into the bomb slowly until the interior was well cooled. The ammonia was then run in rapidly and the bomb closed immediately. No hydrogen was placed in the bomb in these experiments. When either an amide or imide is prepared (under pressure) from the free acid (Table VI), it is necessary to use dioxane as a diluent for the water formed.

If the amides prepared as above were solids in the bomb they were removed, cooled, filtered and recrystallized from the solvent indicated in Table V. The ethyl alcohol and excess of amine from the filtrate of the reaction product were removed under reduced pressure and the residue purified by recrystallizing. The products which were present as liquids when the bomb was opened were purified by fractionation.

N-Benzyl-β-phenylglutarimide and N-*n*-amylglutarimide were purified by fractionation through a Widmer column. N-Phenethyl-β-methylglutarimide was separated from the amide by fractional crystallization from methyl alcohol. Since the imide is more soluble than the amide it could not be freed entirely from the latter.

The amide present as an impurity was neither converted into the imide nor hydrogenated under the conditions used (Table II), and was recovered unchanged. Some of the amide was insoluble in the dioxane, so when the bomb was opened after hydrogenation of this compound reported in Table II, the catalyst and amide were filtered off. The amide was dissolved immediately in 95% ethyl alcohol and the catalyst filtered off. The two filtrates were combined and fractionated. There was obtained 18.7 g. of 1-β-cyclohexylethyl-4-methylpiperidone-2, b. p. 158–162° (3 mm.). The residue from the first fractionation was 3.9 g. On recrystallization from methyl alcohol it melted at 180–185°, and mixed with di-N-phenethyl-β-methylglutaramide it melted at 186–188°. Since 30.1 g. of the mixture of amide and imide was used, 13% of the mixture was amide. Thus 26.2 g. of imide was present in the mixture, and the yield of piperidone calculated on this basis was 74%.

All the **amides, and the imides of β,β-dimethylglutaric acid,** were prepared by heating the corresponding diethyl ester (1 mol) with four moles of the amine at temperatures of from 180–250° under 125 atm. of hydrogen. Twice the calculated amount of amine is necessary because some of it is alkylated by the ethyl alcohol set free.[24] The esters were previously treated with about 5% of their weight of Raney nickel under 100 atm. of hydrogen at 150° for about six hours to remove any impurities which might poison a catalyst, and to ensure the purity of the amides. It was found that in most cases a temperature of 200° was sufficient for the preparation of amides, but since there were a few exceptions it was considered preferable to carry out the reactions at 250°. Also, most of the reactions were probably complete in much less than the time indicated, but since longer heating does no harm, no particular attempt was made to stop the reactions as soon as they were complete.

β-Phenylglutarimide, m. p. 174–175° (from methanol), was prepared by the method of Vorländer[15] in yields of 62 to 72%. β-Methylglutarimide, m. p. 144–145° (from acetone and ether), was similarly prepared in 72% yield.[13]

Preparation of Acids, Esters and Glycols

Diethyl glutarate was prepared by the hydrolysis of ethyl methylene–dimalonate with 38% sulfuric acid.[25] By this procedure 67–75% of the ester could be obtained directly. Three hundred thirty-two grams (1.0 mole) of the ester and 532 g. of 38% sulfuric acid (prepared from 330 cc. of water and 110 cc. of concentrated sulfuric acid, sp. gr. 1.84) were placed in a 2-liter round-bottomed flask and refluxed vigorously for ten hours. The contents of the flask should be shaken vigorously several times until refluxing starts. Otherwise the bottom layer may become greatly superheated, causing the material to boil out through the condenser. The solution became clear in six hours, but if the reaction was stopped at this point the yields were greatly reduced. When the contents of the flask had cooled to room temperature, the oily layer was separated and the aqueous layer extracted three times with 150-cc. portions of benzene. The benzene and ester were combined, dried over anhydrous sodium sulfate and the benzene distilled at atmospheric pressure. The residue was placed in a flask under a Widmer column and heated in an oil-bath at 150° under reduced pressure until the evolution of carbon dioxide ceased. The ester was then fractionated. This distillation is accompanied by con-

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(21) Ziegler and Orth, *Ber.*, **66B**, 1867 (1933).

(22) Müller and Sauerwald, *Monatsh.*, **48**, 526, 730 (1927).

(23) Müller and Wachs, *ibid.*, **53**, 420 (1929).

(24) Winans and Adkins, THIS JOURNAL, **54**, 306 (1932).

(25) Welch, *J. Chem. Soc.*, 673 (1931).

siderable foaming so a column of some sort is necessary. The material boiling at 104–108° (8 mm.) was collected. On refractionation the ester boils at 105–106° (8 mm.). The refractionation of four runs of the size described above gave 563 g. (75% of theoretical) of pure diethyl glutarate, b. p. 105–106° (8 mm.).

β-Phenylglutaric acid was prepared from benzylidenebismalonic ester by hydrolysis with hydrochloric acid.[26] The reaction was carried out in a manner similar to that described in "Organic Syntheses" for the preparation of tricarballylic acid.[27] Three hundred and seventy grams (0.9 mole) of the ester, 125 cc. of water, and 125 cc. of concentrated hydrochloric acid were placed in a 2-liter round-bottomed flask carrying a Widmer column and a condenser set for downward distillation. The mixture was boiled at such a rate that the temperature at the head of the column remained at 80–100°. In this manner the alcohol was removed as formed, but very little water was allowed to distil. This was continued until the solution became clear and no more carbon dioxide was evolved (thirty hours). Twice during this time further 100-cc. portions consisting of 50 cc. of water and 50 cc. of concentrated hydrochloric acid were added.

The flask was cooled in an ice-bath and the crystals were filtered and dried by suction. The dried acid was dissolved in 200 cc. of hot acetone, treated with charcoal and filtered. Half the acetone was distilled and an equal volume of benzene added. One hundred twenty-five grams (67%) of pure β-phenylglutaric acid separated, m. p. 139–140°. (Melting points of 138 and 143° are given in the literature.) The filtrate gave an additional 44.5 g. of acid, m. p. 138–139° (24%). The total yield was 91% of the theoretical.

In preparing diethyl β-phenylglutarate the above procedure was followed except that the crude acid was not purified. Four hundred five grams (1 mole) of benzylidenebismalonic ester was hydrolyzed as above. To the crude, dry acid was added a mixture of 460 cc. of 95% ethyl alcohol and 25 cc. of concentrated sulfuric acid. The mixture was refluxed for six hours on the steam-bath. Then the excess alcohol and the water formed were removed under reduced pressure by warming on the steam-bath until the temperature of the residue was 50° (20 mm.). Then 200 cc. of absolute ethyl alcohol and an additional 10 cc. of concentrated sulfuric acid was added and the mixture refluxed for three hours. The excess alcohol was removed under reduced pressure and the residue poured into water. The oily layer was separated and the aqueous layer extracted twice with ether. The ether solution of the ester was extracted twice with 5% sodium carbonate solution, twice with water and dried over anhydrous sodium sulfate. The ether was removed at atmospheric pressure and the residue distilled *in vacuo*. One hundred sixty grams of ester was obtained (85%) which distilled at 143–145° (1.5 mm.); von Braun and Weissbach[28] report the boiling point of this ester as 148–150° at 0.5 mm.

β-Methylglutaric acid was made as by Boorman, Linstead and Rydon except that the triethyl 2-methylpropanetricarboxylate obtained as an intermediate was purified before hydrolysis. The triester b. p. 117–119° was obtained in 80–85% yield. The yield of acid m. p. 86.5–87.5° was 80%, based on the triester used.[29]

Diethyl-β-methylglutarate was prepared in a manner analogous to that used in the preparation of diethyl-β-phenylglutarate, in a yield of 90% from the pure acid. It boils at 117–118° (13 mm.).

Diethyl-β,β-dimethylglutarate was obtained through the kindness of Dr. Roger Adams.

β-Methylglutaric anhydride was prepared by the method of Darbishire and Thorpe[30] in a yield of 92%, b. p. 141–142° (8 mm.) and m. p. 41–43°.

The glycols were prepared by the hydrogenation of esters.[31]

Summary

Glutaramide gave a 70% yield of piperidine by treatment with hydrogen under 200–400 atm. pressure over copper–chromium oxide at 250° in dioxane solution. Eight N-monosubstituted amides of glutaric, β-methyl-, β-phenyl- and β,β-dimethylglutaric acid in which the substituents on the nitrogen atom were the *n*-amyl, benzyl or phenethyl group, gave 65–80% yields of piperidines substituted in the 1 and 4 positions. Glutarimides gave yields of piperidines of the same order of magnitude. The di-N-pentamethylene amides of glutaric, β-methyl- and β,β-dimethylglutaric acid gave rise to 45–71% yields of di-N-pentamethylenecadaverines.

Under the same conditions two 2-pyrrolidones and one 2-piperidone have been converted to the corresponding pyrrolidines and piperidine in yields of 88–96%.

Primary amines have been found to react with 1,4- or 1,5-glycols under the conditions used for the hydrogenation of amides, to give 68–77% yields of pyrrolidines or piperidines.

The hydrogenation of di-N-*n*-amyladipamide was shown to give a 45% yield of 1-*n*-amylhexahydroazepine. Thirty-four per cent. of this material was isolated in the pure state from the di-*n*-amylamine which was formed to the extent of 41%.

Treatment of hexanediol-1,6 with benzylamine gave a 23% yield of 1-benzylhexahydroazepine which was converted to hexahydroazepine by treatment with hydrogen over copper–chromium oxide at 275°.

Two N-substituted succinimides and one glutarimide have been converted to the corre-

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[26] Kötz, *J. prakt. Chem.*, [2] **75**, 486 (1907).

[27] "Organic Syntheses," 508 (1932).

[28] Von Braun and Weissbach, *Ber.*, **64**, 1787 (1931).

[29] Auwers, Köbner and Meyerburg, *ibid.*, **24**, 2888 (1891); Day and Thorpe, *J. Chem. Soc.*, **117**, 1469 (1920); Boorman, Linstead and Rydon, *ibid.*, 573 (1933).

[30] Darbishire and Thorpe, *ibid.*, **87**, 1717 (1905).

[31] Adkins, Folkers and Wojcik, THIS JOURNAL, **54**, 1145, 4939 (1932).

sponding pyrrolidone-2 or piperidone-2 by treatment with hydrogen over Raney nickel at 200–220°.

When diethyl glutarate, or diethyl β-methyl- or β-phenyl-glutarate, was heated with four moles of a primary amine at 250°, amides were formed to the extent of 83–94%. When diethyl β,β-dimethylglutarate was so treated, yields of 39–71% of the glutarimides were formed.

Glutarimides were formed in yields of 42 to 62% by heating glutaric, β-methyl- or β-phenylglutaric acid with one mole of primary amine at 250°. This is appreciably less than the yields of succinimides obtained from succinic acid and primary amines.

An improved method for preparing diethyl glutarate has been developed.

MADISON, WIS. RECEIVED OCTOBER 1, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Rates of Alcoholysis of Acyl Chlorides

G. E. K. BRANCH AND A. C. NIXON

We have recently published the results of a study[1] in which we investigated the effect of the para-substitution of certain groups on the rates of alcoholysis of triphenylmethyl chlorides. In this paper we pointed out that predictions concerning rates in which I and T effects are used merely on the direction of electrical forces tending to prevent or assist the separation of an ion are not necessarily sound, although the actual results we obtained with the trityl chlorides could have been predicted on this basis. As we strongly suspected that this crude method of using I and T effects would be entirely erroneous when applied to the alcoholysis of acyl chlorides, we have used an identical method to measure the rates of alcoholysis of some acyl chlorides. The compounds studied are mainly para substituted benzoyl chlorides but measurements on some aliphatic compounds are also included.

We employed the same solvent as before, namely, a mixture containing by volume at 25°, 60% ether and 40% absolute ethyl alcohol. The reactions were followed by observing the rate of change of the electrical conductivity of solutions containing acid chloride. This method was used on the assumption that the hydrochloric acid produced had a much higher conductivity than any of the other constituents of the solution and hence the concentration of the acid could be determined from the conductivity of the solution by reference to a previously determined conductivity–concentration curve for hydrochloric acid. The concentration of the organic chloride at any time could then be determined as the difference between the hydrochloric acid concentration at that time and the final hydrochloric acid concentration after completion of the reaction. This method is very suitable for measuring low concentrations. We used concentrations around 0.001 *M*, and could follow the reactions accurately to more than 95% completion.

The reaction was found to be irreversible at the concentrations used since the conductivity of a 0.001 *N* hydrochloric acid in the alcohol–ether mixture was found to be unchanged by the addition of an equivalent quantity of ethyl *p*-nitrobenzoate. The irreversibility of the reaction has been shown more definitely by Norris and his co-workers,[2] who showed that ethyl *p*-nitrobenzoate was unaffected when hydrogen chloride gas was bubbled through the molten ester. Their tests also showed the absence of side reactions.

A detailed description of the method and apparatus used is given in our previous communication.[1] The method consisted essentially of mixing 20 cc. (25°) of alcohol with 30 cc. (25°) of an ether solution of the chloride at the bath temperature and then measuring the resistance of the solution at convenient intervals. The cell resistance was determined by means of the usual Wheatstone bridge arrangement, an a. c. galvanometer being used as a null instrument.

Preparation of Materials

(a) Alcohol and Ether.—These were prepared as reported previously and had within limits of error the same physical constants.

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[1] A. C. Nixon and G. E. K. Branch, THIS JOURNAL, **58**, 492 (1936).

[2] J. F. Norris, E. V. Fasce and C. J. Staud, *ibid.*, **57**, 1415 (1935).

(b) Acid Chorides.—These were obtained, whenever available, by distillation and/or crystallization of the Eastman product. In the other cases they were prepared from the pure acids by use of thionyl chloride. The melting and/or boiling points are given below. The boiling points are at 760 mm. unless otherwise specified.

Chloride	°C.
Trichloroacetyl	117–118 (b. p.)
Dichloroacetyl	108 (b. p.)
Chloroacetyl	106 (b. p.)
Acetyl	55 (b. p.)
p-NO_2-benzoyl	71.5 (m. p.)
p-F-benzoyl	70–71 (6 mm.), 8–9 (m. p.)
p-Br-benzoyl	37.5 (m. p.)
p-I-benzoyl	64.5 (m. p.)[a]
p-CH_3-benzoyl	70–71 (4 mm.)
p-CH_3O-benzoyl	21 (m. p.), 144 (b. p.)

[a] The melting points given for this compound in Beilstein range from 71 to 83° but repeated crystallization from hexane and sublimation did not change this value. It was prepared from two different lots of Eastman *p*-I-benzoic acid (m. p. 278°). It yielded 99.9% of the theoretical quantity of the methyl ester (m. p. 114.5–115.5°).

All the acid chlorides gave, within the limits of error, the theoretical quantity of hydrochloric acid upon alcoholysis as measured by conductivity.

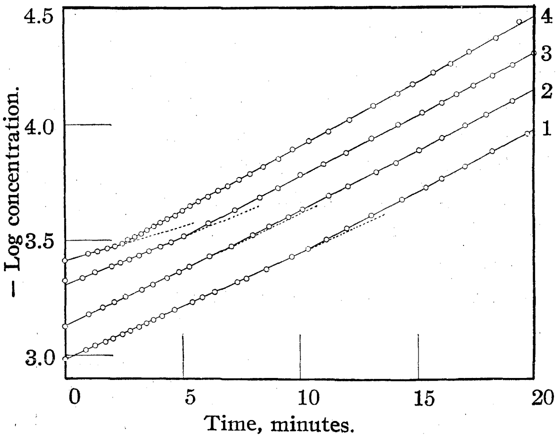


Fig. 1.—The alcoholysis of *p*-nitrobenzoyl chloride. The initial concentrations were (1) 0.00104 *M* *p*-NO_2-benzoyl chloride, (2) 0.000474 *M* *p*-NO_2-benzoyl chloride, (3) 0.000474 *M* *p*-NO_2-benzoyl chloride, 0.000493 *M* HCl, (4) 0.000388 *M* *p*-NO_2 benzoyl chloride, 0.001636 *M* HCl. The points for run (2) have been lowered by 0.2 unit. The curves are ruled lines, the dotted curves being the continuations of the ruled lines through the earlier points.

Kinetics

When the logarithms of the concentrations of the acid chlorides were plotted against the elapsed times, the straight lines characteristic of unimolecular and pseudo-unimolecular reactions were not obtained for the aromatic chlorides. Instead a plot was obtained in which the earlier points fall on one straight line and the later points on another straight line of slightly greater slope, the transition between the two being sharp. The curves in Fig. 1 for *p*-nitrobenzoyl chloride are typical examples. In Fig. 1 the negative logarithms have been plotted, so that the slopes have the same signs as unimolecular rate constants. It would appear that after some time the reaction settles down to a simple pseudo-unimolecular type. We have therefore used the final slopes multiplied by 2.303 for comparing the relative rates of reaction of the various acid chlorides. Norris and his co-workers[2] using 100% alcohol and higher concentrations of acid chlorides found the reactions to be pseudo-unimolecular over their entire course. Our conditions differ from those of Norris and co-workers since we diluted the alcohol with ether and used much smaller concentrations of acid chloride. The difference in the kinetics observed probably arises from the fact that under the conditions employed by Norris considerable hydrochloric acid had already been formed at the time of even the earliest measurements. Thus in the table given by Norris, Fasce and Staud[2] the concentration of hydrochloric acid at the time of the first measurement is 0.005 *N*, while in our experiments the first measurements are only about a hundredth of this value and the final concentrations of hydrochloric acid do not exceed 0.0021 *N*. The conditions used by Norris and co-workers, resulting as they do in simpler kinetics, are better than ours for obtaining relative rates. On the other hand, our conditions might shed some light on the beginning kinetics of the reaction. However, we do obtain approximately the same values for the relative rates of reaction as did Norris for those compounds which are common to both investigations (see Table II).

In seeking an explanation of the effect we must first eliminate the possibility that it is due to experimental error. The most obvious explanation would be that it is due to a lowering of the temperature on mixing the two solutions which would result in a smaller rate at the beginning of the reaction; however, this explanation is not tenable since the effect occurs with compounds whose reactivity is so small that several hours elapse before the final rate is attained. It could be caused by differences between the conductivities of the reaction mixture and those of the standard hydrochloric acid solutions having the same concentrations of hydrochloric acid. These differences might be due either to the conductivities of the acid chloride and ester or, more likely, to their effects on the conductivity of hydrochloric acid. The conductivity of the ester and its effect on the conductivity of hydrochloric acid is easily shown to be quite negligible, at the concentrations we employ, by direct test; but it is impossible to determine directly the effect of the acid chloride since it begins to react immediately. But, irrespective of any effect of this kind, near the end of the reaction the concentration of acid chloride is so small that its effect on the conductivity must be negligible and the observed conductivities must be correct. If the reaction is strictly first order, an extrapolation of the later portion of the curve to zero time should give the initial concentration of the acid chloride, whatever errors had been introduced in the earlier measurements. Such an extrapolation always gives an erroneously high value of the initial concentration. This shows that a real delay in the formation of hydrochloric acid occurs in the earlier stages of the reaction. In the case of acetyl chloride in which no variation from first order was observed, this extrapolation gives the correct value for the initial concentration of acid chloride.

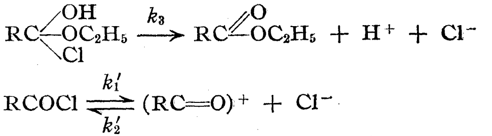
It is unlikely that the delay could be caused by impurities in the solvents such as peroxide or water since runs performed immediately after careful redistillation of the alcohol and ether gave the same results. It is also improbable that it is due to an impurity in the acid chloride since recrystallization produced no change in the effect and the addition of a small amount of the most likely impurity, the organic acid, similarly produced no change.

p-Nitrobenzoyl chloride was selected as a typical compound to use in investigating the rate changing effect and numerous runs were made with this compound under varying conditions. The average value of the constants from the initial slopes for ten runs at concentrations varying between 0.004 to 0.0021 molal was 0.1103 reciprocal minutes, having a mean deviation of 2.5% with a maximum deviation of 4.8%, while the average value for the final constant in 14 runs in the same concentration range was 0.1223 reciprocal minutes, with a mean deviation of 2.0%, the greatest deviation being 3.6%. The position of the transition point decreased from 78% completion in the most dilute solution to 31% completion for the most concentrated solution. The average values of the final constants include those of four runs in which hydrochloric acid was added initially; the values of the initial constants for these runs are not included in the former average. Hydrochloric acid has a slight catalytic effect on the reaction, not noticeable in a single run but appearing as a slight increase in the values of the final rate constants as the initial concentration of either acid chloride or hydrochloric acid is increased. Thus five runs with *p*-nitrobenzoyl chloride at 25° having an average concentration of 0.0008 *M* have an average value for k_f of 0.1205, whereas five runs having an average concentration of 0.0019 *M* show an average value for k_f of 0.1249.

When hydrochloric acid is added initially the initial rate is decreased but the final rate is attained much earlier in the reaction. This is illustrated by plots 2 and 3 in Fig. 1. In run 3 the initial concentration of *p*-nitrobenzoyl chloride was 0.000474 *M* and of hydrochloric acid 0.000493 *M*, which gave an initial constant of 0.088 and a final constant of 0.120, the change occurring at 29% completion, whereas run 2 which started with an identical quantity of acid chloride but no hydrochloric acid gave a value of 0.114 for the initial constant and 0.119 for the final constant, the change occurring at 44% completion. With larger proportions of hydrochloric acid the effect was more pronounced; run 4, in which the initial concentration of *p*-nitrobenzoyl chloride was 0.000388 *M* and of hydrochloric acid 0.001636 *M*, gave 0.069 for the value of the initial constant and 0.127 for the final constant, the transition occurring at 15% completion.

We believe that the results given above may be interpreted on the basis of a mechanism which involves two reaction paths for the acid chloride. This may be expressed as follows

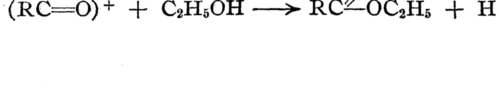
(1)



$$\mathrm{RCOCl} + \mathrm{C_2H_5OH} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{RC}\begin{matrix}\diagup\mathrm{OH}\\ -\mathrm{OC_2H_5}\\ \diagdown\mathrm{Cl}\end{matrix}$$

$$\mathrm{RC}\begin{matrix}\diagup\mathrm{OH}\\ -\mathrm{OC_2H_5}\\ \diagdown\mathrm{Cl}\end{matrix} \xrightarrow{k_3} \mathrm{RC}\begin{matrix}{/\!\!/}\mathrm{O}\\ -\mathrm{OC_2H_5}\end{matrix} + \mathrm{H^+} + \mathrm{Cl^-}$$

(2)



$$\mathrm{RCOCl} \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} \mathrm{(RC{=}O)^+} + \mathrm{Cl^-}$$

$$\mathrm{(RC{=}O)^+} + \mathrm{C_2H_5OH} \xrightarrow{k_3'} \mathrm{RC}\begin{matrix}{/\!\!/}\mathrm{O}\\ -\mathrm{OC_2H_5}\end{matrix} + \mathrm{H^+}$$

If the reaction follows the mechanism outlined above the rate of formation of products would be given by the equation

$$dP/dt = k_1(A)k_3/(k_2 + k_3) + k_1'(A)k_3'/(k_2' + k_3')(\mathrm{Cl}^-)$$

where (A) represents the concentration of acid chloride at any time after the intermediates have reached a steady state concentration. The first term on the right-hand side of the equation represents rate of formation of products through path (1) and the second term the contribution through path (2). The formation of products through path (1) increases in rate until a steady state concentration ratio of intermediate to reactant is reached, the value being $k_1/k_2 + k_3$. If the reaction forming the intermediate, and its reverse, are catalyzed by hydrogen ion but the change from intermediate to product is not, the period over which the velocity constant for path (1) increases is prolonged. Constancy is reached when k_3 becomes negligible with respect to k_2, and $k_1/k_2 + k_3$ becomes equal to K_e, the equilibrium constant for the change of reactant to intermediate. There is thus a limited catalysis by hydrogen ion as is shown by the trend in the final rate constants with increase in final concentration of hydrochloric acid. The final rates which we have obtained are probably a little lower than the maximum rates beyond which the reaction is not increased by acid. The contribution to the reaction by the second path diminishes with hydrochloric acid, and eventually is negligible. The reaction by path (1), were it the only source of electrolyte, would show a short induction period, followed by a more prolonged approach to a maximum rate. The induction period is masked by the reaction by path (2), which is then at its maximum, and the slow rise to a maximum rate of path (1) is to some extent compensated by the falling off in the rate by path (2). These factors tend to make the change from one value of $d \ln c/dt$ to another abrupt. Further, the vagaries of $d \ln c/dt$ that may exist in the earlier part of the reaction are not observable, as the accuracy is not sufficient to allow its evaluation between adjacent measurements, and one is reduced to using the slopes of the best straight lines drawn through the several points on the curve of $\log c$ against time. The apparent first order character of the earlier portion of the reaction is best considered fictitious. We do, however, believe that the lines shown in the figure are drawn through a sufficient number of points to warrant the statement that the earlier part of the reaction is slower than the later part beyond any reasonable doubt. The first order rate constants, heats of activation and probability factors which we obtain by ignoring the first part of the reaction are those for the reaction by path (1). If our theory is correct, Norris and his co-workers must also have obtained the rate constants for the reaction by path (1).

The Effects of Substituent Groups

The first order final rate constants at 0 and 25° in reciprocal minutes are given in columns 2 and 3 of Table I for all compounds for which these quantities could be obtained. The table also gives the heats of activation and the logarithms of the probability factors in the Arrhenius equation, $k = Ze^{-E/RT}$.

Table I

Reaction Rates and Heats of Activation

The values of $\log Z$ were calculated by the use of the equation $\log Z = \log k^{25} + E/2.3\,KT$, in which k^{25} is in reciprocal seconds.

Chloride	k^0, min.$^{-1}$	k^{25}, min.$^{-1}$	E, cal.	Log Z
Trichloroacetyl	(>5)	.....	....	...
Dichloroacetyl	(>5)	.....	....	...
Chloroacetyl	2.89	.....	....	...
Acetyl	0.143	0.986	12,500	7.4
p-NO$_2$-benzoyl	.0222	.1225	11,100	5.5
p-Br-benzoyl	.00167	.0134	13,450	6.2
p-Cl-benzoyl	.00145	.0123	13,850	6.5
p-I-benzoyl	.00158	.0126	13,450	6.2
p-F-benzoyl	.000761	.00732	14,650	7.8
Benzoyl	.000700	.00648	14,400	6.6
p-CH$_3$-benzoyl	.000332	.00386	15,900	7.5
p-CH$_3$O-benzoyl	.000180	.00320	18,650	9.4

Table II

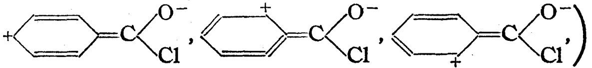
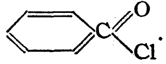
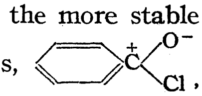
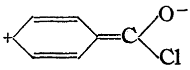
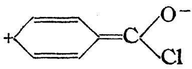
Relative Rates of Alcoholysis at 25°

Chloride	Relative rates in alcohol–ether	Relative rates in absolute alcohol	Relative rates of corresponding trityl chlorides
Trichloroacetyl	(>8000)	..	....
Dichloroacetyl	(>8000)	..	....
Chloroacetyl	(4100)	..	....
Acetyl	171	..	0.00007
p-NO$_2$-benzoyl	19.0	21.6	.011
p-Br-benzoyl	2.1	2.1	.28
p-Cl-benzoyl	1.9	1.9	.32
p-I-benzoyl	1.9	1.9	.34
p-F-benzoyl	1.1	..	.76
Benzoyl	1.0	1.0	1.0
p-CH$_3$-benzoyl	0.60	0.78	4.1
p-CH$_3$O-benzoyl	.49	.81	(>90)

From the data of Table I we have constructed Table II which gives the rates of alcoholysis, at 25°, relative to benzoyl chloride. In column 3 are given the values determined by Norris and co-workers, of the relative reactivities of a number of the same acid chlorides for the reaction in absolute alcohol. It also gives, in column 4, the rates of alcoholysis, relative to triphenylmethyl chloride, of a number of para substituted triarylmethyl chlorides the substituent groups of which are the same as the groups substituted in the benzoyl chlorides, the compounds in each row having the same substituent. Thus the rate of alcoholysis of *p*-nitrotriphenylmethyl chloride relative to that of triphenylmethyl chloride is put in the same row as the relative rate of *p*-nitrobenzoyl chloride. We have taken diphenylmethyl chloride as the analog of acetyl chloride.

It is noticed that the order we have obtained for the relative rates of alcoholysis of the acyl chlorides parallels the order obtained by Norris, except that in our solvent *p*-methoxybenzoyl reacts less rapidly than *p*-methylbenzoyl chloride, while in absolute alcohol the two reactions have approximately the same rate.

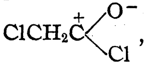
A comparison of columns 2 and 4 in Table II shows that a para substituent affects the alcoholysis of aryl acid chlorides and triarylmethyl chlorides in opposite ways. Groups that increase the rates of alcoholysis of the acid chlorides decrease those of trityl chlorides. In our preceding paper we have shown that in the trityl chlorides the influence of the para substituent follows the ability of the group to transfer a positive charge from the methyl carbon atom to the other parts of the molecule. In this way the groups assist the removal of chloride ion, and increase the rates of alcoholysis. The alcoholysis of a chloride involves not only the removal of chloride ion, but also the addition of alcohol. The influence of the group on the addition of alcohol may be opposite to its effect on the removal of chloride ion, and may be the predominant factor governing the relative rates of alcoholysis. The existence of these two factors is obvious in our suggested equation for the rates, rate = $K_e k_3 A$, in which K_e is the equilibrium constant for an addition of alcohol and k_3 the rate constant for the decomposition of the addition compound into hydrochloric acid and ester. The effect of a para substituent group on k_3 must be assumed to be in the same direction as its effect on the alcoholysis of a trityl chloride, though its magnitude may be much less, as the removal of the chloride ion is largely assisted by the tendency of the unshared electrons of the oxygen atoms to relieve the lack of electrons induced on the carbonyl carbon atom by the removal of chloride ion.

The effect of a para substituent group on K_e is best understood if one uses the combination formula,   instead of the classical formula  The above resonance stabilizes the acid chloride, and does so to a greater degree the more stable the internally ionized structures,   etc., are. In this way the resonance decreases K_e, as it is absent or negligible in the addition compound. Any para substituent which by the direction of its group dipole or by a resonance increases the stability of the structure  decreases the value of K_e. Examples of such groups are CH_3 and OCH_3. On the other hand, strongly negative groups increase the value of K_e. In this way the effect of a para substituent on K_e is opposite to its effect on the velocity constant of alcoholysis of a trityl chloride, or on k_3.

Whether the effect of a para substituent on K_e or on k_3 will be the predominant factor in the alcoholysis can only be decided by experiment. Our experiments show that the first factor is predominant for groups having effects within the range studied. Outside of this range it is possible for the influence on k_3 to become the predominant factor, in which case the order of alcoholysis rates of the acid chlorides would follow those of the trityl chlorides. This possibility is suggested in our results. The increase of rate from *p*-methylbenzoyl chloride to *p*-nitrobenzoyl chloride is thirty-fold, the increase in rate from *p*-nitrotriphenylmethyl chloride to *p*-methyltriphenylmethyl chloride is somewhat larger, about four hundred-fold, but the increase of rates from *p*-methoxy to *p*-methylbenzoyl chloride is only 20% which is very much smaller than the twenty-fold increase from *p*-methyltriphenyl chloride to *p*-methoxytriphenylmethyl chloride. Under the conditions used by Norris and his co-workers *p*-methoxybenzoyl chloride reacts as rapidly as *p*-methylbenzoyl chloride.

We have avoided consideration of ortho groups.

In these derivatives the substituent and reacting groups are brought into very close proximity, and what might be called O-effects are introduced. Norris' results and previous work on so-called "steric hindrances" indicate that O-effects are greatly enhanced by duplication. The alcoholysis rates of 2,4,6-trisubstituted benzoyl chlorides[3] have entirely different orders of magnitude to those of the monosubstituted derivatives. These trisubstituted benzoyl chlorides may react either very much faster or very much slower than the monosubstituted compounds.

The work on the trityl chlorides shows that the phenyl group can lower the positive potential of an adjacent atom more than the methyl group can. Assuming that the addition of alcohol is still the predominant factor, the alcoholysis rates of aliphatic acid chlorides should be faster than those of the aromatic. In chloroacetyl chloride the potential energy of the internally ionized form,  $ClCH_2\overset{+}{C}\left\langle\begin{matrix}O^-\\Cl\end{matrix}\right.$, is increased by the dipole of the α-chlorine atom, its + pole being directed toward the carbonyl carbon atom. This decreases the resonance, and increases the rate of alcoholysis. Further introduction of chlorine atoms should still further increase the rate. These relationships were found, except that di- and trichloroacetyl chlorides reacted so rapidly that it was impossible to determine which was the more reactive.

Heats of Activation

The heats of activation given in Table I were calculated from the values of the final rate constants determined at 0 and 25° by solving for E in the equation $\ln k = \ln Z - E/RT$.

There is a rough correlation between low activation energy and rapid reaction in the alcoholysis of the acid chlorides. In the aromatic compounds the differences in the rates cannot be attributed only to the differences in the heats of activation. In general the differences in the rates are much smaller than would be expected from the differences in the activation energies. This can be seen by comparing the probability factors (Z). These show a trend, being higher for the slower reactions. For instance, if we divide the reactions into four classes, (1) the very fast reaction, that of p-nitrobenzoyl chloride, (2) the moderate reactions, those of para Cl, Br and I benzoyl chlorides, (3) the slow reactions, those of p-F and benzoyl chlorides, and (4) the slowest reactions, those of p-CH_3 and OCH_3, the average values of log Z for these classes are 5.5, 6.3, 7.2 and 8.4. Although errors accumulate in the determination of Z, this trend lies well beyond the experimental limits. In the alcoholysis of the trityl compounds this trend is not noticeable, the figures for the corresponding compounds, in that series, being 8.4, 7.5, 7.9 and 8.0. (The value for the methoxy compound was not obtained.) For acetyl chloride the value of log Z is 7.4, that is, the value is much higher than that of the slower reacting p-nitrobenzoyl chloride. The value of E is also greater for acetyl chloride than it is for the nitrobenzoyl chloride, the difference being greater than any likely experimental error.

The values of Z for the alcoholyses of the acid chlorides are much less than those usually found for reactions of ions with neutral molecules. The alcoholyses of acid chlorides belong to Moelwyn-Hughes' class of slow reactions.

Summary

The rates of alcoholysis of several acyl chlorides have been measured, at great dilutions, in a mixture of 60% ether and 40% alcohol.

The kinetics of the reaction and the relative reactivities of the acyl chlorides are discussed.

Berkeley, Calif. Received September 8, 1936

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[3] J. F. Norris and H. H. Young, This Journal, **57**, 1420 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XVII. Some Heat Capacity, Entropy and Free Energy Data for Five Higher Olefins[1]

BY GEORGE S. PARKS, SAMUEL S. TODD AND C. HOWARD SHOMATE

The heats of hydrogenation of some representative olefins have recently been measured with remarkable accuracy by Kistiakowsky[2] and his collaborators; and in this connection they have kindly loaned us samples of these compounds for the determination of the heat capacities at low temperatures and thereby the calculation of the corresponding entropies and free energies of formation. In the present study we shall present data for *n*-heptene-1, 1,4-pentadiene, tetramethylethylene and the two diisobutylene isomers.

Materials

The preparation and properties of the *n*-heptene-1, 1,4-pentadiene and tetramethylethylene have already been described by Kistiakowsky, Ruhoff, Smith and Vaughan.[2] From the change in melting point during our fusion determinations we have estimated the purity of the heptene-1 to be at least 99.85 mole % and that of the pentadiene 99.90 mole %. While the purity of the tetramethylethylene was probably of a similar high order, a quantitative estimate in this case was prevented by the existence of a transition between its two crystalline forms at a temperature only 1.9° below the melting point, 198.5°K. Incidentally this proximity of the transition and melting points enabled us to perform an interesting qualitative experiment in which a narrow tube containing the olefin was immersed in an alcohol-bath cooled with solid carbon dioxide. By careful maintenance of a suitable temperature gradient in the bath it was then possible to obtain, coexistent in the tube, (1) a supernatant layer of liquid tetramethylethylene, (2) a middle layer of the crystals melting at 198.5° and (3) a bottom layer of the low temperature crystals.

The Harvard investigators also separated the two diisobutylene isomers from a large quantity of commercial material by a series of careful fractional distillations. As they will describe the properties of these compounds in detail in a subsequent paper, we shall simply say here that our fusion determinations indicated a purity of about 99.5 mole % for the low boiling isomer (supposedly 2,4,4-trimethylpentene-1) and about 98 mole % for the high boiling isomer (supposedly 2,4,4-trimethylpentene-2).

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in other places.[3] In view of the accuracy of the various measurements involved, the error in the experimental values thereby obtained is probably less than 0.5% at all temperatures.

These heat capacity data, expressed in terms of the defined calorie[4] and with all weights reduced to a vacuum basis, appear in Tables I and II. The specific heat values are also represented

TABLE I

SPECIFIC HEATS IN CALORIES PER GRAM OF SUBSTANCE

T, °K.	C_p	*T*, °K.	C_p	*T*, °K.	C_p
		n-Heptene-1: Crystals			
80.4	0.1841	105.0	0.2215	128.9	0.2518
85.6	.1922	112.3	.2317	135.8	.2617
91.8	.2017	121.1	.2436	142.7	.2726
98.2	.2120				
		Liquid			
151.1	0.4383	196.9	0.4485	242.5	0.4719
155.5	.4378	201.9	.4515	256.8	.4819
159.8	.4387	206.1	.4511	261.2	.4855
166.5	.4409	215.1	.4557	274.9	.4983
174.8	.4400	219.3	.4588	280.4	.5033
181.1	.4421	234.2	.4656	287.6	.5092
186.2	.4436	238.3	.4695	295.1	.5181
		1,4-Pentadiene: Crystals			
82.4	0.2197	101.0	0.2553	110.7	0.2782
88.3	.2308	103.9	.2620	117.2	.2970
94.5	.2424				
		Liquid			
125.4	0.4506	188.2	0.4471	255.6	0.4830
131.6	.4469	194.6	.4498	260.7	.4870
137.6	.4454	200.3	.4526	265.7	.4913
149.5	.4438	214.4	.4587	275.3	.5002
155.5	.4437	219.7	.4609	284.9	.5065
161.7	.4429	225.0	.4630	288.7	.5091
177.4	.4456	238.4	.4709	292.5	.5144
182.6	.4468	243.6	.4742		
		Tetramethylethylene: Crystals			
82.6	0.2222	115.0	0.2824	156.3	0.3453
87.5	.2330	123.0	.2939	164.7	.3610
93.8	.2461	131.6	.3089	171.6	.3774
101.2	.2596	140.7	.3220	178.2	.3977
108.1	.2709	148.6	.3340	184.2	.4130

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(1) This investigation represents a continuation of Project No. 29 of the American Petroleum Institute Research. Financial assistance in this work has been received from a fund donated jointly by the Standard Oil Company of California and the Shell Development Company.

(2) Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 876 (1935); **58**, 137, 146 (1936).

(3) Parks, *ibid.*, **47**, 338 (1925); also Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

(4) The factor 1.0004/4.185 has been used in converting the international joule to the calorie (defined unit).

TABLE I (*Concluded*)

T, °K.	C_p	*T*, °K.	C_p	*T*, °K.	C_p
		Liquid			
202.4	0.4395	232.3	0.4522	277.0	0.4829
209.8	.4412	241.9	.4570	282.8	.4877
214.6	.4430	247.3	.4605	291.2	.4955
226.8	.4492	263.9	.4722	295.5	.4991
		Diisobutylene (low boiling isomer): Crystals			
80.9	0.1674	111.8	0.2302	148.1	0.2804
86.5	.1765	119.8	.2395	154.2	.2891
92.6	.1884	127.1	.2502	160.3	.3026
98.4	.2091	134.6	.2608	165.8	.3242
105.2	.2220	141.2	.2700		
		Liquid			
178.4	0.4043	216.4	0.4288	265.2	0.4691
187.1	.4102	222.1	.4338	275.2	.4783
192.6	.4137	235.7	.4431	280.9	.4844
200.8	.4185	253.3	.4575	288.3	.4919
206.1	.4227	259.5	.4637	296.0	.5013
		Diisobutylene (high boiling isomer): Crystals			
81.1	0.1761	104.3	0.2295	131.0	0.2789
86.5	.1853	111.3	.2409	137.6	.2986
92.3	.1962	116.8	.2487	143.8	.3256
98.1	.2095	123.9	.2604		
		Liquid			
170.0	0.4085	216.7	0.4411	260.8	0.4744
175.0	.4121	222.1	.4445	276.3	.4898
190.8	.4233	236.7	.4551	282.1	.4952
200.3	.4293	241.9	.4585	289.6	.5021
205.6	.4335	255.6	.4696	298.6	.5116

TABLE II

FUSION DATA

Substance	M. p., °K.	Heat of fusion (cal. per g.) I	II	Mean
n-Heptene-1	153.4	30.77	30.86	30.82
1,4-Pentadiene	124.3	21.55	21.54	21.55
Tetramethylethylene	198.5	15.50	15.53	15.51
Diisobutylene, l. b.	178.9	18.68	18.67	18.67
Diisobutylene, h. b.	166	14.44	14.49	14.47

graphically in Figs. 1 and 2. It is interesting to note that the curve for liquid pentadiene shows a marked minimum similar to that found previously with butene-1, *cis*-butene-2 and propylene.[5] Another noteworthy point is that the specific heat curves for both diisobutylene isomers exhibit some sort of minor transition with a slight but appreciable rise at about 101°K. The heat effect associated with this transition seemed almost negligible—1.85 cal. per mole in the case of the low boiling isomer. A sample of diisobutylene, which was in reality a mixture of the isomers with the low boiling predominating, has been studied previously by Parks and Huffman.[6] In the present case our values for the low boiling compound agree for the most part to within 1% with these earlier, less reliable data.

In the calculation of the fusion values, the somewhat more rapid rise in the specific heat of the crystals as the melting point is approached was attributed to premelting; and the heat absorbed in this region in excess of that obtained by extrapolation of the specific heat data at lower temperatures was added to the heat absorbed at the melting point. In the case of tetramethylethylene the transition point in the crystals at 196.6°K. was so close to the melting point that entirely independent determinations of the heat of transition and heat of fusion were impractical. Accordingly the sum of these heat effects was measured and from the relative time intervals for these two steps the fusion results in Table II were then derived. The corresponding values obtained for the heat of transition of tetramethylethylene were: I, 13.00 cal.; II, 13.01 cal.; mean, 13.00 cal. per g.

Entropy Data

Using the heat capacity data contained in the preceding section in conjunction with the third law of thermodynamics, we have calculated the entropies at 298.1°K. for these five substances. The detailed entropy values are given in Table III. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman[7] for estimating the entropy increases for the crystals (Column 2) from 0 to 80°K. The various increments from 80 to 298.1°K., which appear in the next three columns, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree per mole are then given in the sixth column under the heading "S°_{298} olefin"; they are probably reliable to within 1.0 e. u. in an absolute sense and to 0.5 e. u. for comparative purposes.

In the seventh column of Table III we have tabulated entropy values,[6,8] derived previously in this Laboratory, for *n*-heptane, *n*-pentane, and 2,2,4-trimethylpentane, the paraffin hydrocarbons produced on the hydrogenation of four of these olefins. The last column then shows the

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[5] Todd and Parks, THIS JOURNAL, **58**, 134 (1936).

[6] Parks and Huffman, *ibid.*, **52**, 4381 (1930).

[7] Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

[8] Parks, Huffman and Thomas, THIS JOURNAL, **52**, 1032 (1930). Corrections made since this earlier publication have altered the entropy values for *n*-heptane and 2,2,4-trimethylpentane by −0.1 to +0.2 e. u., respectively.

TABLE III

ENTROPIES OF THE LIQUID OLEFINS PER MOLE

Substance	Crystals		Fusion	Liquid	S°_{298} olefin	S°_{298} paraffin	ΔS paraffin–olefin
	0–80°K.	Above 80°K.					
n-Heptene-1	14.00	14.70	19.71	30.18	78.6	78.8	0.2
1,4-Pentadiene	11.26	7.65	11.80	27.44	58.2	62.0	1.9 × 2
Tetramethylethylene	13.97	23.24	12.13[a]	15.80	65.1	..	.....
Diisobutylene, low boiling	14.28	21.79	11.70	25.44	73.2	75.4	2.2
Diisobutylene, high boiling	14.94	20.10	9.77	29.68	74.5	75.4	0.9

[a] This value includes the entropy of transition (5.56 e. u.) between the two crystalline forms at 196.6°K.

differences between the molal entropies of these corresponding paraffins and olefins or, in other words, the entropy decreases for the formation of the olefin double bond. Undoubtedly this effect depends considerably upon the position of the double bond in the molecule and upon symmetry considerations.[9] In the present case the average entropy decrease per double bond is 1.4 e. u. and this figure, while it cannot be considered very significant, is probably preferable to the decrease of 2.7 e. u. suggested previously by Parks and Huffman[6] from data pertaining mainly to crystalline unsaturated acids and various cyclic compounds.

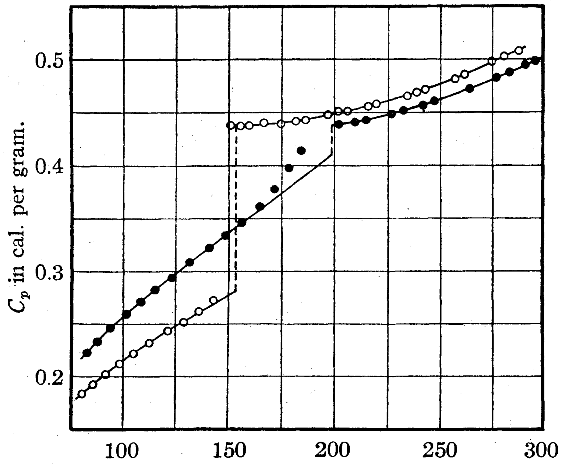

Fig. 1.—The specific heat curves for *n*-heptene-1 (circles) and tetramethylethylene (heavy dots).

Free Energy Data

We have also calculated the free energies of formation of four of these olefins in the liquid state by means of the fundamental equation, $\Delta F = \Delta H - T\Delta S$. The essential thermal data are given in Table IV.

TABLE IV

THERMAL DATA AT 298.1°K. FOR THE OLEFINS

In calories per mole with all weights reduced to a vacuum basis.

Substance	ΔH°_{298}, cal.	ΔS°_{298}, e. u.	ΔF°_{298}, cal.
n-Heptene-1 (l)	−25,520	−149.5	19,050
1,4-Pentadiene (l)	18,060	− 73.5	39,970
Diisobutylene l. b. (l)	−36,360	−187.5	19,530
Diisobutylene h. b. (l)	−35,250	−186.2	20,260

The values for the ΔH°_{298} of formation of these compounds were obtained by a combination of the ΔH°_{298} values for the corresponding or parent paraffins with the heats of hydrogenation of Kistiakowsky and collaborators.[10] The heats of formation of these particular liquid paraffins have already been calculated by Parks[11] with the aid of the highly accurate combustion data obtained in recent years by Rossini and his collaborators at the U. S. Bureau of Standards. To these values for the parent paraffins we have then added

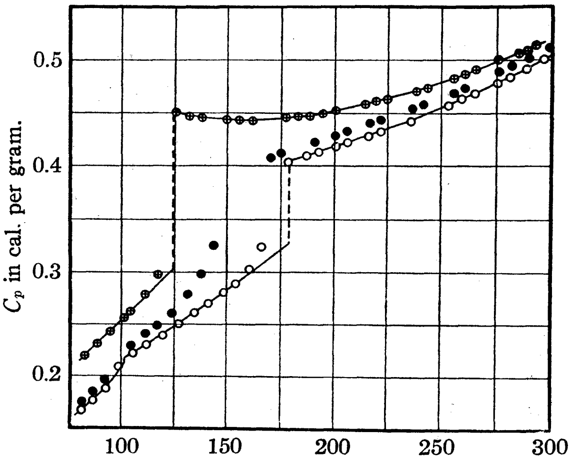

Fig. 2.—The specific heat curves for 1,4-pentadiene (crossed circles) and the low boiling diisobutylene (plain circles). The specific heat values for the high boiling diisobutylene (m. p. 166°) are represented by the heavy dots without a curve.

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(9) In this connection see Kassel, *J. Chem. Phys.*, **4**, 435 (1936).

(10) The heats of hydrogenation for the diisobutylene isomers have not been published yet. A private communication from the Harvard laboratory gives these as 27,236 cal. per mole for the low-boiling and 28,352 cal. per mole for the high-boiling isomer in the gas phase at 355°K. In the latter case there is considerable uncertainty as to the effect of the impurities on this hydrogenation value. The data for the three other olefins are available in ref. 2.

(11) Parks, *Chem. Rev.*, **18**, 325 (1935).

Kistiakowsky's hydrogenation results, reduced by a uniform 250 cal. (500 cal. in the case of pentadiene) to convert the data from 355 to 298° K. In this connection we have assumed that these heats of hydrogenation, although determined for the gas-phase reaction, can be applied without alteration to the process involving the hydrocarbons in the pure liquid state.

The ΔS°_{298} values represent simply the differences between the S°_{298} for each olefin and the corresponding values for the entropies of the elements contained therein. For this purpose we have used 15.615 e. u.[12] for the entropy of $^1/_2H_2$ and 1.36 e. u.[13] for C (β-graphite).

The molal free energies appear in the last column of the table. The errors in these values are probably within 800 cal. for *n*-heptene-1 and 1,4-pentadiene, within 1500 cal. for low boiling diisobutylene and within 2000 cal. for high boiling diisobutylene.

Comparing the free energy of heptene-1 with that calculated by Parks[11,8] for *n*-heptane, we find $\Delta F^\circ_{298} = 20{,}620$ cal. for the dehydrogenation process

$$n\text{-heptane} \longrightarrow n\text{-heptene-1} + H_2$$

Likewise in the case of 1,4-pentadiene and *n*-pentane the difference is 2 times 21,400 cal. Previously Parks[11] has estimated 21,040 cal. and 21,360 cal., respectively, for the propylene–propane and butene-1–*n*-butane differences. Hence, the free energy change in the formation of a normal α olefin by dehydrogenation of a paraffin is apparently around 21,000 cal. irrespective of the length of the paraffin chain.

The addition of more methyl or other radicals to the carbon atoms adjacent to the double bond, however, leads to definitely lower values for this ΔF°_{298} of dehydrogenation. Thus with branched molecules, such as isobutene and 2,4,4-trimethylpentene-1, the free energy difference drops noticeably, being 18,180 cal. in the latter case. The same trend appears also when the double bond is shifted from the α- to the β-position, as shown by Todd and Parks[5] in the cases of *cis*- and *trans*–butene-2. Next with the trimethylethylene–methylbutane combination, involving three methyl substituents on the ethylene group, we calculate $\Delta F^\circ_{298} = 17{,}360$ cal., using the hydrogenation data of the Harvard laboratory[2] in conjunction with the proper experimental entropy values.[14] Of course, the end-point in this series is the tetramethylethylene–tetramethylethane combination for which an exact calculation of the ΔF°_{298} of dehydrogenation is at present impossible in the absence of an experimental entropy value for the paraffin compound. However, for the dehydrogenation in this case ΔH°_{298} is only 26,380 cal. and, if we assume equal entropies for the olefin and parent paraffin (an assumption that cannot involve us in any serious error), ΔF°_{298} is estimated as approximately 17,100 cal.—a figure about 4000 cal. lower than with the dehydrogenations that yield the normal α olefins. In other words, with additional spatial protection to the ethylene group the olefins become progressively less unstable with reference to the parent paraffin hydrocarbons.

Summary

1. The specific heats of *n*-heptene-1, 1,4-pentadiene, tetramethylethylene and the two diisobutylene isomers have been measured between 80 and 298°K. The corresponding heats of fusion have also been determined.

2. The entropies of these five olefins in the liquid state at 298.1°K. have been calculated from the foregoing heat capacity data.

3. The corresponding free energies (except in the case of tetramethylethylene) have also been calculated. Among the α olefins the free energy difference between an olefin and the corresponding paraffin is uniformly about 21,000 cal. As the number of radicals attached to the carbon atoms of the ethylene linkage increases this free energy of dehydrogenation falls off progressively to about 17,100 cal. as a limit.

STANFORD UNIVERSITY, CALIF.

RECEIVED OCTOBER 19, 1936

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[12] Giauque, THIS JOURNAL, **52**, 4825 (1930).

[13] Jacobs and Parks, *ibid.*, **56**, 1513 (1934).

[14] It should be noted here that S°_{298} for liquid 2-methylbutane is 59.5 e. u. instead of 60.8 e. u., as erroneously reported in References 6 and 8.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF UNION COLLEGE]

Heats of Solution and Heats of Reaction on Liquid Ammonia[1]

BY FREDERIC C. SCHMIDT, JOSEPH SOTTYSIAK AND HERMAN D. KLUGE

In order to study more thoroughly the properties of electrolytes and other compounds in aqueous solution, thermochemical characteristics of these solutions have been examined. Among these, the heats of solution and dilution have been determined experimentally. Such data are scarce in the study of the properties of liquid ammonia solutions.

Kraus and Ridderhof designed a liquid ammonia calorimeter and some heats of solution and reaction were measured.[2]

In the present work the authors have made some measurements of the heats of solution of several electrolytes and non-electrolytes over a fairly wide range of concentrations with this same calorimeter. From the curves obtained the heats of dilution may be calculated.

Experimental Details

The calorimeter described by Kraus and Ridderhof[2] was used and was further improved by silvering, thus making the correction for the heat flow out of or into the instrument practically negligible. The new radiation constant was found to be 0.125 cal./deg./min. The other constants and the experimental procedure were the same as in the earlier investigation of Kraus and Schmidt.[3]

Temperatures were measured by means of a copper–constantan thermocouple (0.0385 mv./deg.) similar to that of Kraus and Prescott,[3] in conjunction with a "Queen" potentiometer and a matched sensitive galvanometer. Temperatures were read directly from the calibration curve of this thermocouple and were accurate to 0.01°; the heat capacity of the calorimeter being 6.73 cal. The error in heat measurement was 0.33 cal. The calorimeter contained 24.89 g. of liquid ammonia.

The heats of solution of ammonium bromide and ammonium chloride; lead iodide and absolute ethyl alcohol were measured over the maximum range of concentration allowed by the construction of the calorimeter. Trial heat effects were made on a few other electrolytes and on pyridine. The ammonium salts were of reagent quality and were recrystallized three times from distilled water. They were pumped and dried at 100° to constant weight. The ethanol was dried over lime and then anhydrous copper sulfate. It was then distilled into weighed bulbs out of contact with the air, and introduced directly into the calorimeter for measurement.

Experimental Results

The heats of solution of ammonium chloride and ammonium bromide are presented in Table I, those for absolute ethyl alcohol in Table II, and those of lead iodide and miscellaneous compounds in Table III.

TABLE I

MOLAR HEATS OF SOLUTION OF AMMONIUM CHLORIDE AND BROMIDE

Wt., g.	Mols NH_3 per mol salt	Obsd. heat effect	Molar heat effect
	(A) AMMONIUM CHLORIDE		
0.2888	270.5	36.5	6754
.4592	169.6	57.3	6663
.7710	101.6	93.3	6475
.7773	99.8	96.6	6652
1.2599	61.2	146.9	6240
1.4486	53.1	166.9	6165
1.5547	49.4	174.3	5993
1.5559	49.3	176.9	6083
1.7948	42.7	196.9	5870
2.5665	29.6	240.4	5009
3.0565	25.4	258.9	4532
	(B) AMMONIUM BROMIDE		
0.4957	228.4	52.6	10435
.8101	175.4	83.3	10066
1.2523	112.9	121.6	9512
1.4959	94.4	135.5	8873
1.8070	78.0	157.9	8560
2.4423	57.4	195.9	7858

TABLE II

MOLAR HEATS OF SOLUTION OF ABSOLUTE ETHANOL

Wt. sample, g.	Mols NH_3 per mol alcohol	Obsd. heat effect	Molar heat effect
2.3784	28.3	60.9	1180
2.1062	32.0	52.0	1137
1.8322	36.8	43.3	1086
1.7695	38.0	42.5	1160
1.6539	40.8	36.6	1020
1.4357	46.9	25.0	803
1.4327	47.0	27.0	867
1.3139	51.3	15.0	530

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(1) This present investigation was made possible by a Grant-in-Aid from the Society of the Sigma Xi and by aid received from the Warren Fund of the American Academy of Arts and Sciences.

(2) C. A. Kraus and J. A. Ridderhof, THIS JOURNAL, **56**, 79 (1934).

(3) Kraus and Schmidt, *ibid.*, **56**, 2297 (1934); Kraus and Prescott, *ibid.*, **56**, 86 (1934).

TABLE III

SOME MOLAR HEATS OF SOLUTION

Subs.	Wt., g.	NH_3 vap. g.,	Obsd. heat effect	Molar heat effect
Lead iodide	2.4281	0.4077	137.0	26020
Lead iodide	2.1772	.3429	123.5	26151
Lead iodide	1.0755	.1616	63.8	27370
Lead iodide	0.7733	.1067	45.9	27360
Mercuric iodide	2.0202	.2598	97.0	20123
Lithium iodide	0.9225	.3231	124.7	18090
Lithium bromide	.5454	.3317	123.8	19715
Rb bromide	.6271	.0000	1.7	440
Pyridine	1.1150	.0000	−17.6	−1250

Discussion

As will be noted on examining Fig. 1, the heats of solution of the ammonium salts vary regularly over the range of concentration measured, increasing with decreasing concentration. These curves are similar to the heat of solution curves of the strong acids in aqueous solution. These results are in accord with the view that the ammonium salts are ammoniated acids in the nitrogen system of compounds.[4]

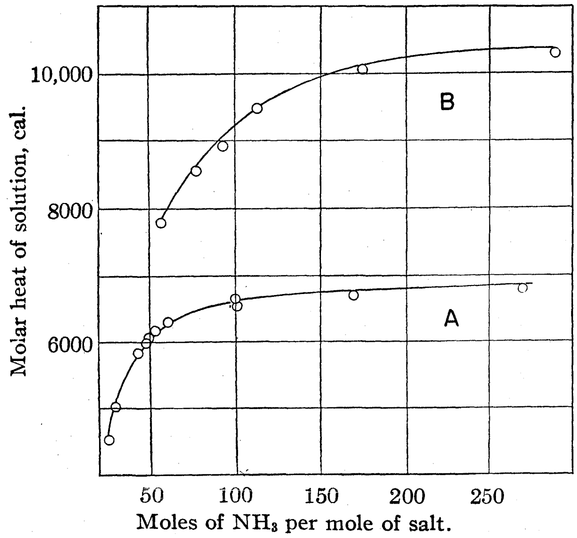

Fig. 1.—Showing variation in the molar heat of solution with concentration: (A) ammonium chloride; (B) ammonium bromide.

From these heat of solution curves it is possible to obtain the heats of dilution of these salts in liquid ammonia. The heat of solution of ammonium chloride in dilute solution is approaching 6800 calories per mole, while that of ammonium bromide at infinite dilution has a value of about 10,500 calories per mole. The absolute ethanol shows also a positive molar heat of solution which varies decidedly with the concentration. The slope of the curve for this compound, as is shown by Fig. 2, is negative. Ethanol has a negative heat of dilution in contrast with the positive dilution heat effect displayed by the ammonium salts. Apparently, energy must be supplied in order to disassociate the ethyl alcohol aggregates as the solution is diluted. The heats of solution of lead iodide, mercuric iodide and the lithium salts are high and are of the order of magnitude of heats of reaction. The lead and mercury salts are known to react with ammonia to form fairly stable ammoniates. The lithium salts, no doubt, show a high heat effect due to the solvation of the positive lithium ion with ammonia molecules. Metallic lithium itself has the highest heat of solution in liquid ammonia of all the alkali metals measured so far.[3]

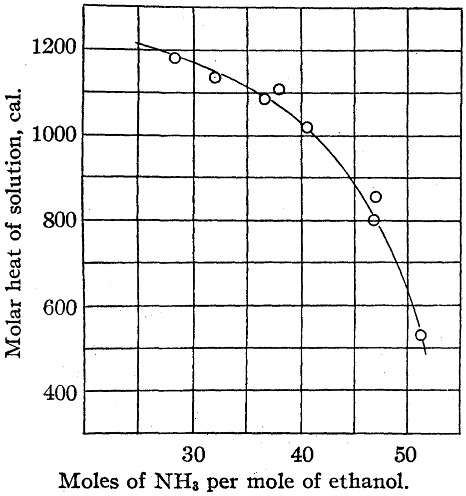

Fig. 2.—Showing variation in the heat of solution of ethanol with the concentration.

The authors wish to thank Dr. C. A. Kraus of Brown University for his kindness in the loan of the liquid ammonia calorimeter.

Summary

The molar heats of solution of ammonium chloride and ammonium bromide have been measured in liquid ammonia over a fairly wide range of concentration and show a marked heat of dilution.

The molar heat of solution of ethyl alcohol has been measured over a range of concentration and it has been shown that this compound has a decided negative heat of dilution.

SCHENECTADY, N. Y. RECEIVED AUGUST 22, 1936

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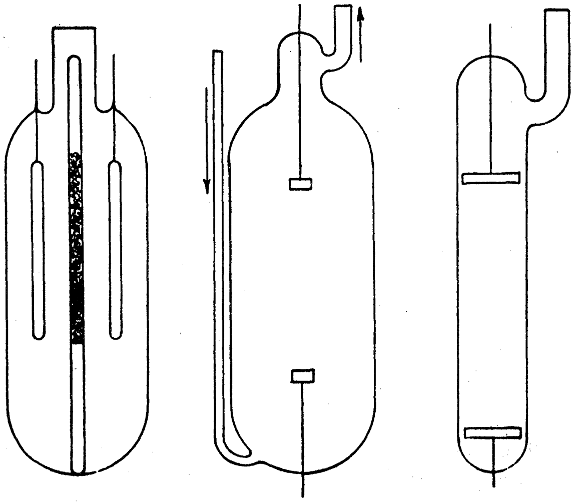
[4] Franklin, "Nitrogen System of Compounds," Reinhold Publishing Corp., New York, 1935, p. 26.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Oxidation of Selenium in the Glow Discharge. II. A Study of Variables and Further Characterization of Product[1]

BY EARL OLSON AND V. W. MELOCHE

In a previous study of the oxidation of selenium in the glow discharge,[2] it was found that a mixture of selenium dioxide and selenium trioxide was produced. Since very little was known concerning the mechanism of the reaction, it was thought that the study could be extended profitably. The present paper includes a description of the effect of variables, pressure, current, electrode distance, shape of tube, and distance of selenium from the electrodes on the production of selenium trioxide, and also gives some general facts concerning chemical action in the glow discharge.



Tube I Tube II Tube III

Fig. 1.

Apparatus.—The apparatus was essentially the same as that used by Kramer and Meloche.[2] A 25,000-volt transformer served as the source of alternating current. For direct current, a single phase full wave rectifier circuit (two RCA-866 tubes) was used. Three types of discharge tubes were used in this investigation.

Materials and Analysis.—The preparation of materials and the methods of analysis are the same as the ones described by Kramer and Meloche. Ordinary analytical methods were later augmented by X-ray examination of the product.

Procedure.—In general, the procedure used was the same as that described by Kramer and Meloche, *viz.*, elementary selenium was supported between the two electrodes of a tube and subjected to the glow discharge at a definite oxygen pressure, the walls of the tube being at the temperature of liquid air. In order to provide a constant pressure for a given experiment, pure dry oxygen was allowed to enter the apparatus through a Hoke micro-valve at such a rate that the inflow of oxygen was balanced by its removal with the pumps. It should be noted that it was possible to pass a current of oxygen into the bottom of tube II by sealing the small side-arm to the micro-valve and sealing the large exit to the pump line of the apparatus. In this manner a current of oxygen passed over the sample whereas in tubes I and III the oxygen reached the sample by diffusion. Other details of procedure will be given in connection with the individual experiments.

Effect of Pressure.—Using tube I, a 25,000-volt transformer and a constant alternating current of 44 m. a., elementary selenium was melted on a rod which was supported in a vertical position between the electrodes and subjected to the action of oxygen at a definite pressure. The curves shown in Fig. 2 represent the analyses of various products which were obtained at various pressures of oxygen.

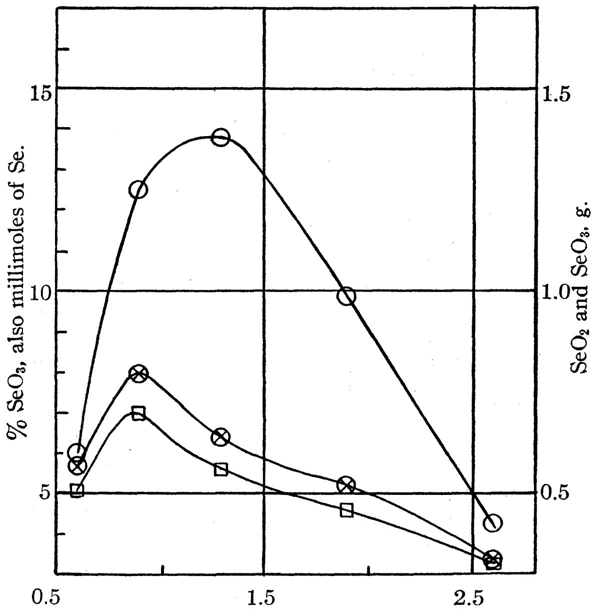


Fig. 2.—○, % SeO_3; ⊗, SeO_2 and SeO_3, g.; □, millimoles of Se.

Kramer and Meloche have reported a maximum in selenium trioxide concentration at a pressure of 1.2 mm. This maximum is shown in Fig. 2 at 1.1 mm. Curves 2 and 3 show the variation of weight of product and the variation of millimoles of selenium in the product with the change in pressure. For these two curves, maxima are found at 0.9 mm. pressure. A difference in the maxima for

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(1) This investigation was supported in part by the Wisconsin Alumni Research Foundation. This paper is presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Kramer and Meloche, THIS JOURNAL, **56**, 1081 (1934).

curves 2 and 3 as contrasted to curve 1 is to be expected since the weight of product depends primarily upon the vaporization of selenium while the percentage of selenium trioxide depends upon both vaporization and activation of selenium.

Two factors affect the vaporization of selenium, thermal radiation from the cathode and electron bombardment. The percentage of selenium trioxide depends to a large extent upon activation by electron bombardment after vaporization. Using tube I, thermal vaporization of selenium is greatest at 0.9 mm. Maximum activation of the selenium is obtained at 1.1 mm. pressure.

Maxima may also be noted in Fig. 3. In this case tube II was used and selenium was suspended on a glass holder midway between the electrodes. The maximum concentration of selenium trioxide was produced at 0.8 mm. pressure. Since the electrodes were farther apart than in tube I, a lower pressure was required to keep the selenium vapor in the negative glow, which is the most reactive region of the discharge.

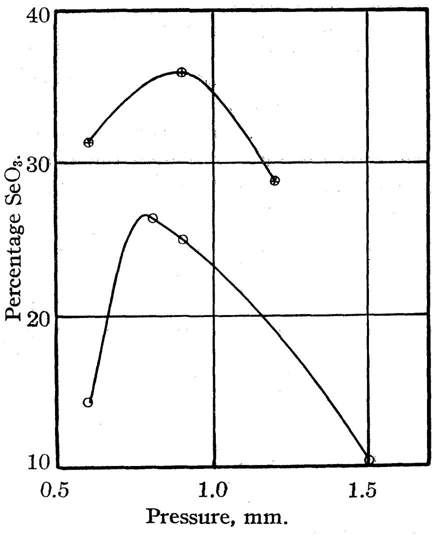

Fig. 3.

Shape of the Tube.—The curves of Fig. 2 using tube I and of Fig. 3 using tube II show that a higher concentration of selenium trioxide was obtained in tube II, identical conditions of current and temperature having been maintained. This was probably due to the fact that the electrodes in tube II were smaller than those in tube I and since the discharge column in tube II was smaller, the current density was higher.

When tube III was used, large amounts of selenium were found mixed with the oxides of selenium. In this tube, the walls were very close to the discharge column. It is therefore likely that some of the deposited product was decomposed or that some elementary selenium condensed on the walls before combination with oxygen could occur.

Still another factor exists other than the proximity of the walls to the region of glow. As has been noted, the small side-arm of tube II could be connected to the Hoke microvalve and the large opening of the tube could be connected to the pump side of the apparatus, thereby making it possible to have a positive flow of oxygen through the tube in the direction of the pumps. It was also possible to seal off the small side-arm and when the large outlet of the reaction tube was sealed to the system, the oxygen reached the sample by diffusion. In Fig. 2, the upper curve shows that a steady flow of oxygen through tube II caused a marked increase in the percentage of selenium trioxide. The lower curve represents results obtained when the oxygen diffused into the tube. If it may be assumed that the flow of oxygen through the tube provides an excess of unactivated oxygen, whereas, in the second case, the oxygen diffuses into the tube and is largely activated, the above results probably indicate that selenium combines more readily with unactivated oxygen than with activated oxygen to form selenium trioxide.

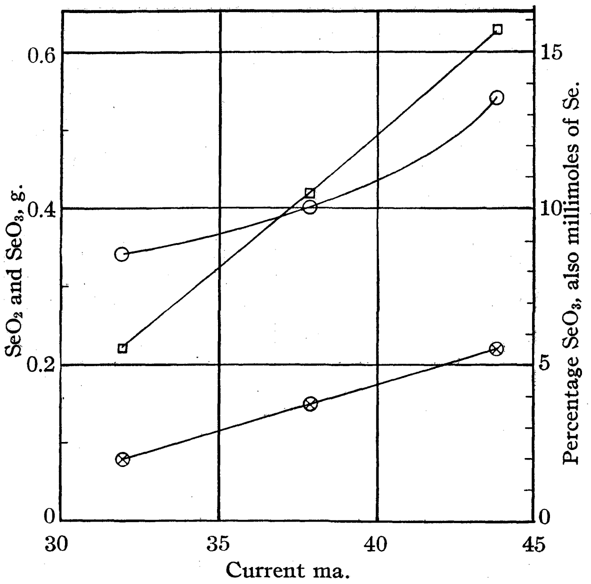

Fig. 4.—○, Percentage SeO_3; ⊗, millimoles of Se; □, SeO_2 and SeO_3, g.

Electrode Distance.—It is well known that the extent of the negative glow is independent of the distance between the electrodes and is dependent on the nature of the gas and the pressure. In tube I a relatively large selenium surface is exposed and the region of negative glow represents a relatively large volume. In contrast the electrodes in tube II are smaller and, therefore, for the same power, the region of negative glow is smaller in volume but more concentrated in electrons for the same current. Results obtained under identical conditions of pressure and current show consistently a larger amount of product for tube I than for tube II and a higher percentage of selenium trioxide for tube II than for tube I. As might be expected, the change of distance between the electrodes of tube II does not affect the percentage of selenium trioxide in the product, pressure and current being the same.

Distance of Selenium from the Electrodes.—It was found that no perceptible reaction took place unless the selenium was in the region of the negative glow. Using direct current, excessive volatilization of selenium took place when the selenium was too near the cathode and selenium was found in the product.

Effect of Current.—The curves of Fig. 3 show distinctly that the percentage of selenium trioxide, the weight of

TABLE I

Pressure, mm.	Current, ma.	Electrode distance, cm.	Distance of Se from cathode, cm.	Wt. of product, g., behind		% SeO_3, behind	
				Anode	Cathode	Anode	Cathode
				Tube I			
1.5	45 d. c.	2	1	0.1169	0.1736	4.66	11.15
1.5	45 d. c.	2	1	.1663	.2996	3.35	7.69
				Tube II			
				Between electrodes	Behind cathode	Between electrodes	Behind cathode
1.0	44 a. c.	6.5	1.2	0.0151	0.1633	16.16	19.9
0.9	45 d. c.	4	1	.0317	.0302	8.15	13.23
1.2	45 d. c.	4	1	.0381	.0700	4.47	14.58

product, and millimoles of selenium increase with an increase of current. In these experiments special care was taken to maintain identical conditions, varying only the amperage and voltage. Using the same tube, the voltage must be increased to produce a higher current. Brewer,[3] in his studies of various reactions, also has reported a larger rate with an increase of current. Particularly significant is the relation between percentage of selenium trioxide and current. Evidently the percentage of selenium trioxide is dependent on the power factor, which would lead one to believe that the activation of selenium is an important factor in the production of selenium trioxide. Calculations of m/N ratios have not been attempted because of the complications introduced by the solid reactant and the heterogeneous product.

Deposition of Product.—Using tube I, Kramer and Meloche[2] have reported a higher percentage of selenium trioxide in the product behind the electrodes. Using direct current instead of alternating current, as was the case in the above experiments, a higher percentage of selenium trioxide and a larger weight of product was found behind the cathode. Some typical results, using tubes I and II, as shown in Table I, show conclusively that the product concentrates behind the cathode.

Using tube II, the deposit, in many cases, formed in diffuse rings. The majority of the product was usually concentrated in a ring just below the cathode.

Characterization of the Product.—In the earlier work with alternating current, the products of the oxidation of selenium in the glow discharge were analyzed chemically and reported to be a mixture of selenium dioxide and selenium trioxide. In the present study using direct current the same type of product was obtained. However, since it was realized that chemical analyses could not alone establish the character of the product, X-ray powder photographs were taken of typical samples. A characteristic which interfered with chemical analyses also made the X-ray examination difficult, namely, the strong affinity of the product for water. In the solution of samples for chemical analysis it was necessary to place the weighed dry sample in a weighing bottle and place a drop of water on the wall of the bottle, allowing the sample to stand long enough for the water vapor to reach the product and thus provide slow hydration. When this occurred the sample could be moistened and diluted to the desired volume. If this precaution was not taken and water was added directly to the fresh sample, the reaction was so violent that some sample would be lost.

When samples were prepared for the X-ray examination, the usual thin-walled tubes were filled in a desiccator box to avoid contamination of the sample with water. It was necessary to prepare a standard photograph of selenium dioxide, as there is no X-ray data on this oxide in the literature. A molybdenum target tube was used with a zirconium oxide filter, thereby producing monochromatic light of 0.70997 Å. wave length. An unusually long exposure was required, discernible lines appearing after twenty-four hours.

The data in Table II give the actual diameters of diffraction rings and the calculated interplanar distances of the planes producing these rings.

TABLE II

SeO_2		Discharge product	
Distance between lines, cm.	Interplanar distance, Å.	Distance between lines, cm.	Interplanar distance, Å.
..	....	6.24	1.1560
5.92	1.2164	..	....
5.66	1.2710	5.66	1.2710
5.44	1.3213	5.44	1.3213
5.18	1.3865	5.18	1.3865
4.58	1.5643	4.54	1.5780
..	....	4.00	1.7865
..	....	3.64	1.9602
3.22	2.2163	3.26	2.1889
2.76	2.5773	2.82	2.5247
2.38	2.9909	2.38	2.9909
2.20	3.2350	2.20	3.2350
1.90	3.7375	1.90	3.7375
1.74	4.0864	1.74	4.0864

The above table shows that selenium dioxide crystals are produced by the oxidation of selenium in the glow discharge since selenium dioxide lines are found in the photograph of the glow discharge product. It is doubtful that a double oxide forms, since the selenium dioxide lines on the two photographs were of practically equal intensity (a double oxide would decrease the selenium dioxide percentage). It is more reasonable to suppose that, since there are three additional lines in the selenium dioxide and selenium trioxide photograph, selenium trioxide exists as crystals.

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(3) Brewer, *et al.*, *J. Phys. Chem.*, **36**, 2133 (1932); and earlier papers.

Acknowledgment

The authors with to express their indebtedness to Dr. A. T. Lincoln for the use of the X-ray diffraction apparatus at Carleton College.

Summary

In the reaction between selenium and oxygen in the glow discharge, the effects of the variables, pressure, current, electrode distance, shape of tubes, were studied. From these studies, optimum conditions for the production of selenium dioxide and trioxide were ascertained. The characterization of these products, by means of chemical analysis, was supplemented by X-ray diffraction studies.

The reaction is best initiated in the negative glow and is completed by the deposition of product on the cold tube walls.

MADISON, WIS. RECEIVED AUGUST 28, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Oxidation of Selenium in the Glow Discharge. III. Striated Deposits and Possible Mechanism[1]

BY EARL OLSON AND V. W. MELOCHE

Although the glow discharge may be said to comprise a rather complex field for chemical reaction, the use of solid selenium as one of the reactants and the cooling of the walls of the tube in liquid air greatly reduce the complexity of the system. In a homogeneous system, it is difficult to determine the nature of the reaction in the various parts of the discharge column. Since the products of the oxidation of selenium are solids, it has been possible to study the deposits which formed as striations *in the column* and to study the effect of the change of pressure and power on these striations. We propose to describe the results of this study and use these data together with results published in a previous paper in support of a proposed mechanism for the oxidation of selenium in the glow discharge.

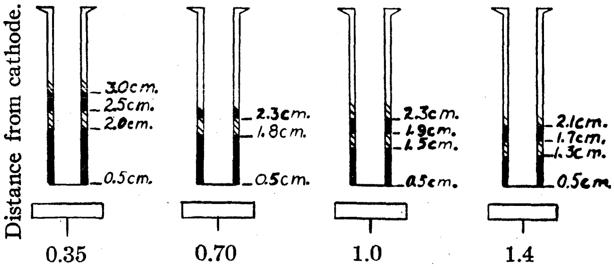

Fig. 1.—▨, Oxides of selenium; █, elementary selenium.

Apparatus.—The apparatus used in this research was the same as that described in previous papers.[2,3] The data to be presented were obtained with the discharge tube III, illustrated in the second paper, having a distance of 10 cm. between the electrodes. Direct current was used.

Striated Deposits in the Discharge

Selenium was fused on the bottom of a glass suspension 0.5 cm. from the cathode as shown in Fig. 1. The basket was suspended in the center of the discharge column. After subjecting the selenium to the glow discharge for an hour and a half, it was found that oxides and elementary selenium deposited not only on the walls of the tube but also on the vertical glass supports directly in the path of the discharge. Distinct striations of white selenium oxide and elementary selenium were sharply defined if the pressure were held constant during the run. The striation dimensions of four constant pressure runs are given in Fig. 1. The lined areas represent deposits of oxides, while the solid black areas represent deposits of elementary selenium. For example, the striations occurring at 0.35 mm. pressure consisted of a 1.5-cm. deposit of black elementary selenium, then 0.5 cm. of white oxide of selenium, 0.5 cm. of red elementary selenium, and above this another selenium oxide deposit of 0.4 cm. No deposit was detectable higher on the glass support. It is well known that red selenium is transformed to the black variety by heat. In agreement with this is the fact that the black selenium deposited close to the cathode where the temperature was relatively high and the red selenium deposited farther away from the cathode where the temperature was undoubtedly lower.

It is believed that this is the first report of striated depositions occurring directly in the discharge column. Brewer[4] has reported a well defined band of deposit on the wall of the tube in the region of the negative glow; also, under special conditions, striated deposits on the wall in the positive column region. The above figure represents striated deposits in the head of the positive column. The lower black area is in the region of the negative glow and Faraday's dark space. The two oxide deposits (lined areas) and the upper black area are in the region of the head of the

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(1) This investigation was supported in part by the Wisconsin Alumni Research Foundation. This paper is presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Kramer and Meloche, THIS JOURNAL, **56**, 1081 (1934).

(3) Olson and Meloche, *ibid.*, **58**, 2511 (1936).

(4) Brewer, *et al.*, *J. Phys. Chem.*, **34**, 153, 2343 (1930); **35**, 1281, 1293 (1931).

positive column. These striated deposits must have been produced by the luminous and non-luminous regions of the discharge. It is well known that these regions move away from the cathode with decreasing pressure. Figure 1 shows that the deposits of selenium and of selenium oxide were affected in a similar manner, supporting the conclusion that the deposits are regulated by the striations of the discharge.

In order to determine whether the oxides of selenium were deposited in a luminous or non-luminous region, the potential drop between two probes was measured with an electrostatic voltmeter. The two probes were placed at distances 2 and 2.5 cm. from the cathode and the discharge moved past them by varying the pressure. Figure 2 shows the variation of potential drop between the probes as the discharge was moved past them.

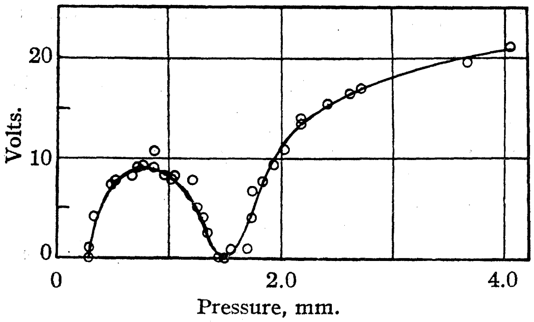

Fig. 2

Figure 3 shows a continuous graph of the striated deposits in Fig. 1.

From the voltage measurements, it can be seen that a non-luminous stratum existed between the probes at pressures of 0.3 and of 1.5 mm. Also, a luminous region filled the space between the probes at a pressure of 0.9 mm. Now, upon inspection of Figure 3, it may be definitely concluded that selenium was deposited in luminous regions and selenium oxide in the non-luminous. This fact gives an indication as to the mechanism of the oxidation of selenium in the glow discharge; the selenium was activated in the negative glow or other luminous regions and then combined with oxygen in a dark space or outside of the discharge column. If any combination of activated selenium and oxygen takes place in a luminous region, decomposition immediately follows.

Facts Pertinent to Mechanism

1. Using a glass suspension located in the d. c. discharge, selenium metal was deposited in luminous portions and selenium oxide deposited in the dark spaces, indicating that selenium was activated in the luminous regions and combined with oxygen in the dark regions.

2. Using a discharge tube with rod electrodes and employing alternating current, higher concentrations of selenium trioxide were found behind the electrodes. This indicated that selenium trioxide was formed near or behind the electrodes; also, the particles were propelled parallel to the electric field.

3. Using the same rod electrodes but employing direct current, larger weights of product and higher percentages of selenium trioxide were found behind the cathode than behind the anode. The larger amount of product behind the cathode indicates that the selenium was attracted toward the cathode and, therefore, was positively charged. Deposition of product in other parts of the tube does not contradict the above for it is certainly feasible that gas neutralization may also take place and, therefore, mere diffusion of product to all parts of the walls.

The higher percentage of selenium trioxide behind the cathode indicates that the selenium was more highly activated in the negative glow, thereby producing a higher concentration of selenium trioxide. This is also indicated by the effect of pressure upon the concentration of selenium trioxide in the product; higher concentrations were obtained at that pressure at which the selenium is in or near the negative glow.

4. A higher concentration of selenium trioxide was produced when a steady current of oxygen was passed through the discharge tube than when oxygen was simply allowed to diffuse into the tube from one opening. (2) This supports the view that the oxides of selenium are formed in the dark spaces or outside the discharge column.

5. Selenium was placed 2 cm. from the cathode and a discharge run at 1.4 mm. pressure; no vaporization or oxidation of selenium occurred. (2) When the pressure was reduced to 0.4 mm. vaporization and the oxidation of selenium took place. Evidently the selenium must be in the region of the negative glow or no appreciable reaction will occur. Brewer[4] has also found the negative glow to be the most reactive region.

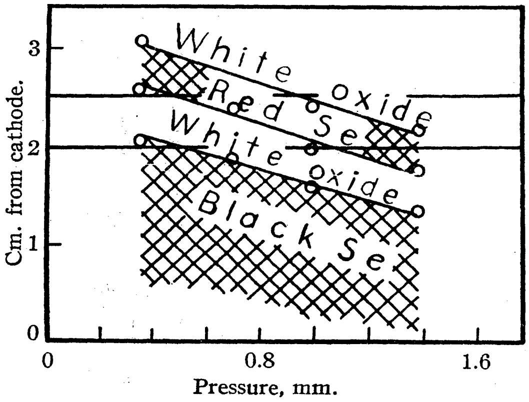

Fig. 3.

6. When pure selenium dioxide was placed in the negative glow, a red coloration developed, indicating reduction to metallic selenium. If selenium dioxide is unstable in the glow, certainly selenium trioxide is unstable and, therefore, only selenium ions exist in the luminous regions, oxides being formed in the dark spaces or outside the discharge column.

7. Increase of power caused an increase of percentage of selenium trioxide and of weight of the product.[2]

8. Previous experiments have shown that selenium trioxide is not formed by the action of ozone on selenium. This fact supports our belief that activated selenium is necessary for the formation of selenium trioxide.

The Mechanism

The selenium is vaporized and activated in the luminous portions of the discharge, the rate being at a maximum in the negative glow. It is highly probable that positive ions are formed and propelled toward the cathode. Once outside the region of the discharge, the activated selenium combines with oxygen forming either the dioxide or trioxide; more trioxide is formed at higher activations of the selenium, as indicated by the effect of current and voltage on the per cent. of selenium trioxide in the product. The particles are positively charged, gas or wall neutralization taking place. Undoubtedly there is decomposition of selenium trioxide occurring. It seems logical that there will be less decomposition of a selenium trioxide particle if it is neutralized on the wall, which is at a low temperature and will take up the heat of neutralization. On the other hand, if gaseous neutralization takes place, the heat cannot be dissipated and therefore might decompose the selenium trioxide molecule. It may be mentioned that only very low percentages of selenium trioxide were found when the tube was at room temperature during the reaction.

Summary

1. Banded deposits of selenium metal and selenium oxide were obtained in the glow discharge column. This afforded a means of determining the region in which the oxidation of selenium takes place. A correlation of voltage measurements and the character of the striated deposits shows that vaporization and activation of selenium takes place in the luminous regions. Combination with oxygen takes place in the dark regions.

2. After considering the experimental facts, a mechanism is suggested.

MADISON, WIS. RECEIVED AUGUST 28, 1936

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY No. 568]

The CN Bond in Methyl Cyanide and Methyl Isocyanide

BY L. O. BROCKWAY

The bond between the carbon and nitrogen atoms in methyl cyanide and other organic nitriles has long been regarded as a triple electron pair bond, the structural formula for these compounds, $R{-}C{\equiv}N$, being considered satisfactory because in it carbon shows its normal valence of four and nitrogen one of its two normal valences, three. The isocyanides, on the other hand, according to the same considerations might have either one of two formulas, $R{-}N{\equiv}C$ and $R{-}N{=}C$. In the former the carbon atom is again quadrivalent while the nitrogen is quinquivalent; the latter formula is distinguished by the bivalent carbon atom. This formula, suggested by Nef, was favored because it was thought that the unusual chemical reactivity of the isocyanides was perhaps due to the "unsaturated" bivalent carbon atom.

In 1919 Langmuir[1] considered the possibility of a third formula for the CN radical on the basis of the Lewis theory of valency, namely, $R{-}C{\equiv}N$. Langmuir, however, noted the isosterism of cyanide ion and nitrogen molecule and rejected the triple bond structure because of the pronounced chemical differences between nitrogen molecule and acetylene, for which a triple bond structure was accepted. He proposed a structure in which one pair of electrons was shared between the two atoms and the remaining eight formed an octet around the two atoms together. This structure was not generally accepted and Lewis in 1923[2] supported the validity of the triple bond formulation for the cyano radical. In accordance with the octet theory this formula originally considered by Langmuir is preferable to the first two mentioned above since it is the only one of the three in which each of the atoms is surrounded by four electron pairs. This is evident when the formulas are written to show both the shared and the unshared electrons, as follows

$$\mathrm{R:N::::C} \qquad \mathrm{R:\ddot{N}::C:} \qquad \mathrm{R:N:::C:}$$

The interpretation of the octet theory by quantum mechanics in terms of the application of the Pauli exclusion principle to the elements of the first row of the periodic table still excludes the first but admits the second and third structures.

The first direct attempt to decide among these three bond types for methyl isocyanide was made

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[1] I. Langmuir, THIS JOURNAL, **41**, 868, 1543 (1919).

[2] G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923, p. 127.

in 1930 by Lindemann and Wiegrebe,[3] who concluded from a determination of the parachor that only the triple bond structure was correct. Hammick, New, Sidgwick and Sutton[4] measured the parachor of ethyl isocyanide and decided on the same bond type. These authors also measured the dipole moment of several para-substituted aromatic cyanides and isocyanides. By a comparison of the moments they showed that the direction of the moment in the C–N link is different for the two classes of compounds; the nitrogen is negative with respect to the carbon in the cyanides and positive in the isocyanides. Nitrogen in isocyanide with a double bond would be negative but in the triple bond structure nitrogen has become positive by the loss of an electron to the carbon atom, the electron transfer being compensated energetically by the formation of the third electron pair bond. The positive nitrogen in the isocyanide accordingly supports the triple bond structure.

Dadieu,[5] who regarded the foregoing evidence as "indirect," found support for the triple bond structures of both methyl cyanide and isocyanide in the Raman spectra of the two compounds. According to Dadieu every compound which is definitely known to contain a triple bond shows a strong Raman line in the range between 1960 and 2400 cm.$^{-1}$. Each of these compounds shows a strong line in this region; therefore, each has a triple bond structure. Professor R. M. Badger of this Laboratory is making an analysis of the normal vibrations of these molecules in interpreting their infra-red absorption spectra. The evaluation of the force constants of the individual bonds will make the spectral evidence somewhat more satisfactory.

Another test for bond type in covalent compounds is found in the relation between bond type and internuclear distance. The bond distances for single, double and triple bonds are known quite accurately from the table of covalent radii due to Pauling and Huggins.[6] The distances for bonds of intermediate types are known from investigations[7] of the effect of resonance on bond distances.

In the present investigation I have measured the internuclear distances in methyl cyanide and isocyanide by electron diffraction of the vapors. The experimental procedure and methods of interpreting the diffraction patterns have been described in detail.[8]

Methyl Cyanide.—Eastman methyl cyanide was fractionated and a sample boiling at 80.4–80.5° (uncorr.) was used at room temperature for the electron diffraction. The camera distance was 10.85 cm. and the electron wave length was 0.0611 Å. The photographs show five rings of a very characteristic appearance. The first is strong and diffuse, the second weak and sharp, the third strong and sharp with a shelf on the outside edge, the fourth diffuse and the fifth sharp. Reproducible measurements of the diameters could be made only on the sharp rings, *i. e.*, the second, fourth and fifth.

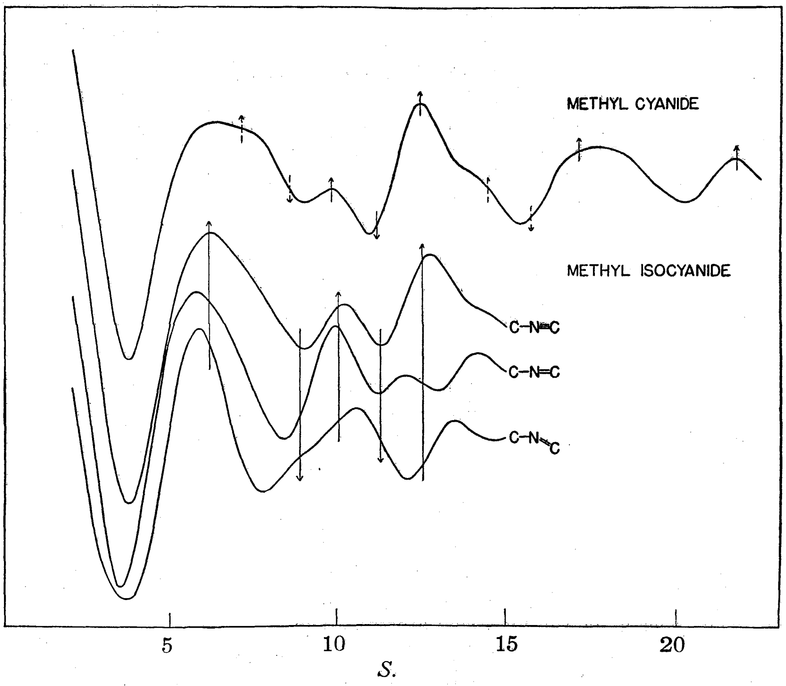

Fig. 1.—Theoretical electron diffraction curves for methyl cyanide and isocyanide with the positions of the maxima and minima measured on the photographs indicated by arrows.

The theoretical curve (Fig. 1) was calculated for a linear arrangement of two carbon atoms and a nitrogen atom with distances of 1.54 and 1.16 Å. for the carbon–carbon and carbon–nitrogen bonds, respectively. The distance 1.06 Å. was used for the carbon–hydrogen bonds in the

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(3) H. Lindemann and L. Wiegrebe, *Ber.*, **63**, 1650 (1930).

(4) D. L. Hammick, R. C. A. New, N. V. Sidgwick and L. E. Sutton, *J. Chem. Soc.*, 1876 (1930).

(5) A. Dadieu, *Ber.*, **64B**, 358 (1931).

(6) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 224 (1934).

(7) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935).

(8) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

methyl group, with H–C–H angles of 109°28′. The linear configuration is supported by the known linear form of HCN[9] and by preliminary results of the analysis of the infra-red absorption spectrum of methyl cyanide now in progress. Non-linear models were not considered.

The characteristic qualitative features observed in the photographs are well reproduced in the curve. The positions of the observed maxima and minima are indicated by the arrows; the points which did not afford reproducible measurements are shown by dashed arrows and were not used in the quantitative comparison in Table I. The final values observed, 1.54 ± 0.02 Å. and 1.16 ± 0.02 Å., are exactly those for a single carbon–carbon bond and a triple carbon–nitrogen bond, respectively.

TABLE I

METHYL CYANIDE

Max.	Min.	s, obsd.	s, calcd. for C–C = 1.54 and C–N = 1.16	C–C, Å.	C–N, Å.
1		7.19	(6.20)		
	2	8.60	9.00	(1.613)	
2		9.84	9.78	1.530	1.152
	3	11.17	10.88		
3		12.44	12.43	1.539	1.159
Shelf		14.53			
	4	15.75	15.40	1.507	1.135
4		17.16	17.65	1.584	1.193
5		21.77	21.68	1.533	1.155
			Average	1.539 Å.	1.159 Å.
			Av. dev.	0.018	0.014

Final value: C–C = 1.54 ± 0.03 Å.; C–N = 1.16 ± 0.02 Å.

Methyl Isocyanide.—Methyl isocyanide was prepared by Dr. C. E. Wilson using methylamine, chloroform, and alcoholic potash. The electron diffraction photographs were taken with a camera distance of nearly 20 cm. and the three rings observed covered the negative. Of these three rings the third is considerably stronger than the second although weaker than the first.

Three molecular models were considered. The first corresponds to the triple bond structure of isocyanide and is linear (except for the hydrogen atoms). The second is also linear but has the double bond N–C distance, 1.31 Å. For the third model a CNC angle of 125° was chosen with the double bond distance since the angle between a single and a double bond is usually observed to have about this value.

The second and third models are quite definitely eliminated. The third maximum in these curves is weaker than the second whereas it is observed to be stronger. In the case of the third curve the second and third maxima both appear to be somewhat asymmetric but in the photographs they are sharply defined. The positions of the outer rings are not correct in either curve as indicated by the arrows showing the observed *s* values.

Model I corresponding to a single and a triple bond in the molecule shows good qualitative and quantitative agreement with the photographs. The quantitative comparison of Table II leads to a CH_3–N distance of 1.48 ± 0.03 Å. and a N–C distance of 1.17 ± 0.02 Å.

TABLE II

METHYL ISOCYANIDE

Max.	Min.	s, obsd.	s, calcd. for C–N = 1.46 and N–C = 1.16	CH_3–N, Å.	N–C, Å.
1		6.17	6.24	1.476	1.173
	2	8.88	9.00	1.480	1.176
2		10.04	10.21	1.485	1.180
	3	11.27	11.26	1.459	1.159
3		12.51	12.73	1.485	1.180
			Average	1.477 Å.	1.173 Å.
			Av. dev.	0.008	0.006

Final value: CH_3–N = 1.48 ± 0.03 Å.; N–C = 1.17 ± 0.02 Å.

Discussion.—The bond distances for single, double and triple carbon–nitrogen bonds are 1.47, 1.32 and 1.16 Å., respectively. The distance 1.16 Å. observed in methyl cyanide supports the triple bond structure and the structure represented by the formula $CH_3—C\equiv N:$ is now well substantiated.

The observed distance of 1.17 Å. in the isocyanide is also very close to the triple bond distance, but the apparent discrepancy of 0.01 Å. suggests the possibility of resonance with the double bond structure. A 60% contribution of this structure would increase the observed bond distance by only 0.02 Å. above the value for a triple bond so that the double bond structure may well be important in the normal state of the isocyanide molecule. The linear configuration indicates, however, that the triple bond structure predominates in determining the properties of methyl isocyanide.

I wish to thank Dr. Chester Wilson for the preparation of the isocyanide and Professor Linus Pauling for his kindly criticism of the investigation.

Summary

The electron diffraction determination of the molecular structures and bond distances of methyl cyanide and isocyanide shows that a triple bond exists in the cyano group of each compound. The observed distances in the first are CH_3–C = 1.54 ± 0.02 Å., C–N = 1.16 ± 0.02 Å.; in the second CH_3–N = 1.48 ± 0.03 Å., N–C = 1.17 ± 0.02 Å. Both compounds are linear except for the hydrogen atoms.

PASADENA, CALIF. RECEIVED SEPTEMBER 28, 1936

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(9) R. Badger and J. Binder, *Phys. Rev.*, **37**, 800 (1931).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Separation of Lithium Isotopes

BY GILBERT N. LEWIS AND RONALD T. MACDONALD

Except in the case of hydrogen the separation of isotopes will always be a laborious and expensive undertaking. However, even a partial separation will in many cases permit an answer to important questions relating to the difference between isotopes in chemical behavior, in spectra, and in nuclear transformations. The methods leading to effective separation will also be interesting in themselves; for even a casual inspection of the literature shows how unsystematic has been the exploration of the methods of separating similar substances.

Most chemical separations have depended upon a difference in the solubility of solids or in the vapor pressure of liquids. Fractionation by selective distribution between two liquid phases is only now being developed in some important industrial processes. The method which we have chosen for the separation of lithium isotopes involves a system of two liquids, but it is not a simple case of selective distribution. In principle it depends, as the first separation of hydrogen isotopes chiefly depended, upon the difference in electrode potentials between the two isotopes.

If a solution of a lithium salt is shaken with an amalgam of lithium, the ratio of Li^7 to Li^6 will not in general be the same in the two phases. The quotient of the two ratios, α, is the fractionating factor. If we use such a system in a continuously operating column of n cells, and equilibrium is established in each cell, then the maximum fractionating effect which can ultimately be obtained from the column is α^n. However, as in the similar case of distillation, when only small quantities of material are employed it is simplest to use a column without definite separation into cells, so that the number of theoretical cells or "plates" depends upon the conditions of operation and can only be determined experimentally.

In our column in which small drops of lithium amalgam fell through a long column containing a solution of lithium salt, we were never able to determine the actual plate efficiency, but several preliminary experiments indicated that the efficiency would be high. For example, when the fine drops of lithium amalgam such as we have used in our experiments fell through one meter of aqueous sodium chloride, analysis of the amalgam which had passed through showed that 96% of the alkali metal in the amalgam was sodium and only 4% lithium. We may assume that this rapid interchange between lithium and sodium indicates a similar rapid interchange between lithium and lithium in our actual column.

The stocks of lithium amalgam, containing from 0.5 to 0.7 mole per liter, were prepared by electrolyzing a saturated aqueous solution of lithium carbonate, in the presence of excess solid carbonate, between platinum and mercury electrodes. The mercury was placed in flat crystallizing dishes, covered with about 2 cm. of water containing powdered lithium carbonate. Horizontal disks of platinum served as anodes. Four such cells were operated in series and these were placed in a trough of ice water to diminish the reaction between the water and the lithium amalgam already formed. Using a cathode current density of about 0.1 amp./sq. cm., the amalgams reached the desired concentration in six or eight hours, provided that reasonable care was taken to exclude such impurities as catalyze the reaction between water and amalgam. The process required little attention, but nevertheless was one of the more onerous parts of the investigation, during which over half a ton of the lithium amalgam was prepared.

The Column

The fractionating column consisted of a vertical glass tube 18 meters high and 4 mm. in internal diameter, which was filled with a solution of lithium salt. Through this solution a fine spray of lithium amalgam fell. It might be thought that the falling drops of mercury would cause serious mixing of the solution at top and bottom, but, on the contrary, when the stream of droplets is properly regulated they actually prevent such mixing. If the drops are of the right size and number they produce a condition of complete turbulence. Each drop of amalgam, as it passes down through the electrolyte, which is itself rising through the tube, assumes a zig-zag course, so that it takes four or five minutes to fall through the length of the column. This condition of turbulence, while causing intimate local mixing, prevents the mixing of the solution in one section of the column with that in another.

A state of turbulence is always very sensitive to slight changes in conditions and if the number of falling drops is increased much above that required for turbulence, the drops begin to pile up, with or without coalescence, thus ruining the whole experiment. In order to avoid dangerous spots it was necessary that the sections of glass tubing used in building the column be welded together with care to prevent any constriction or irregularity.

The top of the column, as shown in Fig. 1, is a continuation and enlargement of the main column, L. The shape of the funnel between L and M is important, since any discontinuity in the stream line causes too great an accumulation of amalgam drops. There is always some accumulation of these drops from the bottom of the funnel to a point which varies with the rate of production of drops at the source M. If the accumulation rises as high as M, or in any case if the droplets remain long enough in the top to coalesce into larger drops, the result is fatal and the whole experiment must be begun anew.

Each experiment was carried out with 10 liters of lithium amalgam, stored in a carboy, and protected against air and moisture. From this carboy the amalgam entered the tube P through a rubber tube fitted with a stopcock, so mounted that the rate of flow of the amalgam could be regulated carefully. Except in one case when a new rubber tube contaminated the amalgam this cock gave a nearly constant rate of flow, although it was customary to make a fine regulation about once an hour.

The amalgam entered the column at M through a fine silk fabric tied at the end of the glass tube. Drops of amalgam about 0.1 mm. in diameter were desired, and many kinds of silk were tried before one was obtained which gave drops of the necessary size and uniformity. As the amalgam falls through the column it displaces an equal volume of the solution which leaves by the overflow at N.

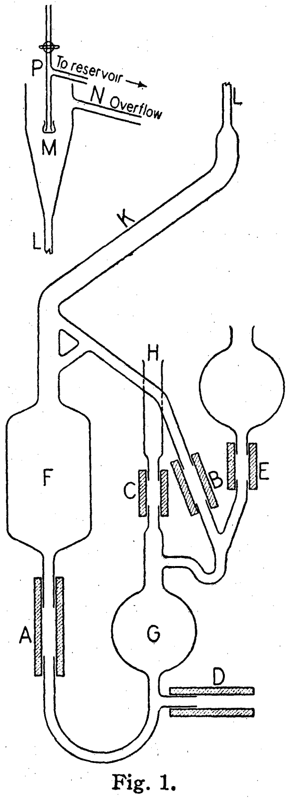

Fig. 1.

The lower end of the column is also shown in Fig. 1. In this part of the apparatus there are five cocks, A, B, C, D and E. The pressure at the bottom is about 2 atmospheres when the whole column is filled with the solution of lithium salt, and this pressure is approximately doubled when the amalgam is streaming down. Pressure stopcocks of glass were tried but it was found that the best cock for our purposes was afforded by a heavy walled rubber tube reinforced on the outside with adhesive tape and closed by a simple screw clamp (not shown in the diagram). The rubber tubing used in the cocks was boiled first with alkali and then with the solution which was to be used in the system. The cocks so prepared caused no appreciable contamination of the mercury and showed no evidence of any rapid deterioration.

At the beginning of the experiment the solution of lithium salt fills the whole column, the bulbs F and G, and connecting tubes as far as the cocks C, E and D. Then, all cocks being closed, the amalgam spray is started at the top of the column. The droplets fall without coalescence as far as the diagonal tube K, which is sealed to, and is larger than, the main column L. Here the coalescence begins and continues as the mercury accumulates in F so that under satisfactory working conditions the amalgam in F becomes a single mass except for a small layer of individual drops at the top. A great deal of time was spent in finding the proper conditions for the coalescence. In one experiment with a solution of lithium chloride in amyl alcohol which was supposed to be ready for a complete run, the drops formed an emulsion in F and no simple method was found which would make the drops coalesce. On the other hand, in some solutions there is danger of too rapid coalescence, for if it begins in the vertical column the experiment is also ruined.

Our present system has one valuable characteristic which is unique. Ordinarily if a material is distributed between two liquid phases the concentration is different in the two, and if a fractionating column is set up it requires a complicated feeding device to ensure that the amount of material rising through the column is just equal to that which is descending. In our present case the concentrations of lithium in the amalgam and in the other phase are independent. We therefore make the concentration of lithium the same in the two phases, and since the falling amalgam displaces an equal volume of the other phase, there is exact equality in the amount of lithium ascending and descending.

The remaining problem is to withdraw a certain volume of amalgam from the bottom of the column, extract its lithium in the form of a salt, dissolve this salt in the same volume of the other solvent, and return this solution to the column without disturbing its operation.

Starting with all the stopcocks closed, the amalgam is allowed to accumulate in the bulb F until it exceeds 100 cc. Stopcocks A and B are then opened until 100 cc. of amalgam flows into the bulb G, being replaced by an equal volume of the solution rising through B. The cocks A and B are now closed, and the cock C is opened to the air, the standpipe H serving to catch any liquid which may be carried up by hydrogen that has been evolved. The cock D is then opened until the amalgam is withdrawn from G. The lithium must now be extracted rapidly from the amalgam, converted into the salt which is being used, and this salt dissolved in 100 cc. of the solvent. The resulting solution is introduced into the system through the cock E, after which, closing E and C, the system is in its original state. This whole maneuver must be executed before the next 100 cc. of the amalgam is collected in the bulb F. This took in our various experiments from thirteen to fifteen minutes.

Attempts were made to find some automatic method of effecting, at the bottom of the column, the exchange from lithium amalgam to a solution of lithium salt. One method which seemed promising was to allow the amalgam drops to fall through a saturated solution of the corresponding salt of a heavy metal such as zinc. In such experiments, however, the zinc, instead of entering the amalgam, often formed a precipitate in the solution itself. Such methods were finally abandoned and we returned to the laborious but reliable methods of hand control.

If we are using, for example, a solution of lithium chloride in one of the alcohols, the simplest plan would be to treat the amalgam with an equivalent amount of an alcoholic solution of hydrochloric acid, but this process proved to be too slow. The reaction is rapid as long as the concentration either of lithium in the amalgam or free acid in the solution is high, especially when the system is kept at the boiling point of the solvent. However, even with amyl alcohol boiling at 130° it was found impossible to remove all the lithium from the amalgam by an equivalent amount of the acid solution during the fourteen or fifteen minutes available. Even a slight excess of acid could not be tolerated as it caused a violent evolution of hydrogen from the stream of amalgam drops. This evolution of hydrogen occurred to some extent in all of our experiments, but every effort had to be taken to keep it at a minimum.

The method finally employed is illustrated in Fig. 2. Two vessels A and B, operating on the counter current plan, are provided with small centrifugal stirrers which draw in amalgam at the bottom and spray it violently into the acid solution through a number of small openings. The burets C and D permit the introduction of measured volumes of a molal acid solution in the chosen solvent. In the vessel B, amalgam, from which most of the lithium has been removed in the vessel A, comes in contact with fresh acid until the last trace of lithium is removed. Through the stopcock F the mercury is withdrawn and discarded while the still acid solution is transferred to vessel A. Here 100 cc. of fresh amalgam enters directly from the column through the tube G.

The stirrer is then set in motion and a certain volume of acid introduced from the buret C. After a few minutes this acid is used up, as shown by an indicator, more acid is added, and the process repeated as long as time permits. The indicators used were phenolphthalein and chlorphenol red. Both are destroyed by violent agitation with lithium amalgam, so that they must be added near the end-point. At one of these end-points the stirrer is stopped, the nearly spent amalgam is transferred to vessel B, and the neutral solution is made up to 100 cc. and introduced into the column. The whole operation with both stirrers operating simultaneously took about ten minutes, leaving three or four minutes for the handling of the material at the bottom of the column.

All these operations had to be continued on schedule time and without the slightest departure from routine throughout the twenty-four hour run. At the end of each run, when the whole 10 liters of original amalgam had passed through the column, the two last samples of amalgam were withdrawn for analysis, as well as the solution which remained in the bottom of the apparatus and the lower end of the column.

The Isotopic Analysis

After the method of fractionating lithium isotopes had been developed it became an equally difficult task to ascertain the degree of enrichment of the light lithium isotope in the samples obtained from the column, for it is necessary to determine the atomic weight in a sample which contains originally only about 0.4 g. of lithium even before the processes of purification are begun.

Formerly, in an entirely different attempt to separate the isotopes of lithium, we had met the problem of determining the atomic weight in a sample containing less than a milligram of lithium, and we used a simple method which would only be able to show a large change in the isotopic ratio. In that method the sample was purified as lithium fluoride and the fluoride was fused on a platinum foil in an inert atmosphere. The drop of fluoride, on freezing, was usually transparent in the center with some opacity at the edges. By breaking the crystal into small pieces and selecting the transparent ones, it was possible to determine their density by a flotation method, using a mixture of a heavier and a lighter organic liquid. The reproducibility thus obtained was about 0.1%. With the larger samples available in the present research a higher degree of accuracy was sought by some more conventional method of atomic weight determination.

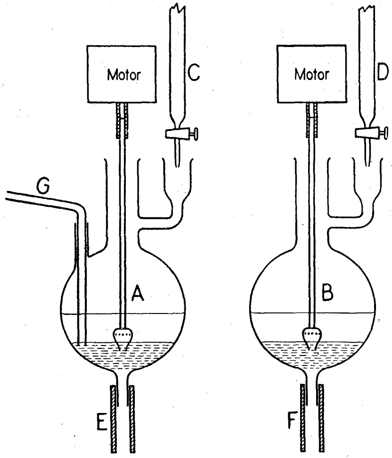

Fig. 2.

The method chosen consisted in titrating a weighed quantity of pure dry lithium carbonate against a solution of hydrochloric acid about 1.8 *N*. Since it was desired to obtain results reproducible to 0.01% it was necessary to take special precautions in the purification, the drying and the titration.

In order to test the method three samples of ordinary lithium carbonate containing 3 or 4 g. each were independently purified in the following manner. Each sample was dissolved in the requisite amount of pure water in a quartz flask. The solution was filtered through a small fine hardened filter paper, fastened by a clean rubber band to the end of a quartz tube. The filtrate was placed in a platinum flask of 900-cc. capacity and was then boiled until only 10 cc. of liquid remained. Most of the lithium carbonate was now in the form of a granular solid or a coherent layer on or near the bottom of the flask. The liquid was poured off and the remaining solid was rinsed with 10 cc. of pure water. The flask was next refilled with water to dissolve the carbonate and again boiled down for a second recrystallization. Each sample was crystallized three or four times. After two or three crystallizations the material gave every evidence of purity. It showed no flame test for sodium and in certain other experiments in which Br^- and SO_4^{--} were originally present, these ions could no longer be detected. All of the water used in these recrystallizations was prepared in a still of block tin and was free from non-volatile impurities.

The purified sample consisting of 1 or 2 g. of lithium carbonate was dried in a platinum crucible at 200°. It was then transferred to a weighed crucible and heated in an electric furnace for thirty minutes at a temperature about 50° below the melting point. The drying and heating were both carried out in an atmosphere of pure carbon dioxide. Previous experiments had shown that without this precaution some of the carbonate is converted into oxide and causes etching of the crucible. If the carbonate is heated to fusion the crucible is always slightly etched, even in an atmosphere of carbon dioxide. Our method proved to be the only one leading to strictly reproducible weighings.

After the carbonate was so prepared and weighed it was titrated against the standard solution of hydrochloric acid. Aside from the ordinary difficulties inherent in such a titration, the chief source of error lies in the carrying away of carbonate or acid by the spray resulting from the evolution of carbon dioxide. This danger was avoided by allowing the reaction to occur in a closed vessel. The crucible containing lithium carbonate was lowered until it stood upright at the bottom of a 1-liter quartz flask. A small excess of the standard acid was then introduced from a weight buret so as to flow around the crucible without meeting its contents. The flask was then closed with a rubber stopper through which passed a glass tube fitted with a rubber tube and a pinchcock. The flask was exhausted until the first bubbles of air began to rise from the acid. The cock was then closed, the crucible overturned, and the flask gently agitated until the carbonate was dissolved entirely. The cock was now opened and the stopper removed and tested for traces of acid or alkali. This test was always negative if the flask was so tilted during the neutralization that there was no direct path from the effervescing liquid to the stopper. The drops adhering to the sides of the flask were washed down and the small excess of acid remaining was now titrated with no more than ordinary precautions, the carbon dioxide being boiled off from the acid solution and phenolphthalein being used as indicator. Dilute solutions of barium hydroxide and hydrochloric acid, standardized with respect to the standard solution of concentrated hydrochloric acid, were used.

The titration of the three samples gave as the ratio of the weight of the standard acid solution to the weight of the lithium carbonate the three values 13.129, 13.127 and 13.128. In later experiments the standard acid was checked against ordinary lithium carbonate prepared from ordinary lithium amalgam, in order to follow the exact procedure used in preparing the samples of lithium carbonate of unknown isotopic composition from the amalgam taken at the bottom of the column. The procedure was as follows. The lithium amalgam was treated with pure distilled water in a wax bottle. After a day or two the reaction was complete and the solution of lithium hydroxide was filtered into a quartz flask through fine hardened filter paper attached to the end of a quartz tube. This treatment will remove any impurity of magnesium, which is the hardest element to separate from lithium. The filtrate was then immediately transferred to the platinum flask, converted into carbonate by a stream of carbon dioxide, and recrystallized by the method that we have already described.

The Three Operations of the Column

The First Run.—We first operated with half normal lithium amalgam and the same concentration of lithium chloride in ethyl alcohol. The method of transferring lithium from the amalgam to the electrolytic solution was in an experimental stage and broke down early in the run. In consequence a very crude and laborious method was necessary. The amalgam was treated with an excess of concentrated hydrochloric acid in a casserole which was heated until the excess acid had been driven off and the alcohol was added while the material was still hot and then brought to the proper concentration. About half way through the run one of the amalgam samples was lost completely. In addition to these difficulties the alcohol was not entirely free from water and there was therefore a large evolution of hydrogen in the column. This evolution of hydrogen does not seriously disturb the lower part of the column, for here the gas is under pressure and rises as small bubbles with the ascending solution, but as the bubbles rise they not only expand, but coalesce to form larger bubbles which produce much irregularity in the falling of the amalgam drops. In spite of these vexations the experiment was continued until the whole 10 liters of amalgam had passed through the column and the final amalgam at the bottom was analyzed. This analysis showed that Li^6 was being carried preferentially by the amalgam and that the ratio of Li^6 to Li^7 had approximately doubled. We were therefore encouraged to continue the experiments, avoiding as far as possible the difficulties of this run.

The Second Run.—Many experiments were now made with a variety of solvents and lithium salts, chiefly with the purpose of limiting the evolution of hydrogen. It was found in general that a solution which could be kept for hours in contact with lithium amalgam without appreciable reaction would react rapidly with the amalgam in the form of a fine spray. The rate of this reaction proved to be nearly independent of temperature, but depended markedly upon the presence of water and other impurities in the solvent, and was greatly increased by even a slight acidity.

Pure dioxane, which we prepared by a method similar to that of Kraus,[1] gives no reaction with lithium amalgam, but it is too poor a solvent to give the desired concentration of lithium salt. The system which seemed to suit our purpose best was a solution of lithium bromide in a mixture of four parts dioxane to one of ethyl alcohol, and our second run was started with this solution. However, the amalgam drops would not coalesce at the bottom of the column and it was necessary to begin anew with a solvent composed of two parts of dioxane and one of ethyl alcohol. This caused a somewhat greater evolution of hydrogen but not enough to cause serious trouble. One reason for using dioxane was that it seemed likely, on theoretical grounds, that it would enhance the separation of the two isotopes

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(1) Kraus, THIS JOURNAL, **55**, 21 (1933).

We shall see, however, that this proved not to be the case.

At the bottom of the column the lithium was transferred from the amalgam to the electrolytic solution by the new method which we have already described. The stock acid solution was made by passing dry gaseous hydrogen bromide into absolute alcohol at −40° and this solution was then mixed with dioxane and kept at 0°, since at higher temperatures the hydrogen bromide reacts rapidly with both dioxane and alcohol. The run was satisfactory in every respect and two samples of amalgam were obtained at the end. These were purified carefully.

The pure lithium carbonate obtained in this experiment was titrated against our standard acid and its weight was compared with the weight of lithium carbonate of ordinary isotopic composition neutralizing the same amount of standard acid. For the ratio of the equivalent weight of the latter to the equivalent weight of the former we found in the first sample 1.0015, and in the second sample 1.0014. The calculation of the isotopic composition from these figures will be made presently.

The Third Run.—Since we found that contrary to our expectations the dioxane–alcohol mixture gave less fractionation than pure alcohol, it was decided to make one more run with lithium chloride in absolute ethyl alcohol, although the evolution of hydrogen is greater in this solvent. In the third run ten liters of 0.6 *N* amalgam were passed through the column in twenty-three hours. At the end, two 100-cc. samples of amalgam were obtained, and also a third sample containing the alcohol solution remaining in the bottom, together with some from the column itself.

The lithium carbonate from the first sample of amalgam was purified and at the end of the recrystallization 1.37 g. was left. The ratio of the weight of ordinary lithium carbonate to the equivalent weight of this sample was 1.0022. With the second sample of amalgam the process of recrystallization was carried further than we intended, leaving only 0.69 g., which gave 1.0026 as the ratio of equivalent weights.

On account of the small amount of the second sample a new determination seemed desirable. Therefore the material left from the titration of these two samples, containing chiefly lithium chloride and barium chloride, was treated with sulfuric acid and evaporated nearly to dryness. To the residue, water and an excess of barium carbonate were added, and carbon dioxide was bubbled through overnight. The solution was boiled, filtered and subjected to the usual recrystallizations. The resulting carbonate gave the lower ratio 1.0016. It is to be noted that every impurity that can be imagined to be present will diminish the value of the ratio. It seems probable that this sample, which was obtained by a different procedure from the others, still contained some impurity.

Finally, the lithium chloride which was present in the electrolytic solution at the bottom of the column was purified by the following method. An aqueous solution of the lithium chloride was treated with an excess of silver oxide, and carbon dioxide was bubbled through for many hours. The solution was then filtered, boiled and refiltered. To remove the last traces of silver carbonate 2 cc. of 0.01 *N* hydrobromic acid was added. After filtration the treatment was continued as in previous cases through four recrystallizations, during which all traces of Br^- disappeared. This carbonate gave, for the ratio of equivalent weights, 1.0019. Since this sample contained some liquid from the column where there would be less separation of the isotopes, this experiment tends to confirm the higher ratio obtained in the first two analyses.

Unfortunately at this point it was necessary to discontinue the experiments owing to the departure of one of the authors, but it seems that we can make no great error in taking as our final ratio for this run the weighted mean of the first two ratios, namely, 1.0023.

Interpretation of the Results

The ratio of Li^7 to Li^6 in ordinary lithium is 11.6, according to the most recent work of Brewer.[2] This identical value is also obtained by comparing the accepted atomic weight of lithium, 6.940, with the values 7.0182 for Li^7 and 6.0170 for Li^6, obtained from mass spectra and nuclear disintegrations.[3]

In our third run, in which the highest concentration of Li^6 was obtained, we found the value 1.0023 as the ratio between the equivalent weights of ordinary lithium carbonate and of that from the column. Using the latest International atomic weights, we thus find that in our experiment the atomic weight of lithium was brought from 6.940 to 6.855. This means that the concentration of Li^6 has been raised from 8% in the original lithium to 16.3% in our new material. In other words, the ratio of Li^7 to Li^6 in our sample has been reduced to 5.1.

In our second run, using lithium bromide in a solvent containing one part of ethyl alcohol to two parts of dioxane, the ratio of Li^7 to Li^6 was brought to the value 6.6. Whether the smaller fractionation in this case was due to a smaller fractionating factor or to a lower efficiency in the column we cannot state.

Concerning the theory of the fractionation in our column, there is little to be said. In some experiments on the separation of the nitrogen isotopes, which will shortly be published by Lewis and Schutz, it was found possible to make in advance a rough calculation of the sign and the magnitude of the fractionating effect. In the present case there was no sure way even of predicting whether Li^6 would be concentrated at the top or bottom of the column. Since the fractionation must depend chiefly upon differences in zero-point energy, the zero-point energy always being greater in a substance containing a heavier isotope,

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(2) Brewer, *Phys. Rev.*, **49**, 635 (1936).

(3) See, for example, Bonner and Brubaker, *ibid.*, **50**, 308 (1936).

our experiments indicate that lithium is held more tightly to oxygen in the electrolytic solution than it is to mercury in the amalgam. Since, presumably, in alcohol the lithium is held between two or more atoms of oxygen and attached ordinarily to only one oxygen in dioxane, it seemed likely that the fractionating effect would be higher with dioxane than with alcohol; but, as we have seen, this proved not to be the case.

Our experiments did not proceed far enough to enable us to determine either the exact fractionating factor or the number of theoretical plates in our column. We can, however, obtain a minimum value for the fractionating factor, as follows. We estimate that in our last run 0.012 equivalent of Li^6 accumulated at the bottom of the column in excess of the amount present in ordinary lithium. This figure is to be compared with the total of 0.48 equivalent of Li^6 which was present in the original ten liters of amalgam. If the column is assumed to have an infinite number of theoretical plates, the fractionating factor is then 1.025. If, on the other hand, the column was less efficient, and some of the excess Li^6 found its way to the overflow at the top of the column, then the fractionating factor is larger. Corresponding to a fractionating factor of 1.025, the electrode potential between lithium amalgam and a solution of lithium chloride in alcohol would, at room temperature, and under equivalent conditions, be 0.0006 volt higher for Li^7 than for Li^6. Hence we may conclude that the difference in potential is at least as great as this.

The material obtained in this investigation will be used in several experiments to determine the difference in physical and chemical properties of the two lithium isotopes. Recently Mr. Brewer,[2] studying positive rays, has obtained indications of the existence in ordinary lithium of the isotope Li^5. If we attribute the concentration of Li^6 in our experiments mainly to differences in zero-point energy, a simple calculation shows that if Li^5 exists in the original lithium, it would be concentrated five-fold by our fractionation. We have, therefore, sent a sample of material from our third run to Mr. Brewer, who has been kind enough to examine it. He writes that in his first experiment conditions were unfavorable for observing Li^5, but it is interesting that he finds in this sample exactly the same ratio of Li^7 to Li^6 which we found by the atomic weight method, namely, 5.1.

Summary

From the ordinary mixture of lithium isotopes, Li^6 has been enriched in an 18-meter column, where fine drops of lithium amalgam fall through a solution of lithium chloride in absolute ethyl alcohol or of lithium bromide in a mixture of alcohol and dioxane. At the bottom of the column, the lithium is extracted from the amalgam and added as lithium salt to the ascending electrolytic solution. After the passage of 10 liters of amalgam through the solution, the material at the bottom of the column is removed for the analysis, which consists in determining the atomic weight of this lithium relative to that of ordinary lithium. This was accomplished by the exact titration of dry lithium carbonate against a solution of hydrochloric acid. In the final experiment, the isotopic ratio Li^7 to Li^6 was changed from 11.6 in ordinary lithium to 5.1 in our material. The results show that, under equivalent conditions, the electrode potential between amalgam and alcohol solution is greater for Li^7 than for Li^6 by at least 0.0006 volt.

BERKELEY, CALIF. RECEIVED SEPTEMBER 28, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reaction of Hydrogen Peroxide with Chromic Anhydride in Dry Ethyl Acetate

BY DOUGLAS G. NICHOLSON

The chemical literature contains many references to the deep blue colored metastable compound formed when acidified chromate solutions are treated with hydrogen peroxide. Many of these references[1–6] imply that the chromium in this compound is in a valence state higher than six; while others[7–10] show quite conclusively that the chromium is present in the hexavalent state.

An investigation was undertaken to prepare and, if possible, study the properties of this peroxychromic compound in a non-aqueous medium. The solubility of chromic anhydride and hydrogen peroxide in dry ethyl acetate led to the selection of this material as the solvent for this work.

Experimental

A solution of hydrogen peroxide in ethyl acetate was prepared by shaking a mixture of 100 ml. of 30% hydrogen peroxide, 3–5 ml. of water, and 900 ml. of ice cold ethyl acetate for about fifteen minutes, allowing the liquids to separate, then carefully pouring off the acetate layer. This acetate solution of hydrogen peroxide was then dried over anhydrous copper sulfate for at least thirty minutes. After filtration, to remove the cupric sulfate, a small portion of this solution was titrated (in dilute aqueous sulfuric acid solution) with standard permanganate solution. This titration showed the peroxide content of the ethyl acetate solution to be between 0.95–0.99 normal. Upon standing for several days this solution showed no material loss in peroxide content.

From one-half to one gram of solid chromic anhydride was added to the remaining bulk of the ethyl acetate peroxide solution. The resulting intensely blue colored solution was maintained at the temperature of the ice-bath, while a solution of ammonia in absolute alcohol was added in slight excess. This alcoholic ammonia solution was prepared by adding liquid ammonia to absolute alcohol. Upon the addition of the ammonia, the intensely blue color faded leaving a water clear solution and a tan colored precipitate.

The peroxide solution was maintained in excess at all times in order to retain the chromic anhydride in combination as the blue colored peroxy compound.

The tan precipitate was carefully washed with cold ethyl acetate and dried in an atmosphere of nitrogen while retained in a vessel jacketed with dry ice. Samples of the dry material were analyzed for ammonia as well as for the chromium content.

Discussion

Since chromic anhydride unites with water forming chromic acid, it seems likely that the anhydride may unite with hydrogen peroxide in a non-aqueous medium to form a peroxy acid analogous to Caro's acid in the case of sulfur trioxide. Addition of the alcoholic ammonia solution should form an ammonium salt of this acid. The tan precipitate which formed upon addition of the ammonia was studied to evaluate some of its physical and chemical properties.

The ammonia content of the tan precipitate was determined using the standard method of absorbing the ammonia in a known volume of standard acid, then back titrating with standard alkali solution.

The chromium was determined by reduction and precipitation of chromic hydroxide, with subsequent ignition to chromic oxide; as well as by oxidation to chromate, precipitation of mercurous chromate, and ignition to chromic oxide.

On the basis that hydrogen peroxide would unite with chromic anhydride forming a peroxychromic acid thus: $H_2O_2 + CrO_3 \longrightarrow H_2CrO_5$, and that the tan precipitate would have the formula $H_2CrO_5 \cdot 2NH_3$, the calculated chromium content would be 30.95% while the ammonia content would be 20.23%. The average chromium content found by analysis was 30.93%, and the average ammonia content 20.15%.

Considerable difficulty was encountered in the analysis of the tan material due to its extremely unstable nature. Several samples took fire spontaneously during the course of weighing. Other samples gave poor results due to absorption of moisture and subsequent decomposition.

The tan colored ammonium salt dissolves in water with evolution of oxygen, forming a yellow-orange chromate solution. When added to acidic solutions it evolves oxygen with the formation of the unstable blue peroxychromic acid, and the resulting decomposition gives rise to a green chromic salt. At temperatures slightly above room temperature, the salt decomposes spontaneously

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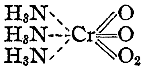
(1) Riesenfeld, *Ber.*, **41**, 3941–51 (1908).
(2) Riesenfeld, *ibid.*, **38**, 4068 (1905).
(3) Riesenfeld, *ibid.*, **47**, 548, 553 (1914).
(4) Schwarz and Giese, *ibid.*, **65B**, 871–76 (1932).
(5) Rumpf, *Compt. rend.*, **198**, 1694–7 (1934).
(6) Riesenfeld, *Chem.-Ztg.*, **32**, 914 (1908).
(7) Moissan, *Compt. rend.*, **97**, 96 (1883).
(8) Schwarz and Giese, *Ber.*, **66**, 310 (1933).
(9) Rosenheim, *Z. anorg. Chem.*, **209**, 175 (1932).
(10) Bancroft and Murphy, *J. Phys. Chem.*, **39**, 377–397 (1935).

and bursts into flame. This decomposition takes place in two stages—swelling and ignition. The particles appear to swell considerably, and finally flash rapidly leaving a residue of finely divided chromic oxide. If struck a sudden blow the material decomposes with explosive violence. If allowed to remain for some time below, or at room temperature, the material becomes more stable and behaves in much the same manner as does ammonium dichromate. X-Ray diffraction patterns show the tan colored material to have a structure quite different from that of ammonium chromate or ammonium dichromate.

The physical and chemical properties of this material resemble those described by Riesenfeld[11] for the compound chromic tetroxide triammine. The formula given this compound is



$$\begin{matrix} H_3N\searrow & & \nearrow O \\ H_3N\rightarrow & Cr & = O \\ H_3N\nearrow & & \searrow O_2 \end{matrix}$$

Since the molecular weight of this material would be 167, and that of $H_2CrO_5 \cdot 2NH_3$ 168, it follows that the chromium content would not be a deciding factor in the determination of structure. Since but two ammonia groups could be accounted for by accurate ammonia analysis in the case of the material prepared in this study; it is assumed that these compounds are different in chemical constitution although very similar in chemical properties.

Summary

The reaction between hydrogen peroxide and chromic anhydride has been studied using dry ethyl acetate as the solvent. A tan ammonium salt of the blue colored peroxychromic acid has been prepared. Analyses of this salt are in accord with the formula $H_2CrO_5 \cdot 2NH_3$. From this information the formula of the blue peroxychromic acid probably is H_2CrO_5 or $CrO_3 \cdot H_2O_2$. Some physical and chemical properties of the ammonium salt have been determined.

Urbana, Illinois Received July 29, 1936

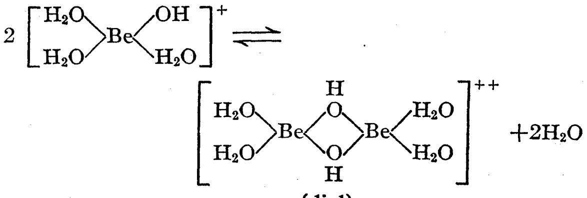
[11] Riesenfeld, *Ber.*, **41**, 3536–52 (1908).

[Contribution from the Department of Chemistry, Columbia University]

Basic Beryllium and Complex Beryllate Hydrosols; an Additional Contribution to the Concept of Polyolated and Polyoxolated Structures

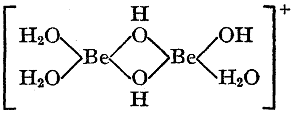
By Arthur W. Thomas and Hoke S. Miller

In previous publications from this Laboratory the properties of certain colloidally dispersed metallic "oxides" have been readily explained according to the concept that the micelles are polyolated and/or polyoxolated structures.[1] Application of this theory which involves the Werner–Pfeiffer ideas of hydrolysis and olation together with Stiasny's concept of the oxolation of ol groups, has produced a new and fundamental knowledge of beryllium "oxide" hydrosols.[2] Accepting the coördination number of 4 usually assigned to beryllium, the formation of a diol from triaquo monohydroxo beryllium ion would be



(diol)

The dissociation of an aquo group in this dinuclear diol ion, or the replacement of one of its aquo groups by OH would produce an ion such as



According to the theory, two of these in turn can olate, the result in this case being a tetranuclear olated ion. Since removal of H^+ ion favors olation, one would expect increase in size of the olated ions when a solution of a beryllium salt is made increasingly basic. Increases in basicity, however, and especially elevation of temperature

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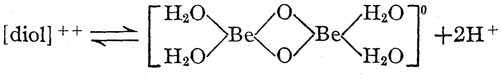
(1) (a) A. W. Thomas and T. H. Whitehead, *J. Phys. Chem.*, **35**, 27 (1931); (b) A. W. Thomas and A. P. Tai, This Journal, **54**, 841 (1932); (c) A. W. Thomas and F. C. von Wicklen, *ibid.*, **56**, 794 (1934); (d) A. W. Thomas and R. D. Vartanian, *ibid.*, **57**, 4 (1935); (e) A. W. Thomas and C. B. Kremer, *ibid.*, **57**, 1821, 2538 (1935); (f) A. W. Thomas and H. S. Owens, *ibid.*, **57**, 1825, 2131 (1935).

(2) For convenience, those hydrosols in which the beryllium is in the cationic micelle will be called *basic beryllium* hydrosols and the name *complex beryllate* will signify hydrosols in which the beryllium exists in the form of an anionic micelle.

favor oxolation, which, taking the diol for simplicity, is represented by the reaction



the intermediate product, containing one ol and one oxo group being omitted to save space. Quite unlike metals having coördination numbers of 6 and 8, it is seen that the complete oxolation of a diol structure of beryllium with its coördination number of 4 produces a complex without a charge. This would suggest that oxolation of colloidal basic beryllium complexes would result in precipitation of the micelles. This prediction has been found to be correct because our basic beryllium hydrosols precipitate immediately when boiled, and in about two hours at 60°.[3]

According to the polynuclear theory proposed at this Laboratory, the formation of a hydrosol by peptization of the hydrous oxide with the acid, HA, consists in the interaction between the H^+ ion of the peptizing acid with OH groups of the hydrous oxide gel, thus converting the polynuclear olated hydrous oxide to a polynuclear cationic micelle. A cationic micelle arises, however, only when the anion, A^- of the acid is not a strong coördinative binder. If it, by displacing aquo groups, becomes coördinatively bound to the same extent that the H^+ ion reacts with the OH groups of the gel, then no colloidal dispersion occurs. However, if A^- has great tendency to displace aquo groups, it may actually produce anionic micelles, and in the case of even neutral salts of such anions, an anionic micelle arises by peptization of the oxide.[1e] Such phenomena previously reported for zirconium and thorium "oxide" hydrosols have also been found in the case of beryllium "oxide" hydrosols.

Preparation of Basic Beryllium Hydrosols.—Three methods were employed as follows:

(a) Sodium hydroxide was added dropwise to a mechanically stirred aqueous solution of beryllium nitrate until a decided turbidity was produced. The stirring was continued for about twenty hours, after which the hydrosol was dialyzed against running distilled water, using nitrocellulose membranes.

(b) Beryllium hydroxide was precipitated from aqueous beryllium nitrate solution, washed by centrifuging and peptized with tenth molar beryllium nitrate solution. During the peptization the system was stirred mechanically. The stirring was continued for twenty hours after the beryllium nitrate was added. The hydrosols thus formed were dialyzed as previously mentioned.

(c) Beryllium hydroxide precipitated by ammonium hydroxide from beryllium nitrate solution was washed by centrifuging until the supernatant liquid no longer gave the ferrous sulfate ring test for nitrate. A known amount of 0.05 *N* hydrochloric acid was added while the solution was stirred mechanically. It was observed that the ratio of equivalents of beryllium as the hydroxide, to the equivalents of chloride, as the acid, should be approximately 50:1. When too much acid was added, deolation seemed to occur. After peptization had continued for about twenty hours the hydrosols were dialyzed against distilled water.

In all cases, the dialysis was carried out by allowing distilled water to flow through nitrocellulose bags which were immersed in the colloidal solutions, the latter being stirred mechanically. All sols were centrifuged after dialysis to remove coarse suspended matter.

Table I summarizes briefly some of the properties of these hydrosols.

TABLE I

DATA CONCERNING HYDROSOLS[a] CONTAINING CATIONIC BERYLLIUM MICELLES

Designation[b]	Method preparation	Hours dialyzed	Be[c]	Cl[c]	NO_3[c]	Ratio equiv. Be/Cl or NO_3	*p*H[d]
cA	a	84	27.2	..	0.1	272	6.1
cB	a	70	41.7	..	5.6	7	5.9
cC	c	360	21.9	[e]	...	...	6.6
cD	b	40	22.3	..	6.0	4	5.6
cE	b	70	12.3	..	1.9	6	5.6
cM	c	72	84.7	0.40	...	212	6.0
cN	c	56	86.3	0.99	...	87	6.1
cO	c	50	60.4	7.88	...	8	5.8
cR	a	72	10.1	..	1.8	6	5.7

[a] All the hydrosols displayed particles in lively Brownian motion in a brilliant Tyndall cone. They were cloudy in appearance. [b] The initial letters (c) and (a) are used in Tables I and III to signify that the beryllium is in the cationic (c) or in the anionic (a) micelle. [c] In milliequivalents per liter. [d] *p*H values were measured immediately after centrifuging the dialyzed hydrosols. [e] 500 cc. of sol cC when decomposed with nitric acid gave no test for chloride with silver nitrate, nor did a portion of it give the ferrous sulfate ring test for the nitrate ion.

Effect of Neutral Salts upon Hydrosols.—In previous publications[1] it was shown that neutral salts raise the *p*H values of certain metallic

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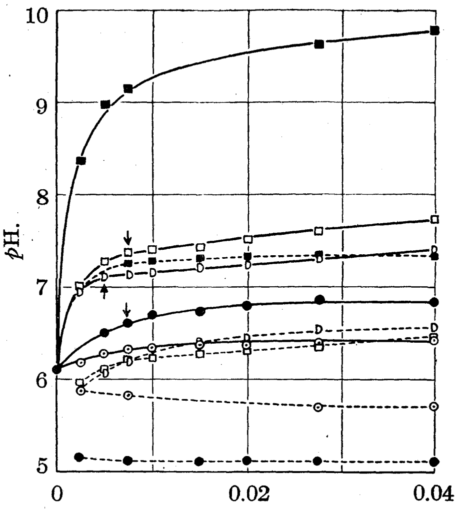
[3] Some of our basic beryllium hydrosols precipitated after storage for two months at room temperature.

"oxide" hydrosols, the action being ascribed to the displacement of OH groups in the micelle by the added neutral salt anions. The relative potencies of neutral salt anions to raise the *p*H value have been ascribed to their relative coördinative binding tendencies.



Final salt concentration in equivalents.

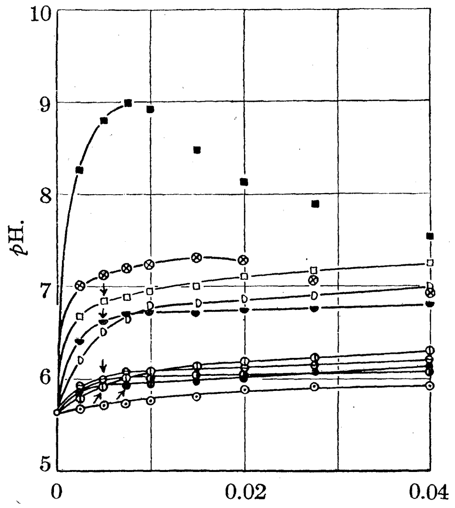
Fig. 1.—Effect of potassium salts on the *p*H of sol cA. Sol six days old. Broken lines represent *p*H values of pure aqueous salt solutions. Continuous lines record *p*H values of sol-salt mixtures. ■, Citrate; ⊙, chloride; □, oxalate; ●, sulfate; D, tartrate.

In the experimental work, with the exception of all the data given in Fig. 1 and that for the potassium citrate solution in Fig. 3, 0.08 *N* stock solutions of the salts were adjusted to *p*H values below 7 and above 6 by the addition of potassium hydroxide or of the appropriate acid. The *p*H values of these stock solutions are recorded in Table II. These solutions with added water, when necessary, were added to equal volumes of the hydrosol in small bottles and rotated at 7 r. p. m. for twelve to twenty hours at 25°.[4] The hydrogen ion activity was then measured by the quinhydrone electrode if the *p*H value was less than 7.5 and by the hydrogen–platinized-platinum electrode when it was above 7.5.

Table II

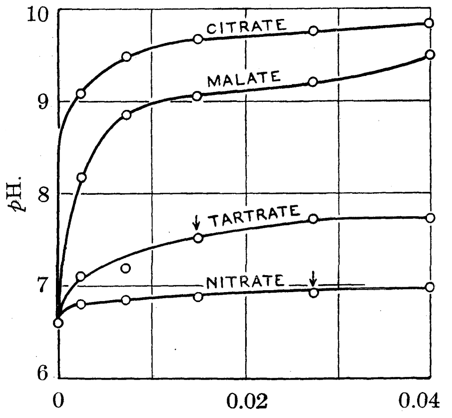
*p*H Values of 0.08 *N* Potassium Salt Solutions

Acetate	6.3	Maleinate	6.5
Citrate	6.3	Malonate	6.7
Chloride	6.3	Nitrate	6.6
Formate	6.1	Oxalate	6.3
Fumarate	6.2	Sulfate	6.2
Lactate	6.7	Tartrate	6.4
Malate	6.4		



Final salt concentration in equivalents.

Fig. 2.—Effect of potassium salts on *p*H of sol cE. Sol one day old. Salt solutions were those described in Table II. ⦶, Acetate; ■, citrate; ⊙, chloride; ⊖, formate; ◑, fumarate; ⊗, malate; ▾, maleinate; □, oxalate; ●, sulfate; D, tartrate.



Final salt concentration in equivalents.

Fig. 3.—Effect of potassium salts on *p*H of sol cC. Sol one day old and apparently devoid of chloride or nitrate ion. Salt solutions used were those described in Table II with exception of the citrate solution which in this instance was at *p*H = 6.9.

Figures 1 to 3 provide some typical results. In Fig. 1, the broken curves show the *p*H values of pure aqueous solutions of the salts while the continuous curves represent the *p*H values of the salt–hydrosol mixtures. There can be no doubt concerning the *p*H increasing effect of the added anions. The marked buffer effect of the *p*H =

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[4] The reaction is practically complete in one to three hours.

6.3 citrate solution used in the experiments plotted in Fig. 2 led us to use a stock citrate solution of $p\text{H} = 6.9$ in the work recorded in Fig. 3. The arrows on Figs. 1, 2, 3 and 7 indicate where precipitation was observed. In the cases of added citrate and malate, precipitation occurred at extremely low concentrations of the added salt, higher concentrations of these salts producing no precipitate but having converted the cationic beryllium micelles to anionic citrato (or malato) beryllate micelles. A summary of all of our measurements showed that the pH raising order for the anions upon cationic beryllium hydrosols is citrate $>$ malonate $>$ oxalate $>$ malate $>$ tartrate $>$ maleinate $>$ acetate $>$ formate $\geqq$ fumarate $\geqq$ sulfate $>$ chloride $\geqq$ nitrate. This series resembles that found in this Laboratory for thorium oxychloride sols[1e] and for zirconium oxychloride sols.[1f]

With the *cis-trans* isomers, potassium maleinate proved to be more effective than potassium fumarate. This is in agreement with the action of these salts on thorium oxychloride sols as reported by Thomas and Kremer.[1e]

One might ask whether there is any relationship between the pH raising effect of the added salts and their precipitating potencies upon basic beryllium hydrosols. A few experiments were performed to throw light upon this question.

Liminal Values[5] of Salts.—The procedure adopted for the measurement of liminal values was as follows. Into each of four 30-cc. volume test-tubes was placed 5 cc. of the hydrosol. Five cubic centimeter portions of varying concentrations of the salt were placed in four other tubes. The salt solution was poured into the hydrosol; the contents were poured back into the salt solution tube; then back to the hydrosol tube, after which they were centrifuged for two minutes at 1000 r. p. m. (radius, 21 cm.). This procedure was repeated until the liminal value was finally obtained.

From the results given in Table III it can be seen that the effectiveness of certain potassium salts as precipitants of cationic basic beryllium hydrosols is in general: citrate $>$ malate $=$ tartrate $>$ oxalate $>$ sulfate $>$ fumarate $>$ maleinate $>$ chloride. It is interesting to note that tartrate is a more powerful precipitant than oxalate although the reverse is true for their pH raising potencies. Inasmuch as inorganic micelles are, in general, precipitated when the charge is reduced to a certain extent, and since in this instance the positive charge must be reduced by displacement of aquo groups of negatively charged ions, it would seem that tartrate is a more potent displacer of aquo groups than is oxalate. The same may be said for sulfate as compared with maleinate where the precipitating potency is sulfate $>$ maleinate, the reverse of the pH raising tendency.

TABLE III

LIMINAL VALUES

Sol	Citrate	Tartrate	Malate	Oxalate	Sulfate	Fumarate	Maleinate	Chloride
cA	0.08	0.19	..	0.33	0.53	..	..	600
cB	.41	.62	..	1.08	.78	..	..	>1500
cR	.36	.58	..	0.76	1.64	..	..	>1000
cD	.27	.76	..	1.62	1.64	..	..	>1000
cE	.25	.44	0.44	0.76	0.88	1.24	1.96	>1000

Conductance Titrations.—Another means of comparing the tendencies of anions to displace aquo groups from the central metallic ions of the micelle is offered by measurement of changes in conductivity resulting upon addition of very small amounts of salts to the hydrosol and to water. Such measurements are shown in Fig. 4 where the conductivities of mixtures of hydrosol "cN" and potassium salts (solid lines) are compared with the conductivities of the pure salt solutions (broken lines). If the anion of an added salt enters the micelle, displacing an aquo group therefrom, the conductivity of the salt–hydrosol mixture will obviously be less than if there were no reaction between the added anion and the colloidal micelle. Convergence of the solid line and broken line curves in Fig. 4 is evidence for such displacement, while parallelism of the solid and broken lines for a given salt means no such reaction. Inspection of the figure reveals that the nitrate curves have practically identical slopes and hence at the low concentrations used, nitrate has only a negligible (if any) effect in replacing aquo groups from the central beryllium ions of the micelle. The tartrate curves are not of the same slope, showing that tartrate has an aquo group replacing tendency which is, however, less than that of citrate where the curves converge at the concentration of 15 milliequivalents of potassium citrate per 50 cc. of solution. It must be remembered that some replacement of OH groups also is effected by an ion such as citrate (and to a less extent by tartrate). This

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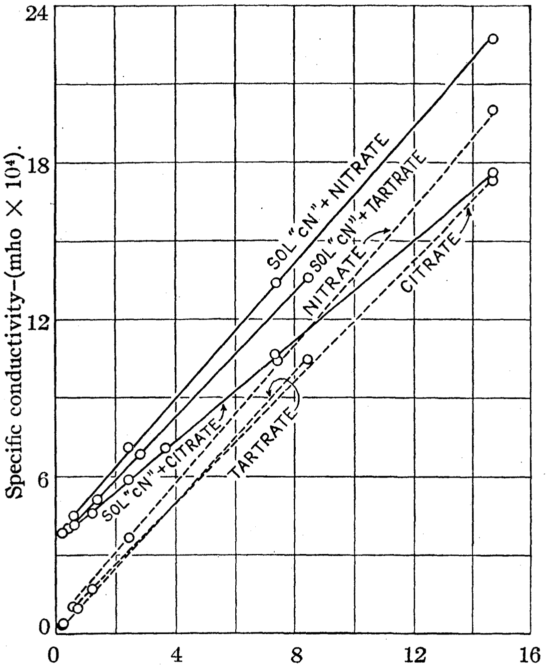
[5] "Liminal value" as used in this paper is defined as the lowest concentration of salt, expressed in millimoles per liter of final mixture, that just completely precipitates the micelles under the described procedure.

would cause the curves to diverge with increasing concentration, however. In view of the fact that both OH replacement and aquo group replacement may occur, one is obliged to be content with the solely qualitative nature of the evidence given in Fig. 4, namely, aquo group replacement potency is citrate > tartrate > nitrate.[6]



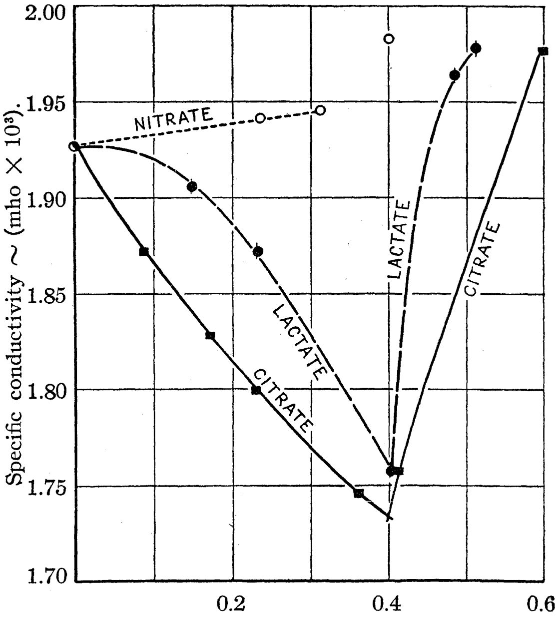
Milliequivalents of salt in final solution, 25 cc. sol "cN" + 25 cc. salt.

Fig. 4.—Potassium salt conductivity titrations of sol cN. Sol three days old. Continuous lines represent mixtures of sol and salt solutions. Broken lines represent salt solutions diluted with water.

Another method of measuring the tendency of anions to replace aquo groups is by means of the observation of the effect of added silver salts upon the conductivity of the hydrosol. By means of a technique previously described[1b] the results shown in Fig. 5 were given by sol "cM."

All the chloride in the hydrosols was precipitated by each of the silver salts added since the value of the chloride content determined by the conductivity method agreed with the gravimetric results. When an amount of silver salt just in excess of equivalence to the chloride content of the hydrosol was added, a sharp change in direction of the curve occurred.

It is seen that added amounts of silver nitrate caused an increase in conductivity in the first segment of the curve, while the reverse was found true for lactate and citrate. These experimental data may be explained as follows. When silver ion is added to the hydrosol it combines with the unbound chloride ion to form silver chloride. As the chloride ion is removed from solution, any coördinatively bound chloride moves out of the micelle. This reaction continues until all the chloride has been converted to silver chloride, when the inflection point occurs; further additions of silver salt obviously increase the conductivity of the system. Since the nitrate ion has only a very feeble tendency to become coördinatively bound, we may assume that as the chloride groups move out of the micelle, aquo groups enter to satisfy the coördination number of the beryllium atom, thus the positive charge of the micelle increases, and consequently the conductivity increases also. This is, of course, superimposed upon the increase in conductivity resulting from the addition of silver and nitrate ions.



Milliequivalents of silver salts added.

Fig. 5.—Conductivity titrations of sol cM with silver salts. Sol three days old.

The decrease in conductivity when either silver lactate or silver citrate is added may be explained in the following manner. As the coördinatively bound chlorido groups move out of the complex they are replaced by negatively charged lactate or citrate ions as the case may be. The combination between chloride and silver ions reduces the

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(6) The reaction between citrate ion and the micelle was rather slow, four hours being required for attainment of equilibrium at the highest concentration of added citrate.

conductivity of the system as in the first instance. At the same time, since lactate or citrate ions displace aquo groups, the charge of the micelle is reduced. These ions no longer contribute to the conductivity of the system and hence there are introduced two additional conductivity-lowering factors.

The steeper slope for citrate is ascribed to its greater tendency than lactate to become coördinatively bound to the central beryllium ions and to replace aquo groups therefrom.

A similar series of titrations of sol "cO" is given in Fig. 6. This sol differed from "cM" in its lower basicity or higher ratio of chloride to beryllium. It is noted that nitrate ion showed a slight tendency to combine with the micelles.

Complex Beryllate Hydrosols

Thomas and Owens[1f] and Thomas and Kremer[1e] found that a reversal of the sign of charge of cationic zirconium "oxide" and thorium "oxide" micelles occurred upon the addition to the hydrosols of specified concentrations of salts and acids of strong coördinative binding anions. These authors also demonstrated that upon direct peptization of zirconium or thorium hydrous oxides with certain salts or acids, anionic basic "oxide" sols were produced. Thomas and Owens reported also that anionic zirconium micelles could be produced by boiling a crystalloidal solution of a complex zirconeate.

Search of the literature failed to locate any statement concerning the reversal of the sign of the charge of cationic beryllium "oxide" micelles other than the report that attempts to accomplish such a result by use of potassium ferrocyanide[7] did not meet with success. Following the theoretical prediction that anions which are powerful coördinative binders should produce anionic micelles provided that they replace a sufficient number of aquo groups from the cationic micelle or from the hydrous oxide, it was found that stable hydrosols of anionato complex beryllate micelles could be produced. Some remarks concerning these systems follow.

Preparation of Complex Beryllate Hydrosols.—These hydrosols can be prepared by either of the following methods: (1) by the addition of either potassium citrate, malate or tartrate to a cationic beryllium hydrosol, producing a precipitate which redisperses;[8] (2) by the peptization of freshly precipitated hydrous beryllium oxide with an aqueous solution of either potassium citrate or malate, or tartrate; (3) by dropwise addition of ammonium hydroxide solution to a complex crystalloidal beryllate, prepared by adding potassium tartrate to beryllium nitrate solution, with immediate and subsequent dialysis. Care must be exercised not to add too much ammonium hydroxide. An excess of this reagent precipitates the beryllium as hydroxide.[9]

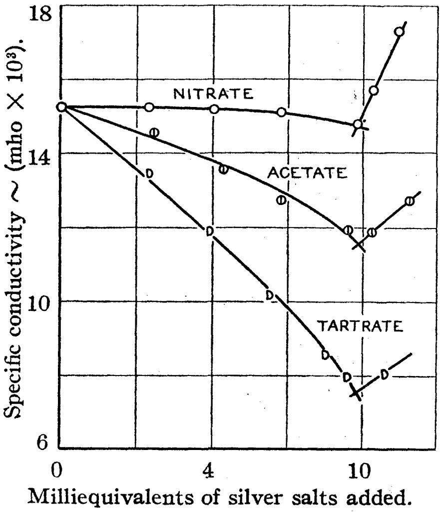

Fig. 6.—Conductivity titration sof sol cO with silver salts. Sol three days old.

A description of a few of these sols is given in Table IV.

TABLE IV

DATA CONCERNING COMPLEX BERYLLATE HYDROSOLS[a]

Designation	Method of preparation	Hours dialyzed	Be[b]	pH[c]
aJ	3	186	40.1	7.8
aK	2 (citrate)	237	19.5	6.3
aH	2 (tartrate)	113	41.6	6.4
aL	2 (malate)	223	29.1	6.9
aQ	2 (tartrate)	77	74.5	6.9

[a] These hydrosols were cloudy in appearance, displaying particles in lively Brownian motion in a brilliant Tyndall cone. [b] In milliequivalents per liter. [c] The pH values were measured immediately after centrifuging the dialyzed hydrosols.

Some Properties of Complex Beryllate Hydrosols.—It was found that addition of potassium salts to these hydrosols results in an increase in pH value. A typical result is shown in Fig. 7

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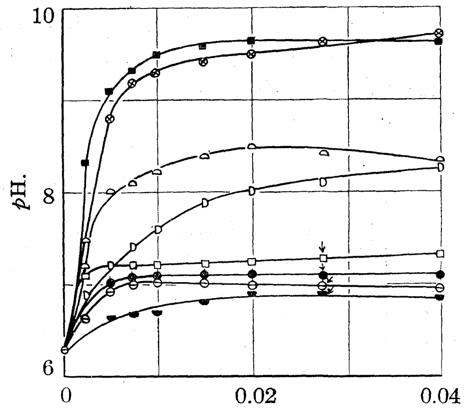
(7) W. H. Madson and F. C. Krauskopf, *J. Phys. Chem.*, **35**, 3237 (1931).

(8) The redispersion of the precipitate with potassium tartrate is slow, several days being necessary for the formation of a hydrosol.

(9) This affords a means for the separation of beryllium from certain other metals which is to be described by one of us (H. S. M.) in a subsequent paper.

where the effectiveness of the anions is seen to be citrate > malate > malonate > tartrate > oxalate > lactate > formate > maleinate. In the concentration range shown in Fig. 7, precipitation of the micelles occurred only with the last four salts mentioned and then only slightly at a concentration of 0.028 milliequivalent.

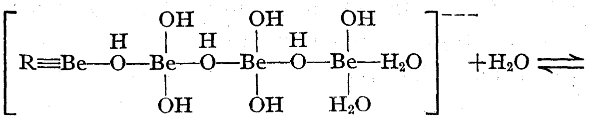


Final salt concentration in equivalents.

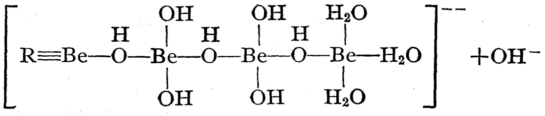
Fig. 7.—Effect of potassium salts on the pH of sol aK. Sol five days old. Salt solutions used were those described in Table II. ■, Citrate; ⊖, formate; ●, lactate; ⊗, malate; ▾, maleinate; ⌓, malonate; □, oxalate; D, tartrate.

It will be recalled that hydrosols of the cationic metallic micelles become more acid on storage at room temperature owing to oxolation and possibly to dissociation of aquo groups. The complex beryllate hydrosols, on the contrary, become less acid on aging at 25°. The pH value of sol "aK" which was 6.3 at the conclusion of dialysis rose to 7.2 in one month. Six weeks later it was 7.4. Sols "aL" and "aQ" also increased in pH value but to a less extent.

This increase in pH might be ascribed to the action of free citrate, malate or tartrate ions (possibly present) in replacing coördinatively bound OH groups. But the phenomenon of aquotization would seem to offer a more plausible explanation. An aquotization reaction of a hypothetical basic citrato beryllate[10] may be illustrated as follows, where R = $C_6H_5O_7^{---}$



$$\left[\mathrm{R{\equiv}Be{-}\overset{H}{O}{-}\underset{OH}{\overset{OH}{Be}}{-}\overset{H}{O}{-}\underset{OH}{\overset{OH}{Be}}{-}\overset{H}{O}{-}\underset{H_2O}{\overset{OH}{Be}}{-}H_2O}\right]^{---} + H_2O \rightleftharpoons$$



$$\left[\mathrm{R{\equiv}Be{-}\overset{H}{O}{-}\underset{OH}{\overset{OH}{Be}}{-}\overset{H}{O}{-}\underset{OH}{\overset{OH}{Be}}{-}\overset{H}{O}{-}\underset{H_2O}{\overset{H_2O}{Be}}{-}H_2O}\right]^{--} + OH^-$$

As a precedent for this type of reaction we would cite Sandved's[11] measurements of the equilibrium constants of the reversible aquotization reactions

$$\left[\mathrm{Co}^{\chi}_{(NH_3)_5}\right]^{++} + H_2O \rightleftharpoons \left[\mathrm{Co}^{H_2O}_{(NH_3)_5}\right]^{+++} + \chi^-$$

where χ = Cl or NO_3

Heating of beryllate sols produced an unexpected change in that cationic beryllium micelles arose. Sols "aK" and "aL" were heated at 95° in sealed containers for ninety-six and fifteen hours, respectively. As a result of the heating, the conductivities rose in the case of "aK" from 4.24×10^{-5} to 5.84×10^{-5} mho and in the case of "aL" from 13.76×10^{-5} to 13.98×10^{-5} mho.

Upon electrophoresis of the sols which had been heated, it was observed that about half the beryllium in the case of sol "aK" and about four-fifths in the case of "aL" migrated to the anode, the remainder being cationic.[12] These results may be explained on the assumption that heating causes some of the citrato or malato groups to move out of the micelles, thus reducing the negative charge and even reversing it on some of the particles. The citrato or malato groups which move out of the micelles cause an increase in conductivity, the increase depending upon the length of time of heating the hydrosols. Thus, oppositely charged micelles may exist in basic beryllium hydrosols as previously mentioned for basic zirconium complexes.[1f]

Action of Acids upon Hydrous Beryllium Oxide.—It was shown previously that acids containing weakly coördinative binding anions peptize hydrous alumina at room temperature to the colloidal state while those whose anions have powerful coördinative binding tendency do not.[1d] The following experiment was performed in order to see whether hydrous beryllium oxide acted similarly. A suspension of freshly precipitated and washed hydrous beryllium oxide (precipitated from the nitrate with ammonium hydroxide) equal to 0.1 g. equivalent of beryllium oxide was agitated for forty-eight hours at 25° with 195 cc. of water containing 0.005 g. equivalent of acid. The reaction mixtures were filtered and examined.

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(10) It is to be understood that the hypothetical compound formulated is not intended to describe the structure of a complex beryllate micelle.

(11) K. Sandved, *Tids. Kjemi Bergvesen*, **15**, 21 (1935).

(12) The colloidal nature of the migrating particles was evidenced by the turbid appearance of the contents of both arms of the electrophoresis U-tube.

In the cases of citric and malic acids (citrate and malate ions have powerful coördinative binding affinity for beryllium) the filtrates contained some beryllium ion but no colloid. In the case of tartaric acid (tartrate ion is not so powerful a coordinative binder as citrate or malate), the slightly turbid filtrate was found to consist of a dispersion of colloidal complex beryllate micelles ("negatively charged beryllium oxide"). In the case of lactic acid (lactate ion is not a strong coordinative binder to beryllium), the very turbid filtrate was a dispersion of cationic basic beryllium micelles ("positively charged beryllium oxide").

Thus, it is indicated that the reaction of hydrous beryllium oxide to acids can be included under the same theoretical treatment as aluminum oxide. More will be reported on this topic in a subsequent publication.

Summary

For convenience of expression the term "beryllium hydrosol" will be used to designate hydrosols wherein the beryllium is in the complex cationic micelles; and the term "beryllate hydrosol" will refer to those hydrosols wherein the beryllium is in the anionic micelles.

1. Some methods for the preparation of beryllium and beryllate hydrosols have been described.
2. Addition of neutral salts to beryllium and to beryllate hydrosols produces marked decreases in hydrogen ion activity, the decrease being dependent upon the nature and concentration of the anion of the salt added.
3. The effectiveness of potassium salts in decreasing the hydrogen ion activity of beryllium hydrosol–salt systems was in general: citrate > malonate > oxalate > malate > tartrate > maleinate > acetate > formate ≧ fumarate ≧ sulfate > chloride ≧ nitrate; while that for a beryllate hydrosol–salt system was: citrate > malate > malonate > tartrate > oxalate > lactate > formate > maleinate.
4. Heating to 60° precipitated the beryllium hydrosols, whereas the beryllate hydrosols did not precipitate[13] when raised to 100°.
5. Aging at 25° caused an increase in hydrogen ion activity of the beryllium hydrosols, while in case of the beryllate hydrosols a decrease in hydrogen ion activity was noted on aging.
6. The order of silver salts in decreasing conductivity is: nitrate < lactate < citrate; and nitrate < acetate < tartrate.
7. Conductance titrations of beryllium hydrosols with potassium salts indicate the following order with respect to the tendency of the anions of the salts to become coördinatively bound to the beryllium atom: citrate > tartrate > nitrate.
8. It has been shown that heat increases the conductivity of beryllate hydrosols, converting some of the anionic beryllium to the cationic state.
9. It is evident that the order of peptization of hydrous beryllia with acids is the reverse of the *p*H raising potencies of the corresponding neutral salts of the acids.

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(13) After standing for two months at room temperature tartrato beryllate began to precipitate, while the citrato and malato beryllates were still stable.

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Rearrangement of Sugar Acetates by Aluminum Chloride. Crystalline Celtrobiose and Some of its Derivatives[1]

BY NELSON K. RICHTMYER AND C. S. HUDSON

Although it is stated in well-known texts[2] that celtrobiose is *d*-glucosido-*d*-altrose, the evidence rests on the single observation[3] that after hydrolysis of acetochloroceltrobiose with 0.5 *N* hydrochloric acid for two and a half hours at 98° the solution is levorotatory. By analogy with neolactose (*d*-galactosido-*d*-altrose),[4] both in its preparation through the rearranging action of aluminum chloride, and in its behavior on hydrolysis, whereby a levorotatory solution also is obtained, such a formulation seemed probable. We now know that this negative rotation is due, not to *d*-altrose itself which rotates[4c,5] +32.6°, but to a non-reducing derivative, and that the rotation −98° originally ascribed to *d*-altrose[4b] refers to the equilibrium mixture of *d*-altrose and its anhydro form that results from sufficiently strong acid conditions. The present report, dealing with celtrobiose and some of its derivatives, proves conclusively that celtrobiose is *d*-glucosido-*d*-altrose.

Acetochloroceltrobiose has now been obtained in yields of 40–45% by the action of a mixture of aluminum chloride and phosphorus pentachloride on a chloroform solution of cellobiose octaacetate. From this acetochloro compound with acetic anhydride and sodium acetate the α-octaacetate was prepared; by converting the acetochloro derivative to the β-heptaacetate with silver carbonate and aqueous acetone, and then acetylating with acetic anhydride and pyridine the β-octaacetate was prepared. The rotations of these carefully purified substances are recorded in Table I, and from them values for the rotations of the end asymmetric carbon atoms (A_{Ac} and A_{Cl}) have been obtained in the usual way.[6]

It is noted that the value for A_{Ac} is in agreement with those obtained for cellobiose, lactose, and neolactose, and the two octaacetates may be assumed to represent a normal α,β-pair. The value for A_{Cl} is much smaller than in the case of cellobiose and lactose, but agrees closely with that found for neolactose; it seems probable that this A_{Cl} value is a characteristic of the acetochloro-*d*-altrose portion of the disaccharide derivative, and that the A_{Cl} value for acetochloro-*d*-altrose itself will be of the same magnitude, namely, about 30,000.

Although aluminum chloride was originally suggested as being the reagent which causes the double epimerization at the second and third carbon atoms, the best yields of rearrangement products have been obtained by using a mixture of aluminum chloride and phosphorus pentachloride. On the other hand, the use of aluminum chloride alone is recommended for the preparation of the normal chlorination product; for example, acetochloroceltrobiose has been obtained in 90% yield by warming a chloroform solution of celtrobiose octaacetate with twice its weight of commercial aluminum chloride.

In our study of the α- and β-octaacetates of celtrobiose six different crystalline modifications were isolated. The α-octaacetate separates from alcohol in large prisms which melt at 130°, or in prisms which melt at 112°, then resolidify and melt at 130°; either form can be obtained at will. The β-octaacetate crystallizes from aqueous alcohol in prisms as a monohydrate melting at 87–93°, or as solvent-free needles melting at 114°; from ether it separates in fine needles melting at 103-105°. Here also any of the three forms is obtainable as desired. In addition to the pure α- and β-forms, a double compound is known, and serves to identify readily one octaacetate in the presence of the other. It crystallizes from ether in typical rectangular plates melting at 70° with evolution of gas; it has the composition 2α-octaacetate·1β-octaacetate·3ether, as shown by analysis, and rotation of +24.9° as compared with the value +25.0° calculated from the known rotations of the two octaacetates. This appears

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service. Presented in part before the Division of Organic Chemistry, at the Pittsburgh meeting of the American Chemical Society, Sept. 7–11, 1936.

[2] *E. g.*, Tollens–Elsner, "Kurzes Handbuch der Kohlenhydrate," 4th edition, Johann Ambrosius Barth, Leipzig, 1935, p. 476; Abderhalden "Biochemisches Handlexikon," Vol. XIII, edited by Zemplén, Verlag von Julius Springer, Berlin, 1931, p. 606.

[3] Hudson, THIS JOURNAL, **48**, 2002 (1926).

[4] (a) Kunz and Hudson, *ibid.*, **48**, 1978 (1926); (b) Kunz and Hudson, *ibid.*, **48**, 2435 (1926); (c) Richtmyer and Hudson, *ibid.*, **57**, 1716 (1935).

[5] Throughout the article the rotations are specific rotations at 20° for sodium light.

[6] Hudson, THIS JOURNAL, **46**, 462 (1924).

TABLE I

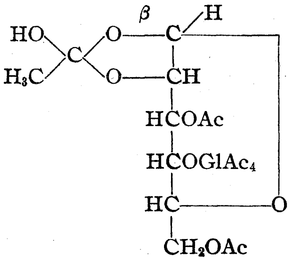
Derivative of celtrobiose		α-Octaacetate	β-Octaacetate	α-Acetochloro
Molecular weight		678	678	655
$[\alpha]^{20}\text{D}$ in $CHCl_3$		+48.0	−13.0	+64.2
$[M]^{20}\text{D}$		+32,540	−8810	+42,050
Rotation of end carbon		$A_{\text{Ac}} = +20{,}700$		$A_{\text{Cl}} = +30{,}200$
A for corresponding derivatives of	Cellobiose	19,100[a]		37,600[b]
	Neolactose	20,500[c]		30,900[c]
	Lactose	19,800[d]		38,400[e]

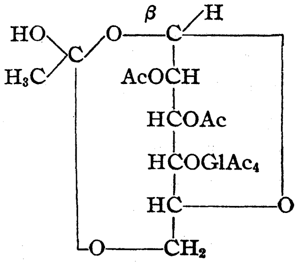
[a] Hudson and Johnson, THIS JOURNAL, **37**, 1276 (1915). [b] Calculated from the rotation +71.7° for acetochlorocellobiose, found by Brauns, *ibid.*, **48**, 2776 (1926). [c] Kunz and Hudson, ref. 4a. [d] Hudson and Johnson, THIS JOURNAL, **37**, 1270 (1915). [e] Kunz and Hudson, *ibid.*, **47**, 2052 (1925).

to be the first example of a double compound of two octaacetates, and indicates that considerable caution is required lest two isomers crystallizing together be mistaken for a pure chemical individual. Similar molecular compounds reported from this Laboratory include the novel modifications of methyl-*d*-xyloside,[7] lactose,[7] anhydrous *l*-rhamnose,[8] and the so-called neolactose "α"-heptaacetate.[4c] Also, Fischer's rhamnose β-triacetate rotating −19.4° was considered by him to represent a mixed compound.[9]

Exchange of the Cl atom in acetochloroceltrobiose by an OH group leads to the formation of celtrobiose β-heptaacetate which has been crystallized only in combination with one mole of ether; on a solvent-free basis the β-heptaacetate in chloroform rotates +3.9° changing to +15.1°. The α-heptaacetate crystallizes as a dietherate and also solvent-free; it mutarotates downward in chloroform from +22.3 to +15.1°.

Another heptaacetate of celtrobiose has been obtained, in very small yield, through the silver carbonate–aqueous acetone reaction with the chloro compound; it melts considerably higher than the other acetates, rotates +1.0° in chloroform without mutarotation, and on cautious acetylation with acetic anhydride and pyridine is transformed quantitatively to celtrobiose β-octaacetate. These properties, combined with the fact that the normal α- and β-heptaacetates are known, lead to the belief that this acetate may well have an ortho ester structure involving the 1,2- or even the 1,6-positions of the altrose molecule which are spatially much closer than the customary formula would indicate.





The previously known ortho esters of the sugar series in which one hydroxyl group remains unsubstituted appear to be limited to the heptaacetate of the ketone sugar turanose described by Pacsu[10] and to a tetraacetate of glucose described by Helferich and Klein[11] as 1,2,3,6,(?)-tetraacetyl-β-*d*-glucose, but to which Haworth, Hirst and Teece[12] have assigned a 1,6-ortho ester structure. Reactions which were expected to prove an ortho ester linkage in these compounds were disappointing because derivatives of the normal form were usually obtained. Methylation with silver oxide and methyl iodide produced the normal acetylated β-glycoside in each case. Acetylation of the glucose tetraacetate did not lead to a new glucose pentaacetate but only to the well-known β-pentaacetate. In these reactions it has been assumed that a facile rearrangement from the ortho ester to the normal form has been brought about by the reagents employed. The lack of reactions suitable for proving an ortho ester structure together with the scarcity of our own extra heptaacetate make necessary a postponement of its further study.

Deacetylation of the hepta- or octaacetates with barium methylate solution resulted in crystallization of the parent disaccharide. Celtrobiose monohydrate, well-formed prisms from 75% alcohol, rotates +13.6° in water; although mutarotation was not observed the sugar is undoubtedly the β-form since on cautious acetylation it produced an 85% yield of celtrobiose β-octaacetate. The component hexoses liberated from celtrobiose by hydrolysis with dilute hydro-

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(7) Hockett and Hudson, THIS JOURNAL, **53**, 4454, 4455 (1931).

(8) Jackson and Hudson, forthcoming publication.

(9) Fischer, Bergmann and Rabe, *Ber.*, **53**, 2362 (1920).

(10) Pacsu, THIS JOURNAL, **55**, 2451 (1933).

(11) Helferich and Klein, *Ann.*, **450**, 226 (1926); **455**, 177 (1927).

(12) Haworth, Hirst and Teece, *J. Chem. Soc.*, 1408 (1930).

chloric acid at 100° had a rotation of −22.8°; the value −22.7° would be expected from an equilibrium mixture of *d*-glucose (+52.5°) and *d*-altrose (−98° in acid solution).[4c] The oxidation of celtrobiose with bromine water, followed by acid hydrolysis of the bionic acid, yielded crystalline *d*-glucose, and *d*-altronic acid which was isolated as the crystalline calcium salt. Since the biose linkage should not be affected by the aluminum chloride rearrangement of cellobiose octaacetate, these data prove conclusively that celtrobiose is 4-β-*d*-glucosido-*d*-altrose.

Preliminary experiments have shown that calcium *d*-altronate, obtainable through the aluminum chloride rearrangement of lactose or cellobiose octaacetates, is a convenient source for the preparation, by degradation, of *d*-ribose.

Experimental

α-Acetochloroceltrobiose.—The modified procedure is as follows. To a solution of 50 g. of recrystallized cellobiose octaacetate[13] in 400 cc. of alcohol-free dry chloroform in a one-liter flask is added 100 g. of powdered commercial aluminum chloride and 50 g. of powdered phosphorus pentachloride. The flask is shaken for a few minutes to ensure thorough mixing, then heated for one hour in a bath at 60–63°. The granular mixture is decomposed carefully with ice and water, the resulting solution extracted with chloroform, and the chloroform extracts washed several times with water, dried with granular calcium chloride and concentrated *in vacuo* to a thin sirup. Dry ether is then added cautiously in order to obtain a small crop (*ca.* 10 g.) of acetochlorocellobiose which carries down most of the colloidal impurities derived from the cellulose. After a few minutes the solid is removed by filtration, and the mother liquor diluted to 500 cc. with dry ether. Crystallization is allowed to proceed overnight at room temperature and then for a week in the refrigerator. The mixture of acetochloro derivatives thus obtained is separated mechanically; partial disintegration of the crystals with a spatula allows the fine needles of acetochlorocellobiose to be floated away in ether suspension, leaving the heavier prismatic crystals of the celtrobiose compound. A small additional crop of the latter may be obtained by combining the two fractions of crude acetochlorocellobiose and shaking them with ether for several hours at room temperature; the more soluble celtrobiose derivative is dissolved, together with some of the cellobiose compound, and the two are separated by crystallization. The yield of crude acetochloroceltrobiose is 19–22 g. (40–45%). Two recrystallizations from chloroform–ether give a product, rotating about +61°, which is pure enough for subsequent transformations. However, thirteen recrystallizations brought the rotation to +63.9°, a figure which was not appreciably changed by eight additional recrystallizations, and the value +64.2°, obtained after the twenty-first recrystallization is accepted for the rotation of α-acetochloroceltrobiose in U. S. P. chloroform (*c*, 4). The m. p. is 141–142°, with no visible decomposition.

α-Acetochloroceltrobiose from Celtrobiose α-Octaacetate.—A solution of 25 g. of pure α-octaacetate (see below) in 200 cc. of alcohol-free dry chloroform was heated with 50 g. of powdered commercial aluminum chloride for two hours at 60–63°, then decomposed carefully with ice and water. The chloroform extracts, after being washed with water and dried with calcium chloride, were concentrated *in vacuo* to a thin sirup. Upon the addition of dry ether the solution deposited typical hexagonal plates of acetochloroceltrobiose in a yield of 21.6 g. (90%) plus a few centigrams of the acicular crystals of acetochlorocellobiose. After five recrystallizations the acetochloroceltrobiose melted at 141–142°, and rotated +64.2° in U. S. P. chloroform (*c*, 4); these values were unchanged by five additional recrystallizations.

Celtrobiose α-Octaacetate.—A mixture of 25 g. of acetochloroceltrobiose, 25 g. of fused sodium acetate and 200 cc. of acetic anhydride was heated on the steam-bath for two hours, then boiled gently for five minutes and poured into two liters of ice and water. The solution was neutralized by adding solid sodium bicarbonate, whereupon most of the octaacetate separated as a spongy, light brown mass. This was extracted with chloroform, and the chloroform solution washed with water, dried with granular calcium chloride, and concentrated *in vacuo.* The resulting sirup was dissolved in alcohol and the solution, inoculated with a crystal already obtained, deposited 22.1 g. of heavy clusters of prisms, melting at 127–129°. Recrystallized from three volumes of warm alcohol, it melted at 129–130° and rotated +48.0° in U. S. P. chloroform (*c*, 4); these values were unchanged by eight additional crystallizations.

A second modification of the α-octaacetate, melting at 112°, was obtained in a preliminary experiment; the same form appeared during recrystallizations when the 130° form was left in contact with its mother liquor, especially in a cool place, the original sharp-edged prisms assuming a "weather-beaten" appearance and showing the lower melting point. It was later discovered that either the 112° or the 130° modification could be obtained at will by seeding an alcoholic solution of the octaacetate with a crystal of the desired form. This second modification crystallizes in prisms which melt at 112°, then resolidify and melt again at 129–130°; it contains no solvent of crystallization, and its melting point was unchanged after four hours of heating at 100° *in vacuo.* After five recrystallizations it rotated +48.0° in U. S. P. chloroform (*c*, 4).

Anal. Calcd. for $C_{28}H_{38}O_{19}$: C, 49.54; H, 5.65; acetyl, 11.79 cc. of 0.1 *N* NaOH per 100 mg. Found: (130° form) C, 49.39; H, 5.64; acetyl, 11.83 cc.; (112° form) C, 49.31; H, 5.63; acetyl, 11.84 cc.

Celtrobiose β-Octaacetate.—A mixture of 50 cc. of acetic anhydride and 125 cc. of pyridine, cooled to −10°, was added to 25 cc. of twice recrystallized celtrobiose β-heptaacetate monoetherate (see below), also at −10°. The solution was kept in the refrigerator overnight, then poured into ice water and extracted with chloroform. The chloroform solution was washed in succession with water, cold dilute hydrochloric acid until free from pyridine, water,

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[13] Prepared in about 30% yield by the acetolysis of alpha sulfite, soda, or kraft paper pulp which had been furnished through the courtesy of Mr. Warren E. Emley of the Division of Organic and Fibrous Materials of the National Bureau of Standards.

aqueous sodium bicarbonate, and water, dried with granular calcium chloride, and the chloroform evaporated *in vacuo*. The thick sirup was dissolved in 75 cc. of warm alcohol and treated with a little activated carbon, filtered, and diluted with an equal volume of water. After being inoculated with a crystal obtained in a preliminary experiment the solution deposited 21.9 g. of β-octaacetate rotating $-10°$. This material was recrystallized once from dry ether, then four times from 50% alcohol; the rotation in U. S. P. chloroform (c, 6) was $-13.0°$, and was unchanged by four additional crystallizations from 50% alcohol.

The β-octaacetate, like the α-octaacetate, may crystallize in more than one form. Originally it separated from the aqueous alcohol solution in prisms melting at 87–93°; analyses showed it to be a monohydrate. Upon recrystallization from ether it crystallized in solvent-free needles melting at 103–105°. Recrystallization from 50% alcohol then produced a third modification, anhydrous needles melting at 113–114°. Any of the three forms can be obtained as desired, by suitable manipulation.

Anal. Calcd. for $C_{28}H_{38}O_{19}\cdot H_2O$: C, 48.25; H, 5.79; H_2O, 2.59. Found (87–93° prisms): C, 48.36; H, 5.85; H_2O (4 hours in pistol at 100°), 2.49. Calcd. for $C_{28}H_{38}O_{19}$: C, 49.54; H, 5.65; acetyl, 11.79 cc. of 0.1 N NaOH per 100 mg. Found (103–105° needles): C, 49.30; H, 5.83; (113–114° needles): C, 49.36; H, 5.68; acetyl, 11.88 cc.

The Double Octaacetate: 2α-Octaacetate$\cdot 1\beta$-Octaacetate$\cdot 3(C_2H_5)_2O$.—In the preparation of celtrobiose β-octaacetate just described the original alcoholic mother liquor was evaporated *in vacuo* to a thick sirup which was dissolved in the mother liquor from the crystallization from ether, and the solution concentrated. In addition to needles of β-octaacetate it deposited 1 g. of rectangular plates which, after one recrystallization from ether, melted with decomposition at 70°, and rotated $+24.9°$ in U. S. P. chloroform (c, 4). From the known rotations of the α- and β-octaacetates the rotation calculated for a double octaacetate of celtrobiose having the composition 2α-octaacetate$\cdot 1\beta$-octaacetate$\cdot 3(C_2H_5)_2O$ is $+25.0°$. The compound was then synthesized by mixing pure α- and β-octaacetates in the proportions indicated and crystallizing from ether; the product formed in plates melting at 70° with evolution of gas, rotated $+25.8°$ and lost the calculated amount of ether when heated for several days at 56° in a Fischer pistol; the ether-free compound melted over the range 70–85°.

Anal. Calcd. for $C_{28}H_{38}O_{19}\cdot C_4H_{10}O$: ether, 9.85%; acetyl, 10.63 cc. of 0.1 N NaOH per 100 mg. Found: ether, 9.80%; acetyl, 10.66 cc. For the ether-free compound, calcd. for $C_{28}H_{38}O_{19}$: C, 49.54; H, 5.65. Found: C, 49.30; H, 5.66.

Celtrobiose β-Heptaacetate Monoetherate.—The heptaacetates of celtrobiose were prepared by shaking 10 g. of acetochloroceltrobiose with 5 g. of silver carbonate in 190 cc. of acetone and 10 cc. of water for twelve hours. The silver salts were removed by filtration and the clear solution concentrated *in vacuo* at 25° to a sirup from which the crude heptaacetate could be obtained in nearly quantitative yield by adding ether and cooling. The product could not be purified by simple recrystallization, and from a mixture of acetone and ether there usually separated at the same time four crystalline forms melting, when pure, at 60° (dec.), 80° (dec.), 131, and 216°, respectively. However, the several heptaacetates were finally isolated and purified by the following procedure. The crude product was packed into the thimble of a Soxhlet apparatus and extracted with boiling anhydrous ether for two or three hours. The ethereal solution was set aside, and the undissolved residue, containing mostly 80° heptaacetate, was then extracted with fresh ether for six or eight hours; during this extraction the 80° compound crystallized slowly from the warm ether solution in the form of rectangular plates. By decanting the ether while still warm the plates could be separated from the more soluble α-forms which stayed in solution and from the tiny needles of the 216° compound which floated away with the ether. From 50 g. of acetochloroceltrobiose there was thus obtained 25 g. of plates which were purified by two additional crystallizations in the same manner. Analyses showed the substance to be a heptaacetate which contained one mole of ether of crystallization. The rotation of the monoetherate in U. S. P. chloroform (c, 10) was $+3.5°$, changing in the course of a week at 20° to $+13.5°$; calculated for the solvent-free heptaacetate these values become $+3.9°$ changing to $+15.1°$. It could not be obtained crystalline in the absence of ether, and the ether of crystallization could be removed completely only by melting the substance at 80° *in vacuo;* during this process mutarotation took place and the glassy solid when dissolved in chloroform rotated $+14.5°$ changing overnight to $+15.0°$.

Anal. Calcd. for $C_{26}H_{36}O_{18}\cdot C_4H_{10}O$: ether, 10.43%; acetyl, 9.85 cc. of 0.1 N NaOH per 100 mg. Found: ether, 10.19, 10.30%; acetyl 9.95 cc. For the ether-free compound, calcd. for $C_{26}H_{36}O_{18}$: C, 49.03; H, 5.70; acetyl, 11.00 cc. of 0.1 N NaOH per 100 mg. Found: C, 48.84; H, 5.70; acetyl, 10.99 cc.

Celtrobiose α-Heptaacetate.—The ethereal solutions left after isolation of the β-heptaacetate monoetherate as described above were united, concentrated and a mixture of crystalline heptaacetates obtained in which the α-form predominated. The material was placed in the Soxhlet thimble and extracted with ether; this time, after one or two hours of boiling, the α-heptaacetate began to separate in tiny crystals which united to form small granules. By filtering the warm solution most of the β-heptaacetate which had been extracted remained in the mother liquor. Five recrystallizations by this method were carried out, the final product melting at 130–131° and rotating in U. S. P. chloroform (c, 5) $+22.3°$, changing in the course of five days at 20° to $+15.1°$.

Anal. Calcd. for $C_{26}H_{36}O_{18}$: C, 49.03; H, 5.70; acetyl, 11.00 cc. of 0.1 N NaOH per 100 mg. Found: C, 48.83, 48.67; H, 5.83, 5.68; acetyl, 11.07 cc.

Celtrobiose α-heptaacetate may be converted to celtrobiose β-heptaacetate, or *vice versa*, by allowing a chloroform solution to mutarotate until equilibrium is reached, concentrating to a sirup, and isolating the mixture of heptaacetates with ether. Extraction in a Soxhlet with dry ether according to the procedures outlined above will then furnish the desired form.

Celtrobiose α-Heptaacetate Dietherate.—In the ordinary crystallization of the α-heptaacetate there is formed not the 130–131° compound just described but transparent elongated prisms which melt at 60° with the evolution of gas, then resolidify, and melt again at 130–131°. Upon standing in the air, or more rapidly *in vacuo* below 60°, the prisms lose their transparency while retaining their crystalline structure and then show the higher melting point 130–131°. Analyses show the loss of two moles of ether of crystallization from each mole of the heptaacetate (calcd. for $C_{26}H_{36}O_{18}\cdot 2C_4H_{10}O$: ether, 18.89%. Found: ether, 18.79, 18.80%). Crystallization from a warm ethereal solution, as shown above, produces the solvent-free form, but left overnight in the presence of ether at 20°, or below, the granular heptaacetate disappears and beautiful prisms of the dietherate modification are deposited. Under certain intermediate conditions both forms thus are present at the same time.

Celtrobiose β-Heptaacetate with Ortho Ester Structure.—In addition to the α- and β-heptaacetates described above, there always appeared a small amount (5%) of another substance, melting at 216°, which also had the composition of a heptaacetate. It was obtained by the action of silver carbonate in aqueous acetone even from acetochloroceltrobiose which had been subjected to twenty-one recrystallizations, and from acetochloroceltrobiose recrystallized ten times after being prepared by the action of aluminum chloride on purest celtrobiose α-octaacetate. This new heptaacetate is very sparingly soluble in ether, and was recovered from the material left in the Soxhlet thimble after extraction of the more soluble α- and β-forms, or filtered from the ethereal solutions which were decanted during recrystallization of the 80° β-heptaacetate monoetherate. From a mixture of chloroform and ether it separated in small needles, melted at 216°, and after three recrystallizations showed the constant rotation of +1.0° in U. S. P. chloroform (using a 4-dm. tube; *c*, 1). Unlike the normal α- and β-heptaacetates of celtrobiose, which in chloroform solution mutarotate to the equilibrium value +15.1°, this β-heptaacetate showed no evidence of mutarotation on standing eight days. It reduces Fehling's solution readily at 65°. An alkoxyl determination was negative.

Anal. Calcd. for $C_{26}H_{36}O_{18}$: C, 49.03; H, 5.70; acetyl, 11.00 cc. of 0.1 *N* NaOH per 100 mg. Found: C, 48.81; H, 5.74; acetyl, 11.04 cc.

Acetylation of the Heptaacetates.—In order to relate the normal α- and β- and the ortho ester β-heptaacetates with the corresponding α- and β-octaacetates, a 1-g. sample of each of the five compounds was cooled to −10°, and to it was added a mixture of 5 cc. of acetic anhydride and 15 cc. of pyridine, also at −10°; the solution was kept at −10° for one hour, then at 4° overnight. The next morning the temperature was allowed to rise to 20°, the volume adjusted exactly to 25 cc., and the rotation observed. After twenty-four hours a second reading of the rotation showed no change in any case.

Acetylation of the normal α-heptaacetate (m. p. 130–131°) gave a solution of specific rotation +33.3°, as compared with the rotation +38.3° for pure α-octaacetate and −18.6° for pure β-octaacetate in the same acetylating solvent (all rotations calculated on the basis of the amount of octaacetate present). The rotation +33.3° thus corresponds to a mixture containing 91% α-octaacetate and 9% β-octaacetate. By working up the acetylation mixture from 2.09 g. of α-heptaacetate in the usual way and crystallizing from ether there was isolated 1.84 g. of α-octaacetate and 0.20 g. of the 2α-·1β-octaacetate trietherate described above. One recrystallization from alcohol yielded 1.58 g. of α-octaacetate with the correct melting point, and rotating in chloroform +47.4° as compared with +48.0° for the pure compound.

Acetylation of the β-heptaacetate monoetherate (m. p. 80° with decomposition), a method already used in the preparation of celtrobiose β-octaacetate, gave a solution of specific rotation −13.9°, corresponding to a mixture of 92% β-octaacetate and 8% α-octaacetate. How much of this α-octaacetate is derived from α-heptaacetate present as an impurity, and how much is due to mutarotation preceding the acetylation is difficult to estimate; a similar problem arises in considering the acetylation of the α-heptaacetate.

Acetylation of the β-heptaacetate with ortho ester structure (m. p. 216°) produced a solution having the rotation −18.3°, as compared with the value −18.6°, for the pure β-octaacetate; these figures are identical within the limits of error and represent a quantitative transformation to the β-octaacetate. When isolated in the usual way, the product from 2.01 g. of heptaacetate consisted of 2.05 g. of octaacetate (theoretical 2.14 g.). After recrystallization from 50% alcohol it was identified completely as the β-octaacetate by its melting point and mixed melting point of 113–114°, by its rotation in U. S. P. chloroform (−13.2° as compared with −13.0° for the known β-octaacetate), and by its characteristic change of melting point to 103–105° when crystallized from ether and back to 113–114° again on crystallization from 50% alcohol. In addition, a small sample was mixed with twice its weight of pure α-octaacetate and crystallized from ether; typical plates of the double octaacetate etherate were obtained, melting at 70° (dec.), having the rotation +24.9° (calcd. +25.0°) and losing the theoretical amount of ether at 65° *in vacuo* (calcd. 9.85%; found 9.81%).

Celtrobiose Monohydrate.—Deacetylation of any of the hepta- or octaacetates with barium methylate as catalyst in absolute methyl alcohol, followed by removal of the barium by adding the exact amount of dilute sulfuric acid required, led to the isolation of the parent disaccharide in practically quantitative yield. Celtrobiose crystallizes readily as a monohydrate from water, or better by adding three volumes of alcohol to its aqueous solution. The monohydrate is the stable form, and a dehydrated sample quickly reverts to the hydrate on exposure to moist air. It forms large well-shaped prisms which begin to soften at 133°, then slowly melt to a thick sirup which evolves gas at 148°. The rotation was unchanged by three recrystallizations, and the accepted value is +13.6° in water (*c*, 5). No mutarotation was observed in twenty-four hours, the first reading being taken five minutes after adding the water to dissolve the sugar.

Anal. Calcd. for $C_{12}H_{22}O_{11}\cdot H_2O$: C, 39.98; H, 6.72; H_2O, 5.00. Found: C, 39.93; H, 6.88; H_2O, 4.98 (six hours in pistol at 110°).

Acetylation of Celtrobiose.—Since celtrobiose shows no mutarotation, evidence for its designation as the α- or β-form was sought by acetylation studies. To this end a cooled mixture of 5 cc. of acetic anhydride and 15 cc. of pyridine was added to one-half gram of the monohydrate. Most of the sugar dissolved when shaken for an hour at room temperature. After standing overnight the solution was diluted with pyridine to 25 cc. and found to rotate, in duplicate experiments, −11.9° and −11.4°; this corresponds to a mixture containing 88% of the β-octaacetate and 12% of the α-octaacetate. When the solution was poured into ice water and examined in the usual way it yielded 85% of the theoretical amount of octaacetate as the β-form (identified by melting point, mixed melting point and rotation) and about 2% as the double octaacetate etherate.

Hydrolysis of Celtrobiose.—After 0.2594 g. of celtrobiose hydrate was heated with 8 cc. of 1 *N* hydrochloric acid for two and one-half hours at 100° and the solution diluted exactly to 10 cc. at 20°, it rotated −22.8° and did not change when heated for another hour. This rotation is in agreement with the value −22.7° calculated for an equimolecular mixture of *d*-glucose (+52.5°) and *d*-altrose (−98°) under the same conditions.

Oxidation to Celtrobionic Acid and Subsequent Hydrolysis to *d*-Glucose and *d*-Altronic Acid.—The method of Hudson and Isbell[14] was adopted. Thus, to 9.2 g. of benzoic acid and 11.8 g. of barium hydroxide octahydrate, combined by dissolving in 350 cc. of hot water, and cooled, was added 9 g. of the crystalline sugar and 2 cc. of bromine. The solution was kept in the dark, with occasional shaking, for forty-four hours. Excess bromine was expelled with a current of air; precipitated benzoic acid was removed by filtration; the barium ions were completely precipitated by adding a slight excess of sulfuric acid; bromide ions were removed by shaking the solution with 10 g. of silver carbonate; the filtered solution was freed from silver ions with hydrogen sulfide, and the excess hydrogen sulfide blown out with air. The dissolved benzoic acid was completely removed by extraction with chloroform and the solution concentrated to about 240 cc. No attempt was made to isolate the celtrobionic acid, but instead it was hydrolyzed by adding 6.7 cc. of concentrated sulfuric acid to make the solution about 1 normal, and refluxing gently for three hours. To the pale yellowish solution was added 38 g. of barium hydroxide octahydrate, the barium sulfate removed by filtration, and the slight excess of barium precipitated by titration with 0.5 *N* sulfuric acid, using sodium rhodizonate as an external indicator.[15]

The solution should now contain only *d*-glucose, and *d*-altronic acid and its lactone. The acid and lactone were neutralized by adding lime water until the solution would remain faintly alkaline to phenolphthalein for one hour. By concentrating to a small volume and adding alcohol there was obtained 4 g. of crystalline calcium *d*-altronate which was identified completely as described below.

The mother liquor was freed from the remaining calcium altronate by concentrating to a thin sirup and adding methyl alcohol, filtering the granular salts, and repeating the operations. The methyl alcoholic solution of glucose was then evaporated *in vacuo* to a very thick sirup which was extracted with 250 cc. of hot 95% alcohol; from this extract, upon concentrating and inoculating, was obtained 2.2 g. of fine needles. The product was identified as *d*-glucose through the melting point and mixed melting point 146–147°, through its phenylosazone with melting point and mixed melting point 208° (dec.), and finally by a study of its mutarotation. At 23° the initial rotation +70.3° in water (*c*, 5) showed it to be a mixture of the α- and β-forms; the equilibrium rotation +53.0° is in accord with the known value +52.5° for *d*-glucose; and the mutarotation constant 0.0087 is in excellent agreement with the value 0.0085 for 23°, as calculated from the equation $\log (k_1 + k_2) = 11.0198 - (3873/T)$ given by Hudson and Dale.[16]

Identification of Calcium *d*-Altronate·3.5H$_2$O.—The calcium altronate obtained above was recrystallized twice from water, and then found to be identical in its properties with a sample of calcium *d*-altronate prepared from neolactose by oxidation and hydrolysis in the same manner. The air-dried calcium salt contains three and one-half moles of water of crystallization[17] which it loses on heating one hour at 110° *in vacuo;* upon exposure to the moist air of the laboratory it quickly regains its original water content. This property of losing and regaining 3.5H$_2$O as described can be used to distinguish calcium *d*-altronate (and presumably calcium *l*-altronate) from the known calcium salts of other aldohexonic acids except possibly gulonic.[18]

Anal. Calcd. for $(C_6H_{11}O_7)_2Ca\cdot3.5H_2O$: H$_2$O, 12.78. Found: 12.79 for calcium altronate from celtrobiose, 12.78 for calcium altronate from neolactose.

The solubility of hydrated calcium *d*-altronate in water at 20° is very nearly 2 g. in 100 cc Its rotation in water (*c*, 1.8; 4-dm. tube) was determined as −2.36° from celtrobiose and −2.35° from neolactose, as compared with +2.08° for calcium *l*-altronate.[17c]

TABLE II

ROTATION OF CALCIUM *d*-ALTRONATE·3.5H$_2$O IN 1 *N* HCl (*c*, 3)

Time, min.	From celtrobiose	From neolactose	Steiger and Reichstein From *d*-ribose	From "levo-lactone"
5	+11.7	+11.1		
10	14.0	13.8	+14.1	+14.6
15	15.7	16.1		
20	17.5	17.8		
30	20.1	19.4		19.8
45	22.4	21.7	22.3	22.3
60	23.2	23.6		
90	24.3	24.4		
Constant	24.8	24.9	24.7	24.3
Final Rotation, Calculated as Lactone				
	+34.4	+34.5	+34.2[a] 35.1[b]	+33.7[a]

[a] These values have been recalculated from the data given by Steiger and Reichstein.

[b] Levene and Jacobs, *Ber.*, **43**, 3142 (1910).

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(14) Hudson and Isbell, *Bur. Standards J. Research*, **3**, 59 (1929).

(15) Giblin, *Analyst*, **58**, 752 (1933).

(16) Hudson and Dale, THIS JOURNAL, **39**, 320 (1917).

(17) (a) Levene and Jacobs, in *Ber.*, **43**, 3142 (1910), reported 3.5 H$_2$O for calcium *d*-altronate; (b) Austin and Humoller, THIS JOURNAL, **56**, 1152 (1934), reported 3.5H$_2$O for calcium *l*-altronate; (c) Isbell, however, in *Bur. Standards J. Research*, **14**, 308 (1935), wrote calcium *l*-altronate·3H$_2$O.

(18) *Cf.* Fischer and Stahel, *Ber.*, **24**, 528 (1891).

Very convincing evidence of the identity of calcium altronate from celtrobiose with the calcium altronate from neolactose, as well as for their identity with samples of calcium altronate from *d*-ribose and from the 1,4-lactone of *d*-talomucic acid[19] is given in Table II. Here are recorded the changes in rotation which occur when calcium altronate is dissolved in 1 *N* hydrochloric acid and the liberated altronic acid undergoes lactone formation.

This work has been materially aided by a grant to one of us (N. K. R.) from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. Acetochloroceltrobiose has been obtained in 40–45% yield by the action of a mixture of aluminum chloride and phosphorus pentachloride on cellobiose octaacetate in chloroform.

2. Both the α- and the β-octaacetates of celtrobiose have been prepared. A double compound of the two acetates crystallizes with the composition 2α-octaacetate·1β-octaacetate·3-ether.

3. Both the α- and the β-heptaacetates of celtrobiose have been prepared. A third heptaacetate is believed to possess an ortho ester structure.

4. Celtrobiose monohydrate has been obtained in crystalline form. It has $[\alpha]^{20}\text{D} + 13.6°$, without mutarotation. Acetylation shows it to be the β-form.

5. Acid hydrolysis of celtrobiose indicates that the component hexoses are *d*-altrose and *d*-glucose. Oxidation to celtrobionic acid, followed by acid hydrolysis, yielded *d*-glucose, and *d*-altronic acid which was identified as calcium *d*-altronate·$3.5H_2O$. These data lead to the conclusion that celtrobiose is 4-β-*d*-glucosido-*d*-altrose.

Washington, D. C. Received October 19, 1936

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[19] Steiger and Reichstein, *Helv. Chim. Acta*, **19**, 195 (1936).

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The Asymmetric Oxidation of Sugars by Optically Active Alkaline Copper Solutions[1]

By Nelson K. Richtmyer and C. S. Hudson

In a recent paper dealing with neolactose and *d*-altrose[2] we had occasion to compare the reducing powers of the *d*- and *l*-forms of altrose toward the alkaline copper reagent of Shaffer and Hartmann.[3] The *d*-altrose was found to have only about 56% the reducing power of *l*-altrose; similarly, *d*-arabinose was found to have only 76% the reducing power of *l*-arabinose. The suggestion was made that, since the copper carbonate reagent contains an optically active substance, namely, *d*-tartaric acid, the *d*- and *l*-forms of the reducing sugars may behave differently in its presence.

A number of investigators[4] have compared the reducing powers of various sugars as determined by the methods of Hagedorn–Jensen, Folin–Wu, Shaffer–Hartmann, and others, but the behavior of a pair of antipodal sugars toward these reagents, and toward copper reagents containing other than the ordinary *d*-tartaric acid, has not been studied previously. The results of our experiments, in which *d*-glucose, *d*- and *l*-altrose, and *d*- and *l*-arabinose were compared by oxidation with the Hagedorn–Jensen–Hanes ferricyanide reagent, and with four modifications of the Shaffer–Hartmann–Somogyi Reagent 50 with 1 g. of potassium iodide, containing the *d*-, *l*-, racemic, and *meso* tartaric acids, respectively, are shown in Tables I and II.

The first three columns of figures in Table I show clearly that with the ferricyanide reagent, and with the alkaline copper reagents containing *meso* and racemic tartaric acids, the *d*- and *l*-forms of altrose have identical reducing powers, and the same is true of the *d*- and *l*-forms of arabinose, within the limits of experimental error. In the fourth and fifth columns, however, striking differences appear between *d*- and *l*-altrose in their behavior with the alkaline copper solutions containing *d*- and *l*-tartaric acids, respectively. Thus, *d*-altrose (1.2 mg.) requires 5.82 cc. of

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service.

[2] Richtmyer and Hudson, This Journal, **57**, 1716 (1935).

[3] Shaffer and Hartmann, *J. Biol. Chem.*, **45**, 377 (1921).

[4] *E. g.*, Bertrand, *Bull. soc. chim.*, **35**, 1285 (1906); Thomas and Dutcher, This Journal, **46**, 1662 (1924); Willaman and Davison, *J. Agric. Research*, **28**, 479 (1924); Greenwald, Samet and Gross, *J. Biol. Chem.*, **62**, 397 (1924); Rowe and Wiener, This Journal, **47**, 1698 (1925); Pucher and Finch, *Proc. Soc. Exptl. Biol. Med.*, **23**, 468 (1926); Hawkins, *J. Biol. Chem.*, **84**, 79 (1929).

TABLE I

CC. OF 0.005 N THIOSULFATE EQUIVALENT TO AMOUNT OF REAGENT CONSUMED IN 15 MINUTES

	Reagent				
Sugar 1.20 mg.	Ferri-cyanide	Meso tartaric	Racemic tartaric	*d*-tartaric	*l*-tartaric
d-Glucose	7.12	10.50	10.97	10.94	10.82
d-Altrose	5.67	8.44	7.34	5.82	9.47
l-Altrose	5.63	8.34	7.26	9.41	5.78
d-Arabinose	6.58	8.07	8.42	8.00	9.18
l-Arabinose	6.56	8.03	8.29	9.09	7.89

TABLE II

RELATIVE REDUCING POWERS TOWARD VARIOUS REAGENTS, WITH GLUCOSE AS STANDARD IN EACH CASE

	Reagent				
Sugar	Ferri-cyanide	Meso tartaric	Racemic tartaric	*d*-tartaric	*l*-tartaric
d-Glucose	100	100	100	100	100
d-Altrose	79.6	80.4	66.9	53.2	87.5
l-Altrose	79.1	79.4	66.2	86.0	53.4
d-Arabinose	92.4	76.9	76.7	73.1	84.8
l-Arabinose	92.1[a]	76.5	75.6	83.1	72.9

[a] This is in accord with the value of 92 found by Pucher and Finch, ref. 4, and the value of 94 found by the ferricyanide gasometric method of Hawkins, ref. 4.

0.005 N thiosulfate, which is a measure of the amount of oxidation brought about by the reagent containing *d*-tartaric acid, whereas the same amount of *l*-altrose requires 9.41 cc. of thiosulfate; the ratio 5.82:9.41 indicates that toward the *d*-tartaric reagent the *d*-altrose has only 61.8% the reducing power of its *l*-isomer. On the other hand, using the copper reagent containing *l*-tartaric acid, the relations are reversed, the *l*-altrose requiring 5.78 cc., and the *d*-altrose 9.47 cc. of thiosulfate; the ratio of these values shows that toward the *l*-tartaric acid reagent the *l*-altrose has only 61.0% the reducing power of its *d*-isomer. It is noted that the figure for the *d*-sugar with the *d*-reagent, 5.82 cc., is identical, within the experimental limits, with the value 5.78 cc. for the *l*-sugar plus the *l*-reagent; likewise, the *d*-sugar with the *l*-reagent, and the *l*-sugar with the *d*-reagent, give practically identical values of 9.47 and 9.41 cc., respectively.

In the case of the arabinoses, the differences in behavior are strictly parallel, although not so marked. Using the *d*-reagent, the ratio 8.00:9.09 gives the *d*-arabinose 88.0% the reducing power of the *l*-arabinose,[5] with the *l*-reagent the situation is reversed, and the ratio 7.89:9.18 shows *l*-arabinose to have 86.0% the reducing power of its *d*-isomer. For both the altroses and the arabinoses, with the reagent containing racemic tartaric acid, the values lie between those found for the *d*-reagent and those for the *l*-reagent.

In the case of *d*-glucose, the values in Table I show no difference, within the experimental limits of accuracy, between its behavior with the copper reagents containing the *d*-, *l*- and racemic tartaric acids. The value obtained with the *meso* tartaric acid is somewhat smaller; this is not unexpected, since *meso* tartaric acid differ from the other tartaric acids in chemical and physical properties, and a reagent containing it might be expected to differ as much as would a reagent containing citric, trihydroxyglutaric, or other hydroxy acid which might be used to prevent precipitation of the copper hydroxide.

Table II shows the relative reducing powers found for the pairs of altroses and arabinoses, compared with glucose as a standard with each of the five oxidizing agents. The relationships are similar to those already discussed, and show, for example, that each of the two altroses has about 80% the reducing power of *d*-glucose toward the ferricyanide reagent and toward the copper reagent containing meso tartaric acid, and about 66.5% of the reducing power of *d*-glucose toward the racemic tartaric acid reagent. However, toward the *d*-tartaric reagent the *d*-altrose has 53% the reducing power and *l*-altrose 86% the reducing power of *d*-glucose, while toward the *l*-tartaric reagent the reverse situation exists, the *d*-altrose having 87% and the *l*-altrose 53% the reducing power of *d*-glucose.

Having accomplished the primary objects of the research, and having a certain amount of copper reagents on hand, we decided to examine the behavior of other available sugars as far as the supply of reagents would permit. These additional results are presented in Table III. In the last three columns are compared the reducing powers of a single sugar against each of the three alkaline copper reagents employed, which is a somewhat different method of interpreting a portion of the data previously discussed.

The most striking examples were found in the cases of *d*- and *l*-altrose and *l*-allose. For example, *d*-altrose reduces the copper reagent containing *l*-tartaric acid 163% as much as it does the reagent containing *d*-tartaric acid; on the other hand, *l*-altrose reduces the *l*-tartaric reagent

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(5) The discrepancy between the value 88% and the value 76% previously reported may be due in part to the fact that the samples of arabinose used earlier were not purified by us, and in part to the difference in composition of the alkaline copper reagents as used in the two sets of experiments. The present values are believed to be correct at least to within ±2%.

TABLE III

COMPARISON OF SUGARS

Sugar	Time of heating, min.	Cc. of 0.005 N thiosulfate equivalent to amount of reagent consumed by 1.20 mg. of sugar			Relative reducing powers of the sugar toward the three copper reagents, with the *d*-tartaric acid reagent as standard		
		Reagent			Reagent		
		d-tartaric	*l*-tartaric	Racemic	*d*-tartaric	*l*-tartaric	Racemic
d-Glucose	15	10.94	10.82	10.97	100	99	100
d-Mannose	15	8.21	8.69	9.01	100	106	110
d-Mannose	35	10.45	10.62	10.88	100	102	104
d-Galactose	35	9.21	7.64	8.67	100	83	94
d-Altrose	15	5.82	9.47	7.34	100	163	126
d-Altrose	25	5.78	9.50	..	100	164	...
l-Altrose	15	9.41	5.78	7.26	100	61	77
l-Altrose	25	9.41	..	..	100	...	...
l-Allose	35	7.84	4.77	6.37	100	61	81
d-Fructose	15	10.57	10.91	11.23	100	103	106
d-Fructose	35	10.61	10.86	11.29	100	102	106
d-Mannoheptulose	15	7.94	6.99	8.10	100	88	102
d-Mannoheptulose	35	7.94	6.88	8.17	100	87	103
d-Arabinose	15	8.00	9.18	8.42	100	115	105
d-Arabinose	35	8.49	9.83	9.37	100	116	110
l-Arabinose	15	9.09	7.89	8.29	100	87	91
l-Arabinose	35	9.69	8.34	9.50	100	87	99
d-Xylose	35	10.65	10.51	10.76	100	99	101
l-Rhamnose	35	9.07	9.41	9.88	100	104	109
l-Fucose	35	6.86	7.73	7.48	100	113	109
Neolactose	15	5.47	4.95	5.51	100	90	101
Celtrobiose	15	5.86	5.65	6.03	100	96	103
Lactose	15	5.27	4.87	5.25	100	92	100

only 61% as much as it does the *d*-tartaric reagent; yet the fourth column shows that the *d*- and *l*-altrose solutions reduce to the same extent the reagent containing racemic tartaric acid. The *l*-allose also reduces the *l*-tartaric reagent only 61% as much as it does the *d*-reagent.

The arabinose pair of sugars behaves like the altrose pair, although to a lesser extent, the values being 115 and 87%, respectively, for the *d*- and *l*-sugars. *d*-Galactose and *l*-fucose also showed very marked differences in their behavior toward the copper reagents, with values of 83 and 113%, respectively. *l*-Rhamnose, the ketone sugar *d*-mannoheptulose, and the disaccharides lactose, neolactose, and celtrobiose all show differences well outside the limits of error.

The time of heating was varied in several cases, since Shaffer and Somogyi[6] have found that with their Reagent 50, glucose and fructose are oxidized completely in fifteen minutes, while mannose and xylose require thirty-five and thirty minutes, respectively. With the altroses, fructose and mannoheptulose the reaction appeared to be complete within fifteen minutes; with the two arabinoses, and *d*-mannose, a longer period was required, the time of thirty-five minutes being chosen arbitrarily. For the three disaccharides the fifteen-minute period only was tried, while for *d*-xylose, *l*-rhamnose and *l*-fucose a thirty-five minute heating was allowed.

Certain correlations between the configurations of the sugars and the relative reduction of the *d*-, *l*- and racemic reagents may be cited. *d*-Xylose and *d*-glucose, each with the *d*-xylose configuration on the second, third, and fourth carbon atoms, show practically no difference in their behaviors, the ratios being 100:99:101 and 100:99:100, respectively. *d*-Arabinose, *d*-altrose, and *l*-fucose, each with the *d*-arabinose configuration on the second, third and fourth carbon atoms, form a series with the ratios 100:115:105, 100:163:126, and 100:113:109, while *l*-arabinose, *l*-altrose and *d*-galactose, each with the *l*-arabinose configuration, form another series with the ratios 100:87:91, 100:61:77, and 100:83:94, respectively. The other aldoses including lactose, and the two ketoses, are not closely related to themselves or any of the foregoing series, so a further and complete correlation will require more data. All the facts given, however, are in full accord with the recognized theories of stereochemistry.

The above examples of asymmetric oxidation may be considered as belonging to the larger group of phenomena called asymmetric degradations. Pasteur's classical experiment on the preference of *Penicillium glaucum* for the *d*- over the *l*-form of tartaric acid, the selective fermentation of the *d*- but not the *l*-forms of glucose, mannose and fructose, and the peculiarities of other enzymes and micro-organisms in their behavior toward optical antipodes, are well known. A purely chemical asymmetric degradation was first studed by Bredig and his associates.[7] They were able to show that the rates of decomposition of the *d*- and *l*-forms of camphor- and bromocamphor-carboxylic acids were unequally accelerated by the addition of a small amount of optically active base as catalyst; for example, the *l*-camphor carboxylic acid in acetophenone at 75° decomposed about 46% faster than did the *d*-acid

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(6) Shaffer and Somogyi, *J. Biol. Chem.*, **100**, 695 (1933).

(7) Bredig and Fajans, *Ber.*, **41**, 752 (1908); Fajans, *Z. physik. Chem.*, **73**, 25 (1910); Creighton, *ibid.*, **81**, 543 (1913); Bredig and Joyner, *Z. Elektrochem.*, **24**, 285 (1918); Pastanogoff, *Z. physik. Chem.*, **112**, 448 (1924). See also Rona and Reuter, *Biochem. Z.*, **249**, 455 (1932).

when quinine was added, while the reverse effect was produced when quinidine was added.

Recently Y. Shibata and his co-workers[8] have described the asymmetric oxidations brought about by the oxidase-like action of ammonochlorodiethylenediamine cobaltic bromide $[Co-en_2NH_3Cl]Br_2$. Their experiments have led to the conclusion that the *l*-form of 3,4-dihydroxyphenylalanine is oxidized more rapidly than the *d*-form by the *l*-cobalt complex; and that *d*-catechin is oxidized more rapidly by the *d*-cobalt than by the *l*-cobalt complex.

To return to the data in Table III, we find that in the members of the *d*- and *l*-arabinose series, and also in the case of *l*-allose, the reducing power of each sugar toward the racemic tartaric acid reagent was intermediate between the value found for the *d*-reagent and that found for the *l*-reagent. In other cases, notably those of *d*-fructose, *l*-rhamnose, *d*-mannoheptulose and the three disaccharides, the reducing power was not intermediate in value, but was equal to or even greater than the reducing power toward either the *d*- or the *l*-reagent. The reason for this might be learned if we knew more about the mechanism underlying these sugar oxidations. Nef[9] states that the oxidation of *l*-arabinose by alkaline copper hydroxide solution leads to the formation of carbon dioxide, formic and glycolic acids and the optically active arabonic, ribonic, erythronic, threonic and glyceric acids. Thus are produced a number of other optically active acids which would intensify or mitigate the effects already initiated by the tartaric acids, and the reaction becomes so complex that almost any final result would be conceivable.

Similarly, Shibata reports that the oxidation of *d*-catechin by the *d,l*-cobalt complex takes a course closely resembling that of the system *d*-catechin plus *l*-complex as if there were no *d*-complex salt in the solution. Willstätter, Kuhn and Bamann[10] found that if racemic mandelic ester is subjected to the action of an esterase extracted from liver, the (+)-ester is hydrolyzed more rapidly than the (−)-ester, but the relation is reversed if the two forms are examined separately: here the (−)-ester is hydrolyzed faster. This is explained by assuming that the ratio of reaction velocites with which the *d*- and *l*-forms in the racemate are cleaved is conditioned by (1) the ratio of affinities of the esterase for the *d*- and *l*-forms, and (2) the ratio of the velocities at which the esterase—*d*-ester complex and the esterase—*l*-ester complex are hydrolyzed.

It is possible that the asymmetric oxidation of sugars by alkaline copper solutions containing optically active tartrates, or even by alkaline ferricyanide reagents to which tartrates have been added, may become a practical method for identifying sugars, especially in working with very small amounts and before isolation of the crystalline material. The behavior of a *d*-galactose solution toward the *d*- and *l*-reagents would clearly distinguish it from solutions containing *d*-glucose, *d*-mannose, *d*-fructose, *d*-xylose, *l*-rhamnose and *d*-arabinose, although *l*-arabinose would remain a possibility. Because of the difficulties involved in preparing *l*-tartaric acid from the common *d*-acid, it might be advantageous to use other antipodal acids, such as the *d*- and *l*-araboglutaric acids which may be prepared by oxidation of the now readily procurable *d*- and *l*-arabinoses. The use of *d*- and *l*-alanine might also be suggested, since Benedict[11] has substituted alanine for tartaric acid, in part at least, in his sugar reagent.

Experimental

Tartaric Acids.—The **racemic** and **meso tartaric acids** were Eastman Kodak Co. products; the former had no detectable optical activity, while the latter appeared to have the very slight specific rotation of +0.07°. The ***d*-tartaric acid** was a commercial brand, thrice recrystallized from water, having $[\alpha]^{20}D$ +13.5° in water (*c*, 10.1). The ***l*-tartaric acid** was obtained by resolving racemic tartaric acid with cinchonine according to Marckwald.[12] The recrystallized cinchonine *l*-acid tartrate monohydrate was decomposed with excess ammonia and the cinchonine removed by filtration. The filtrate was made barely acid with acetic acid, and lead acetate solution added until no further precipitation occurred. Upon standing overnight the amorphous lead tartrate changed to fine needles which were filtered, washed, suspended in water and the lead removed by hydrogen sulfide precipitation. The clear solution was evaporated *in vacuo* to a small volume and the *l*-tartaric acid allowed to crystallize slowly in a desiccator. After several recrystallizations from water it showed $[\alpha]^{20}D$ −13.5° in water (*c*, 10.3).

Sugars.—The *l*-altrose and *l*-allose were samples kindly supplied by the late Dr. W. C. Austin.[13] The *d*-altrose and the disaccharides neolactose and celtrobiose have been

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(8) Shibata and Tsuchida, *Bull. Chem. Soc. Japan*, **4**, 142 (1929); Shibata, Tanaka and Goda, *ibid.*, **6**, 210 (1931); Shibata and Sakai, *J. Chem. Soc. Japan*, **55**, 841 (1934), in *C. A.* **30**, 6354 (1936).

(9) Nef, *Ann.*, **357**, 251 (1907).

(10) Willstätter, Kuhn and Bamann, *Ber.*, **61**, 886 (1928). *Cf.* Rona and Ammon, *Biochem. Z.*, **181**, 49 (1927).

(11) Benedict, *J. Biol. Chem.*, **92**, 141 (1931).

(12) Marckwald, *Ber.*, **29**, 42 (1896); *cf.* Bremer, *ibid.*, **13**, 351 (1880); Pasteur, *Ann. chim.*, [3] **38**, 437 (1853).

(13) Austin and Humoller, THIS JOURNAL, **56**, 1153 (1934).

described by the present authors.[14] The *d*-arabinose, prepared in this Laboratory by the method of Hockett and Hudson,[15] showed $[\alpha]^{20}{}_{\mathrm{D}}$ −103.4°; the *l*-arabinose, from the Difco Laboratories in Detroit, after one recrystallization, rotated +104.2° in water (*c*, 6). The other sugars were either high grade commercial products or prepared by other workers in this Laboratory. All sugar solutions were made up to contain 1.20 mg. of anhydrous substance in each 5 cc. of solution.

The Alkaline Ferricyanide Reagent.—The procedure of Hagedorn and Jensen[16] as modified by Hanes[17] was used, except that the oxidizing solution contained 6.60 g. instead of 8.25 g. of potassium ferricyanide per liter; thus 5 cc. of this solution was equivalent to 5 cc. of the alkaline copper solutions, each requiring about 20 cc. of the same 0.005 *N* thiosulfate solution in the blank determinations.

The Alkaline Copper Reagents.—According to the latest procedure of Shaffer and Somogyi,[6] four solutions were prepared, the only variation being in the use of an equivalent amount of the sodium tartrates instead of the sodium potassium tartrate (Rochelle salt) recommended. Thus, 3.32 g. of *d*-tartaric acid (or 3.32 g. of the *l*-acid, or 3.72 g. of the *meso* or racemic acid monohydrates) was dissolved in 50 cc. of water, and neutralized with *N* sodium hydroxide, with phenol red as indicator. Then were added in succession 6.25 g. of anhydrous sodium carbonate, 1.875 g. of copper sulfate pentahydrate in 20 cc. of water, 5.00 g. of sodium bicarbonate, 0.25 g. of potassium iodide and 50 cc. of standard potassium iodate solution, 0.1 *N* as to iodine. The mixture was diluted exactly to 250 cc., and allowed to stand for several days before filtering through washed and dried filter paper into a Pyrex flask. This reagent should be the exact equivalent of the "Shaffer–Somogyi Copper Iodometric Reagent 50 with 1 g. KI;" 5 cc. of it required about 20 cc. of 0.005 *N* thiosulfate in a blank determination. The preparation and standardization of the solutions, and the oxidations of the sugars, were carried out as directed, observing all the precautions noted by the original writers. The solutions were kept, and the titrations performed, in a room equipped with a white light and kept constant at 20°.

Summary

1. A study of the oxidation of the *d*- and *l*-forms of altrose and of arabinose by an alkaline ferricyanide reagent and by four modifications of an alkaline copper reagent containing the *d*-, *l*-, racemic and *meso* forms of tartaric acid, respectively, has been made.

2. The reagents which are optically inactive show no difference in their relative oxidizing power on the *d*- and *l*-forms of the sugars.

3. The reagents which are optically active oxidize the *d*- and *l*-forms of the sugars asymmetrically. Striking relationships have been noted in the four systems composed of the *d*- and *l*-sugars with the *d*- and *l*-reagents. The results are in full accord with the classical theories of stereochemistry.

4. The behavior of twelve other sugars toward the *d*-, *l*- and racemic copper reagents has been studied.

5. The practical adaptation of this asymmetric oxidation for the identification of sugars has been suggested.

WASHINGTON, D. C. RECEIVED OCTOBER 19, 1936

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[14] Richtmyer and Hudson, ref. 2, and THIS JOURNAL, **58**, 2534 (1936).

[15] Hockett and Hudson, *ibid.*, **56**, 1632 (1934).

[16] Hagedorn and Jensen, *Biochem. Z.*, **135**, 46 (1923).

[17] Hanes, *Biochem. J.*, **23**, 99 (1929).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS]

On the Formation and Reactions of the Substituted Thiazolidones. IV

BY FLOYD A. EBERLY AND F. B. DAINS

Previous papers from this Laboratory[1] have shown that the alkylation of the 2-arylthiazolidones gave both the 2-aryl-2-alkyl and the 2-aryl-3-alkyl derivatives. This paper is a study of the influence of allyl groups, of acyl groups and of phenyl and diphenylchloroacetyl chlorides in the formation and properties of such thiazolidones. Thus from mono-allylthiourea was obtained the 3-allyliminothiazolidone (the unstable form of Wheeler and Johnson) which did not rearrange; while allylphenylthiourea formed a thiazolidone in which the allyl group assumed position 2 with the phenyl at 3. Allyl iodide and the sodium salt of monophenyl thiazolidone gave the two remaining isomers of phenylallylthiazolidone.

The symmetrical benzoyl and carbethoxyphenylthiourea yielded thiazolidones with the acyl radical at 2. Dixon had erroneously assigned the reverse formula to his carbethoxyphenylthiazolidone.

Our work also indicated that the stable form of phenyl-5-phenylthiazolidone is the 2-phenyl isomer and not the 3-phenyl as was suggested by Wheeler and Johnson since it gave alkylation

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[1] Eberly and Dains, THIS JOURNAL, **55**, 3859 (1933); Davis and Dains, *ibid.*, **57**, 2627 (1935); Long and Dains, *C. A.*, **28**, 2356 (1934); *Kan. Acad. Sci.*, **16**, 119 (1933).

products with the phenyl group at 2 and the alkyl radical entering at either 2 or 3.

The 2-arylthiazolidone from diphenylchloroacetyl chloride was obtained by the action of aniline upon thiocyanodiphenylchloroacetic ester, and not from the acid chloride and phenyl thiourea. The isomeric 2-thio-3-phenyl-5-diphenyl-4-imidazolone unexpectedly resulted from the action of ammonium thiocyanate upon diphenylchloroacetanilide.

Symmetrical phenylmethylthiourea and diphenylchloroacetyl chloride gave the two possible isomeric thiazolidones, the only case noted thus far.

Experimental

1. 2-Imino-3-Allyl-4-Thiazolidone HCl I,

$\overline{\mathrm{SC(NH)NC_3H_5COC}}\mathrm{H_2\cdot HCl}$.

Allyl thiourea and chloroacetic acid on warming, either in water or in alcohol solution, gave an oil, the above labile form of Wheeler and Johnson, which is very easily hydrolyzed to the 2,4-diketo compound II with loss of ammonia. Benzaldehyde condensed with II under the influence of alkali or piperidine yielding 5-benzal-3-allyl-2,4-thiazoledione III, colorless needles melting at 88°. The constitution of III was shown as follows: 2,3-diallyl-thiazolidone, an oil at −10°, prepared from chloroacetyl chloride and diallyl thiourea in acetone and pyridine solution, gave a 5-benzal derivative V, m. p. 53°, which on hydrolysis with hot 50% sulfuric acid yielded allylamine and the diketo compound III.

N-Phenyl-N′-Allyl Thiourea and Chloroacetyl Chloride.—These compounds were refluxed in acetone solution with two moles of pyridine for thirty minutes. The 2-allyl-3-phenyl-4-thiazolidone VI melted at 151° and was soluble in dilute hydrochloric acid. In the majority of cases previously the alkyl group has been found at position 3 and the aryl group at 2. The ring was easily ruptured with alkali but heating with benzaldehyde, sodium acetate and acetic anhydride gave a 5-benzal compound VII (m. p. 141°).

Heating VII with 50% sulfuric acid at 140° gave 5-benzal-3-phenyl-2,4-thiazoledione VIII (m. p. 208°),[2] thus proving the structure.

Further evidence was obtained by the synthesis of the two possible isomers. When the sodium salt of 2-phenylthiazolidone was treated with allyl iodide in absolute alcohol solution, two compounds were isolated: (A) 2-phenyl-2-allylaminothiazolidone IX (95% yield), soluble in dilute acid and melting at 92°; and (B) 2-phenylimino-3-allyl-4-thiazolidone X (5% yield), an oil insoluble in acid which gave a 5-benzal derivative XI (m. p. 106.5°). Hydrolysis of XI with acid yielded the diketo compound III and aniline. The isomeric benzal derivative XII melted at 165°.

2. The Benzoyl and Carbethoxy Thiazolidones.—In these cases it is noteworthy that ring closure occurred with the acyl group at position 2.

2-Benzoylimino-3-*p*-bromophenyl-4-thiazolidone XIII, $\overline{\mathrm{SC(NCOC_6H_5)NC_6H_4BrCOC}}\mathrm{H_2}$, m. p. 213°, was made by heating N-benzoyl-N′-*p*-bromophenylthiourea[3] in acetone solution with chloroacetyl chloride and two moles of pyridine.

Alkaline Hydrolysis.—The compound dissolved in dilute alkali on boiling due to the formation of a thiohydantoic acid, but on continued heating there was deposited N-benzoyl-N′-*p*-bromophenyl urea XIV which melted at 233–234° with decomposition.

Acid Hydrolysis.—The benzoyl compound XIII was treated with boiling concentrated hydrochloric acid for three hours. Benzoic acid and ammonia were split off with traces of *p*-bromoaniline. The residue (m. p. 163°) gave figures on analysis corresponding to 3-*p*-bromophenyl-2,4-thiazoledione, XV. The 5-benzal derivative XVI crystallized from dioxane in needles melting at 253°. Hydrolysis with 60% sulfuric acid at 160° gave 5-benzal-3-*p*-bromophenyl-2,4-thiazoledione XVII (m. p. 247°).

2-Carbethoxy-3-phenyl-4-thiazolidone, XVIII, is best prepared by heating phenylthioallophanic ester with chloroacetyl chloride and pyridine in benzene solution.[4] The plates from dioxane decomposed slowly above 230° and melted completely at 256°. Dixon had formulated it as a 2-phenylimino-3-carbethoxy compound and stated that on hydrolysis it gave phenyl "dioxy thiazole," $\underline{\mathrm{SC(NC_6H_5)OCOC}}\mathrm{H_2}$.

Alkaline hydrolysis disrupted the ring completely but acid treatment gave the known 3-phenyl-2,4-thiazoledione (m. p. 146°), identical with a synthetic preparation. Additional evidence for our structure was afforded by the hydrolysis of its benzal derivative XIX (m. p. 225°), which gave the known 5-benzal-3-phenylthiazoledione, VIII.

Heating the carbethoxy compound XVIII with aniline at 150° or at 180–200° gave only diphenyl urea.

3. Derivatives of 5-Phenyl Thiazolidones

2-Phenylimino-5-phenyl-4-thiazolidone, XX.[5]—Wheeler and Johnson had prepared a diphenylthiazolidone (m. p. 185–186°), by the action of phenylchloroacetic ester on phenylthiourea, to which they assigned a 2-imino-3-phenyl structure since it gave a 3-phenyl-2,4-diketo compound (m. p. 173°) on hydrolysis. This work was repeated and the thiazolidone (m. p. 185°), XX, hydrolyzed by heating with 40% sulfuric acid at 140° for four hours. The acid solution contained both aniline and ammonia while from the solid residue were isolated two compounds; one, soluble in dilute alkali and in cold alcohol, proved to be 5-phenyl-2,4-thiazoledione XXI (m. p. 130°), obtained also by the hydrolysis of 5-phenylthiazolidone (m. p. 233–234°); the other compound was Wheeler's product (m. p. 173°), 3,5-diphenyl-2,4-thiazoledione, XXII. These results are due to the formation of the thiohydantoic acid, loss of either ammonia or aniline and subsequent ring closure. Approximately one part of XXI and two parts of XXII were found.

The original compound XX has the phenyl group at position 2. This was shown by the fact that its sodium salt

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[2] Andreasch, *Monatsh.*, **39**, 419 (1918).

[3] Douglass, THIS JOURNAL, **56**, 719 (1934).

[4] Dixon and Kennedy, *J. Chem. Soc.*, **117**, 74 (1920).

[5] Wheeler, *Am. Chem. J.*, **26**, 353 (1901); Wheeler and Johnson THIS JOURNAL, **24**, 690 (1902).

No.	Thiazolidone	Formula	M. p., °C.	% N	
				Calcd.	Found
I	2-Imino-3-allyl·HCl	$C_6H_5N_2OSHCl$	176	14.58	14.58
II	3-Allyl-2,4-diketo	$C_6H_7NO_2S$	Oil		
III	5-Benzal-3-allyl-2,4-diketo	$C_{13}H_{11}N_2OS$	88	5.71	5.76
IV	2,3-Diallyl	$C_8H_{12}ON_2S$	Oil		
V	2,3-Diallyl-5-benzal	$C_{16}H_{12}N_2OS$	53	9.86	9.80
VI	2-Allyl-3-phenyl	$C_{12}H_{12}N_2OS$	151	12.07	11.85
VII	2-Allyl-3-phenyl-5-benzal	$C_{19}H_{16}N_2OS$	141	8.75	8.71
VIII	3-Phenyl-5-benzal-2,4-diketo	$C_{16}H_{11}NO_2S$	208	4.98	4.92
IX	2-Phenyl-2-allyl	$C_{12}H_{12}N_2OS$	92	12.07	11.89
X	2-Phenyl-3-allyl	$C_{12}H_{12}N_2OS$	Oil		
XI	2-Phenyl-3-allyl-5-benzal	$C_{19}H_{16}N_2OS$	106.5	8.75	8.56
XII	2-Phenyl-2-allyl-5-benzal	$C_{19}H_{16}N_2OS$	165	8.75	8.53
XIII	2-Benzoyl-3-*p*-bromophenyl	$C_{16}H_{11}BrN_2O_2S$	213	7.47	7.40
XIV	N-Benzoyl-N′-*p*-bromophenyl urea	$C_{14}H_{11}BrN_2O_2$	233–234	8.78	8.78
XV	3-*p*-Bromophenyl-2,4-diketo	$C_9H_6BrN_2O_2S$	163	5.15	5.28
XVI	2-Benzoyl-3-*p*-bromophenyl-5-benzal	$C_{23}H_{15}BrN_2O_2S$	253	6.05	6.01
XVII	3-*p*-Bromophenyl-5-benzal-2,4-diketo	$C_{16}H_{10}BrNO_2S$	247	3.89	3.84
XVIII	2-Carbethoxy-3-phenyl-	$C_{12}H_{12}N_2OS$	256	10.61	10.83
XIX	2-Carbethoxy-3-phenyl-5-benzal	$C_{19}H_{16}N_2O_3S$	225	7.95	7.95
XX	2-5-Diphenyl	$C_{15}H_{12}N_2OS$	185	See Wheeler and Johnson	
XXI	5-Phenyl-2,4-diketo	$C_9H_7NO_2S$	130	7.25	7.34
XXII	3,5-Diphenyl-2,4-diketo	$C_{15}H_{11}N_2OS$	173	5.17	5.19
XXIII	2-Phenyl methyl-5-phenyl	$C_{16}H_{14}N_2OS$	144	9.93	9.71
XXIV	2-Thio-3-phenyl-5-diphenyl-4-imidazolone	$C_{21}H_{16}N_2OS$	254	8.14	8.02
XXV	3-Phenyl-5-diphenyl-2,4-imidazoledione	$C_{21}H_{16}N_2O_2$	203.5	8.54	8.26
XXVI	2-Methyl mercapto-3-phenyl-5-diphenyl-4-imidazolone	$C_{22}H_{18}N_2OS$	143	7.82	7.57
XXVII	2-Phenyl-5-diphenyl-4-thiazolidone	$C_{21}H_{16}N_2OS$	253	8.14	8.09
XXVIII	2-Methyl-phenyl-5-diphenyl	$C_{22}H_{18}N_2OS$	191	7.82	7.87
XXIX	2-Phenyl-3-methyl-5-diphenyl	$C_{22}H_{18}N_2OS$	134	7.82	7.88
XXX	3-Methyl-5-diphenyl-2,4-diketo	$C_{16}H_{13}NO_2S$	102	4.95	4.80
XXXI	2-Methyl-3-phenyl-5-diphenyl	$C_{22}H_{18}N_2OS$	119	7.82	7.77
XXXII	3-Phenyl-5-diphenyl-2,4-diketo	$C_{21}H_{15}N_2OS$	150	9.27	9.25

on methylation gave a 2-phenyl-2-methylaminothiazolidone XXIII (m. p. 144°), soluble in dilute acid and identical with the product from phenylbromoacetic ester and unsymmetrical phenylmethylthiourea.

4. Derivatives of Diphenyl Chloroacetyl Chloride[6]

The acid chloride failed to give a thiazolidone with phenylthiourea by the usual methods. However, 2-thio-3-phenyl-5-diphenyl-4-imidazolone, $HNCSN(C_6H_5)COC(C_6H_5)_2$, XXIV, was the unexpected product resulting when diphenylchloroacetanilide[7] was refluxed one hour in dry acetone solution with ammonium thiocyanate, and its formation would seem to be due to the rearrangement of the —SCN grouping in the initial product to —NCS and subsequent ring closure. It was soluble in dilute alkali and crystallized from alcohol in thick needles melting at 254°. It was desulfurized by heating with concentrated nitric acid for thirty minutes, yielding 3-phenyl-5-diphenyl-2,4-imidazoledione, XXV, prisms from alcohol (m. p. 203.5°).

The structure of the 2,4-imidazoledione was proved by its synthesis from monophenyl urea and benzilic acid[8] which were fused together one hour at 180–190°.

2 - Methylmercapto - 3 - phenyl - 5 - diphenyl - 4 - imidazolone, XXVI.—Methylation of the 2-thioimidazolone, either alone or with the aid of potassium hydroxide, gave the thio ether, soluble in acid and melting at 143°. Hydrolysis with 50% sulfuric acid at 150° yielded XXV.

2-Phenylimino-5-diphenyl-4-thiazolidone, XXVII (m. p. 253°).—This compound, prepared according to the method of Wheeler and Johnson,[9] is an isomer of XXIV but mixed melting point and properties showed that they are not identical. This compound behaved as a normal thiazolidone, the sodium salt yielding: (a) 2-methylphenylamino-5-diphenyl-4-thiazolidone XXVIII (m. p. 191°) and (b) 2-phenylimino-3-methyl-5-diphenyl-4-thiazolidone XXIX (m. p. 134°).

The constitution of XXVIII was shown by its synthesis from unsymmetrical methylphenylthiourea and that of XXIX proved by its synthesis from symmetrical methylphenylthiourea and to the fact that it hydrolyzes to give 3-methyl-5-diphenyl-2-4-thiazoledione, XXX (m. p. 102°). The synthesis of XXIX from methylphenylthiourea and diphenylchloroacetyl chloride in benzene solution with two moles of pyridine resulted in the formation in 25% yield of the 2-phenyl-3-methyl compound, insoluble in dilute acid, while the isomeric 2-methyl-3-phenyl derivative, XXXI (m. p. 119°), soluble in dilute acid, was formed in 75% yield. XXXI on hydrolysis gave methylamine and 3-phenyl-5-diphenyl-2,4-thiazoledione, XXXII (m. p. 150°).[10] The isolation of the two isomers is of

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[6] Bickel, *Ber.*, **38**, 1735 (1905); Staudinger, *Ann.*, **356**, 73 (1907).

[7] Klinger, *Ann.*, **389**, 253 (1912).

[8] Method of Biltz, *Ber.*, **41**, 1379 (1908).

[9] Wheeler and Johnson, THIS JOURNAL, **24**, 690 (1902).

[10] Becker and Bistrzyki, *Helv. Chim. Acta*, **2**, 114 (1919).

special interest since in the previous cases, doubtless due to the selective action, only one compound has been isolated from such reactions.

Summary

A study has been made of allyl and acyl substituted thiazolidones and of the use of mono- and diphenyl halogen acetyl chlorides and esters in the synthesis of thiazolidones and in one case of an imidazolone.

The diphenylchloroacetyl chloride gave with methylphenyl thiourea the two possible thiazolidones. It was noted also that the two phenyl groups at position 5 stabilize the thiazolidone ring toward hydrolysis as does the benzal group at the same position.

LAWRENCE, KAN.

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[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

Ethyl Imidocyclopropanecarboxylate Hydrochlorides[1]

BY JOHN B. CLOKE, EDWIN C. KNOWLES AND RAYMOND J. ANDERSON

Preparation.—The imido ester salts were prepared by the general method of Pinner.[2] Thus, the ethyl imidocyclopropanecarboxylate hydrochloride (I) was obtained by the action of dry hydrogen chloride on an ether solution of ethanol and cyclopropyl cyanide as follows

$$\underline{CH_2CH_2CH}CN + HOC_2H_5 + HCl \longrightarrow \underline{CH_2CH_2CH}—C(=NH_2Cl)OC_2H_5 \quad (I)$$

Similarly, the ethyl imido-1-phenylcyclopropanecarboxylate hydrochloride

$$\underline{CH_2CH_2C}(C_6H_5)—C(=NH_2Cl)OC_2H_5 \quad (II)$$

was obtained from 1-phenyl-1-cyanocyclopropane.[3]

Decomposition by Heat.—Pinner[4] many years ago found that the ordinary alkyl imido ester hydrochlorides are decomposed by the action of heat to give an amide and an alkyl chloride. His equation for the pyrolysis was

$$R—C(=NH_2Cl)OR' + \text{heat} \longrightarrow R—CO—NH_2 + R'Cl$$

Several years later, however, Stieglitz[5] in a much more critical study of this reaction pointed out that certain facts are more in harmony with the carbonium, $(R)(NH_2)(OR')CCl$, than with the enammonium structure for the pyrolyzing imidoester salt. His present view, which differs from this one, will be considered in a subsequent communication on this problem.

Following the observation[6] that a cyclopropyl ketimmonium chloride $\underline{CH_2CH_2CH}—C(=NH_2Cl)—R$, rearranges when heated to give the isomeric pyrrolinium chloride, $\underline{CH_2CH_2CH=C(R)NH_2Cl}$, it appeared to be quite possible that the analogous imido ester derivatives such as (I) and (II) might likewise undergo a ring rupture in addition to the Pinner–Stieglitz reaction. However, the work reported in this paper, which was undertaken largely to provide an answer to this question, has demonstrated that (I) and (II) decompose normally according to the Pinner–Stieglitz reaction to give cyclopropanecarbonamide, $\underline{CH_2CH_2CH}—CONH_2$, and 1-phenylcyclopropanecarbonamide

$$\underline{CH_2CH_2C}(C_6H_5)—CONH_2,$$

respectively. No ethoxypyrrolinium salts were detected in the cases thus far investigated. In future work an effort will be made to obtain a definite explanation of this notable ring stability.

Decomposition by Water.—In aqueous solution the imido esters undergo two concurrent reactions. In the first place, they decompose into a nitrile and an alcohol or phenol; and, in the second, they react with water to give the ordinary ester and ammonia, $R—C(=NH)–OR' + H_2O = RCOOR' + NH_3$. The first of these reactions is accelerated by bases, whereas the second is favored by acids. The imido ester hydrochlorides, therefore, are normally decomposed by water to give the ordinary ester and ammonium chloride in accordance with the monomolecular law, although some of them undergo a significant decomposition into nitrile, hydrochloric acid and an alcohol or phenol. Many years ago Stieglitz

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[1] The data reported herein have been taken from theses presented to the Rensselaer Polytechnic Institute by Edwin Chandler Knowles and Raymond J. Anderson. The work on the unsubstituted cyclopropane derivatives was done by R. J. A. and that on the phenylated compounds by E. C. K.

[2] Pinner, "Die Imidoäther und ihre Derivate," Berlin, 1892.

[3] Knowles and Cloke, THIS JOURNAL, **54**, 2028 (1932).

[4] Pinner, *Ber.*, **16**, 355, 1654 (1883).

[5] Stieglitz, *Am. Chem. J.*, **21**, 101 (1899); Lengfeld and Stieglitz, *ibid.*, **16**, 76 (1894).

[6] Cloke, THIS JOURNAL, **51**, 1174 (1929).

and his collaborators[7] made an extensive study of the decomposition of a variety of imido ester salts. The measurements reported in this paper were made in order to compare the characteristics of the cyclopropyl radicals with the alkyl and aryl radicals previously investigated. Upon the basis of these results, the cyclopropyl radicals would be classified with the so-called electronegative aryl radicals.

Experimental Part

Ethyl Imidocyclopropanecarboxylate Hydrochloride.—A solution of 0.2 mole of cyclopropyl cyanide[8] and 0.205 mole of absolute alcohol in four volumes of absolute ethyl ether in a moisture-proof vessel was then cooled in an ice-bath, when a current of carefully dried hydrogen chloride was passed in until no more gas was absorbed, which required about three hours. The solution was then allowed to stand overnight, which led to the separation of a crop of white crystals. These were collected on a filter, which was supported in a moisture-proof housing, when they were washed with anhydrous ether, dissolved in anhydrous acetic acid and reprecipitated therefrom by the addition of anhydrous ether. These crystals, which again were collected on a filter and dried under diminished pressure, melted at 120°, which, however, is actually the melting point of the pyrolysis product, *viz.*, the cyclopropanecarbonamide.[9]

Anal. Calcd. for $C_6H_{12}ONCl$: N, 9.36. Found: N, 9.43, 9.47.

Pyrolysis of Ethyl Imidocyclopropanecarboxylate Hydrochloride.—The imido ester hydrochloride was heated in a test-tube, whereby a white solid condensed on the walls of the tube. The solid melted at 120°, which corresponds to the melting point of the cyclopropanecarbonamide.

Anal. Calcd. for C_4H_7ON: N, 16.45. Found: N, 16.31.

Ethyl Imido-1-phenylcyclopropanecarboxylate Hydrochloride.—A solution of 13.72 g. of 1-phenyl-1-cyanocyclopropane[3] and 4.45 g. of absolute alcohol in 80 cc. of anhydrous ether was treated on several successive days with carefully dried hydrogen chloride. Since only a small amount of white solid had separated at the end of ten days, about 300 cc. of anhydrous ether was added to the mixture, whereby a voluminous white precipitate separated. The crystalline mass was collected on a filter under anhydrous conditions, washed with anhydrous ether and dried in a vacuum desiccator over phosphorus pentoxide for several hours. In view of the fact that the substance, which weighed 11 g., contained 17.6% chlorine as compared with a theoretical value of 15.8%, it was dissolved in warm glacial acetic acid and reprecipitated by the addition of anhydrous ether and petroleum ether. The purified compound was collected and dried as before.

Anal. Calcd. for $C_{12}H_{16}ONCl$: N, 6.21; Cl, 15.72. Found: N, 6.51, 6.37; Cl, 16.1, 15.88.

Action of Heat on above Hydrochloride.—The ethyl imido-1-phenylcyclopropanecarboxylate melted in the vicinity of 110° with some effervescence. When the residue was recrystallized from boiling water and then thoroughly dried, it melted from 98.5–99.5°, which is the melting point of the 1-phenylcyclopropanecarbonamide.

Ethyl Imido-2-methyl-1-phenylcyclopropanecarboxylate Hydrochloride.—A mixture of 7.83 g. of 2-methyl-1-phenyl-1-cyanocyclopropane and 2.3 g. of absolute alcohol was saturated at 0° with dry hydrogen chloride and allowed to stand in a stoppered flask for eight days. The addition of 200 cc. of anhydrous ether to the solution gave 1.5 g. of white crystals, which were washed with dry ether and dried under diminished pressure.

Anal. Calcd. for $C_{13}H_{18}ONCl$: Cl, 14.8. Found: Cl, 15.93.

Reaction Rates of Imido Ester Hydrochlorides with Water.—The velocity with which the imido ester hydrochlorides reacted with water, $R—C(=NH_2Cl)OR' + H_2O = RCOOR' + NH_4Cl$, was ascertained by the method of Stieglitz and Derby[10] for analogous compounds. This method is based upon the fact that an imido ester can be liberated from its hydrochloride by the action of sodium hydroxide and that the free ester is much more soluble in carbon tetrachloride than it is in water, whereas the reverse solubility behavior holds for ammonia. The reaction velocity constant, *k*, was calculated from the equation for a monomolecular reaction

$$k = \frac{2.303}{t_2 - t_1} \log \frac{v_1}{v_2}$$

where v_1 and v_2 represent the relative concentrations of the imido ester hydrochloride at times t_1 and t_2.

In the work which is recorded in the following tables, a 0.05 molar aqueous solution of the imido ester salt was prepared and maintained at a definite temperature in a thermostat. Without delay a 10–20 cc. volume of the reacting solution was pipetted into a Squibb funnel which contained a carefully measured volume of 0.1 *N* sodium hydroxide and a suitable quantity of carefully purified carbon tetrachloride. At once the mixture was well

TABLE I

Reaction: $\overline{CH_2CH_2C}HC(=NH_2Cl)OC_2H_5 + H_2O = \overline{CH_2CH_2C}HCOOC_2H_5 + NH_4Cl$; temp., 25°; concentration of initial solution, 0.05 *M;* volume of individual samples, 10 cc.; t = time in minutes from moment of dissolving; v_b = volume of 0.1 *N* NaOH in cc.; v_a = volume of 0.1 HCl.

t	v_b	v_a	$v_b - v_a$	k
2	7.17	2.19	4.98	....
60	7.17	2.69	4.48	0.00182
180	7.17	3.55	3.62	.00179
420	7.17	4.83	2.34	.00181
780	7.17	5.86	1.31	.00172

Average k = 0.00178

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(7) Stieglitz, *Report International Congress of Arts and Science, St. Louis*, **4**, 276 (1904); *Am. Chem. J.*, **39**, 29 (1908); Stieglitz with Derby, McCracken and Schlesinger, *ibid.*, **39**, 29, 166, 402, 437, 586, 719 (1908); Stieglitz, THIS JOURNAL, **32**, 221 (1910); *ibid.*, **34**, 1687 (1912); *ibid.*, **35**, 1774 (1913); Carr, doctoral dissertation, University of Chicago, 1910.

(8) Cloke, Anderson, Lachmann and Smith, THIS JOURNAL, **53**, 2791 (1931).

(9) Dalle, *Chem. Zentr.*, **73**, I, 913 (1902); Kishner, *ibid.*, **72**, II, 579 (1901), gives 124–124.5°.

(10) Derby, *Am. Chem. J.*, **39**, 439–441 (1908).

TABLE II

Run	Compound	°C.	Successive constants × 10^4					Average k
2	$\underbrace{CH_2CH_2CH}C(=NH_2Cl)OC_2H_5$	25	16.3	17.8	17.4	18.7		0.00176
3		0	0.939	1.054	0.968	1.003		.0000991
4	$\underbrace{CH_2CH_2C}(C_6H_5)C(=NH_2Cl)OC_2H_5$	25	29.7	29.1	26.9	24.2	23.8	.00265
5		25	25.7	24.5	25.0	23.8		.00247
6		25	25.7	24.0	21.8	19.0		.00226
7	$\underbrace{CH_2CH(CH_3)C}(C_6H_5)C(=NH_2Cl)OC_2H_5$	25	17.2	14.3	12.6			.00147
8		25	16.8	12.6	13.3	11.6		.00136

shaken, the carbon tetrachloride layer was drawn off, and the extraction was repeated twice with fresh portions of this solvent. Finally the residual aqueous alkaline solution was titrated with 0.1 N hydrochloric acid. Table I gives the data for a typical run.

Table II presents a summary of runs similar to that recorded in Table I.

In view of the fact that compound (II) appeared to be relatively pure, the drift in the values of the constants of runs 4, 5 and 6 suggests a secondary concurrent reaction, although this has not been ascertained experimentally. Runs 7 and 8 on the methylated derivative are of qualitative value only.

Summary

1. The hydrochlorides of ethyl imidocyclopropanecarboxylate and ethyl imido-1-phenylcyclopropanecarboxylate are pyrolyzed normally according to the Pinner–Stieglitz reaction to give the corresponding amides and ethyl chloride. No evidence was obtained of a ring rupture to give pyrrolinium salts.

2. A study of the reaction velocity constants of our imido ester salts with water and those previously determined by Stieglitz and his collaborators for other compounds shows that by this criterion the cyclopropyl radicals should be classified with the electronegative aryl radicals.

Unfinished work on the free esters and amidines will be completed and reported at a later date.

TROY, N. Y. RECEIVED OCTOBER 5, 1936

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

Acetyl Derivatives of the Monobasic Sugar Acid Lactones

BY FRED W. UPSON, JOHN M. BRACKENBURY AND CARL LINN

The preparation of a number of acetyl derivatives of the monobasic sugar acid lactones is described in this paper and their properties are compared with those of the parent lactones. Since these derivatives are easily prepared, they are useful in identifying the lactones and in synthesizing other compounds.[1] Furthermore, since no other derivatives have been prepared directly from the δ-lactones the preparation of the acetyl derivatives of these lactones is of interest.

It has been shown[2] that the monobasic lactones having an amylene oxide structure, the δ-lactones, are rapidly hydrolyzed in water solution. Loder[3] found that methylation of *d*-mannonic δ-lactone yielded a derivative having the properties of the γ-lactone. A study of the acetyl compounds was undertaken in an effort to prepare derivatives directly from the δ-lactones[4] and this paper is a continuation of the earlier work of Upson and Bartz. A non-crystalline substance identified as the 2,3,4,6-tetraacetyl derivative was obtained by direct acetylation of *d*-gluconic δ-lactone. This compound though non-crystalline, showed a very rapid mutarotation in 80% acetone–water solution, and was otherwise characterized as a derivative of a δ-lactone.

The acetyl derivatives of thirteen sugar acid lactones have been prepared and their specific rotations have been determined in comparison with those of the parent lactones. The following compounds prepared for this study are already described in the literature: 2,3,5-triacetyl-*d*-xylonic[5] and *l*-arabonic,[6] γ-lactones; the 2,3,5,6-tetraacetyl derivatives of the γ-lactones of *d*-gluconic,[4] *d*-mannonic,[4] α-*d*-glucoheptonic,[4] and α-*l*-rhamnohexonic acids;[7] and 2,3,4,6-tetraacetyl-*d*-gluconic δ-lactone.[4] In addition the following

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[1] Paal and Kinscher, *Ber.*, **44**, 3543 (1911); **39**, 1361, 2823, 2827 (1906).

[2] Levene and Simms, *J. Biol. Chem.*, **65**, 31 (1925).

[3] Loder, unpublished thesis, University of Nebraska, 1927.

[4] Upson and Bartz, THIS JOURNAL, **53**, 4226 (1931).

[5] Hasenfratz, *Compt. rend.*, **196**, 350 (1933).

[6] Simon and Hasenfratz, *ibid.*, **179**, 1165 (1924).

[7] Miksic, *Vestnik Kral. Ces., Spol. Nauk.* Cl. II, 18 pp. (1926).

new compounds have been synthesized: the 2,3,5,6-tetraacetyl derivatives of the γ-lactones of *d*-galactonic, *d*-gulonic, *d*-talonic and *l*-rhamnonic acids and the 2,3,4,6-tetraacetyl derivatives of the δ-lactones of *l*-rhamnonic and *d*-mannonic acids.

Experimental

Acetylation was accomplished by means of acetic anhydride in the presence of a catalyst. Anhydrous zinc chloride, pyridine and sulfuric acids have been used. The acetylated product is separated from the catalyst by means of water, a process which tends to cause hydrolysis of the lactones. Dry hydrogen chloride in acetic anhydride was found to be a suitable acetylating agent and the possibility of hydrolysis is avoided since excess reagent may be removed by distillation under reduced pressure.

Preparation of the Acetyl Derivative.—Dry hydrogen chloride was passed into acetic anhydride for several minutes. After cooling to 0° the pure lactone was added, 5 cc. of acetic anhydride being used for each gram of lactone. The lactone went into solution at room temperature, the time required varying from a few hours to two weeks, depending upon the lactone used. After the substance had been completely in solution for at least one day the solution was transferred to a distilling flask of appropriate size and the acetic anhydride excess removed under 15–20 mm. pressure. During this distillation the temperature was controlled by a water-bath, the temperature of which was raised slowly to a maximum of 80°. Occasionally the derivative would crystallize during this process. After all acetic anhydride had been removed, the residue was dissolved in chloroform, filtered and the product finally thrown out of solution by the addition of petroleum ether. The product in most cases was solid at this point and was filtered off, dried in vacuum over potassium hydroxide and finally recrystallized from absolute ethanol. Butanol was usedf or the derivatives of *l*-rhamnonic and α-*l*-rhamnohexonic lactones since these are very soluble in ethanol. If the product thrown down by the petroleum ether was non-crystalline, it was washed several times with petroleum ether, the latter removed by heating at 40° under 20 mm. pressure and the resulting liquid kept in a vacuum over potassium hydroxide, with frequent stirring. Various solvents were tried when the product was persistently non-crystalline.

The following new acetylated lactones were prepared using the method above described. In each instance the corresponding pure lactone was used and the acetylated products were characterized by analyses for carbon and hydrogen as well as by their optical properties.

The acetylation of *d*-gluconic δ-lactone using zinc chloride as the catalyst gives a tetraacetylgluconic acid monohydrate as shown by Upson and Bartz.[4] This possesses a melting point of 114–117° and the specific rotation is very nearly zero. On heating in vacuum for some hours at 100° water is given off and there remains a colorless glass-like solid which analyzes correctly for a tetraacetylgluconic lactone. Furthermore, it exhibits the very rapid mutarotation characteristic of δ-lactones. Acetylation according to the method described in this paper using hydrochloric acid as the catalyst produced the same non-crystalline solid which checked in every particular with the 2,3,4,6-acetylated lactone described by Upson and Bartz. The rotation of this substance is recorded in this paper. The acetyl derivatives of γ-gluconic, γ-talonic and γ-rhamnonic lactones are also liquid, but the non-crystalline character of these compounds does not appear to be related to asymmetric structure.

Two acetyl derivatives prepared in this study, namely, 2,3,5,6-tetraacetyl-γ-*l*-rhamnohexonic lactone and 2,3,5,6-tetraacetyl-*d*-talonic γ-lactone possess unusually low initial rotations, and there is little change in the rotation with time. These low rotations are characteristic of free acids rather than of lactone derivatives. Nevertheless, analyses show that these two compounds are acetylated lactones. Of the remaining compounds the acetyl derivatives of galactonic and glucoheptonic lactones are the only ones which possess significantly lower rotations than do the parent lactones. The acetylated *l*-rhamnonic, γ and δ-lactones have rotations somewhat higher than those of the parent lactones whereas the remaining lactones and acetylated derivatives correspond fairly closely as regards specific rotation.

The mutarotation of the lactones and their acetyl derivatives is recorded by means of graphs in Figs. 1 and 2. The graphs in Fig. 2 are plotted without reference to the sign of rotation. The sign of rotation is negative in the case of rhamnonic lactone and its acetyl derivative and is positive for the mannonic and gluconic derivatives.

Time is plotted in *days* in Fig. 1 and in *hours* in Fig. 2 because of the more rapid change of rotation with time in the case of the delta lactones. Polariscopic readings were taken at intervals during a period of several days and the solutions of the various lactones were maintained at a temperature of 25° during this period. Water was the solvent used in the case of the lactones whereas the solvent for the acetyl derivatives was a mixture of acetone and water in the proportions of 80 and 20%.

An inspection of Fig. 1 brings out a number of points. In all cases the sign of rotation of the lactone and its acetyl derivative is the same. In a number of instances the specific rotation of the acetyl derivative is notably less than that of the parent lactone. The derivatives of galactonic (1 and 1a), gulonic (2 and 2a), talonic (4 and 4a) and rhamnohexonic (10 and 10a) fall in this group. In the case

TABLE I

Tetraacetyl lactone	M. p., °C.	$[\alpha]^{25}\text{D}$				
			Min.			Days
2,3,5,6-*d*-Gulonic γ-	103–104	− 37°	5		−35.5°	5
2,3,5,6-*d*-Galactonic γ-	67–68	− 21.7°	13		−19.9°	6
2,3,5,6-*d*-Talonic γ-	Non-cryst. sirup	− 8°	10		− 3°	5
2,3,5,6-*l*-Rhamnonic γ-	Non-cryst.	− 60.1°	20		−57.9°	5
2,3,4,6-*l*-Rhamnonic δ-	71	−113.8°	10	−89.3° 31 hrs.	−40.8°	8
2,3,4,6-*d*-Mannonic δ-	99–101	+ 96.3°	6	+60° 22 hrs.	+31.3°	6

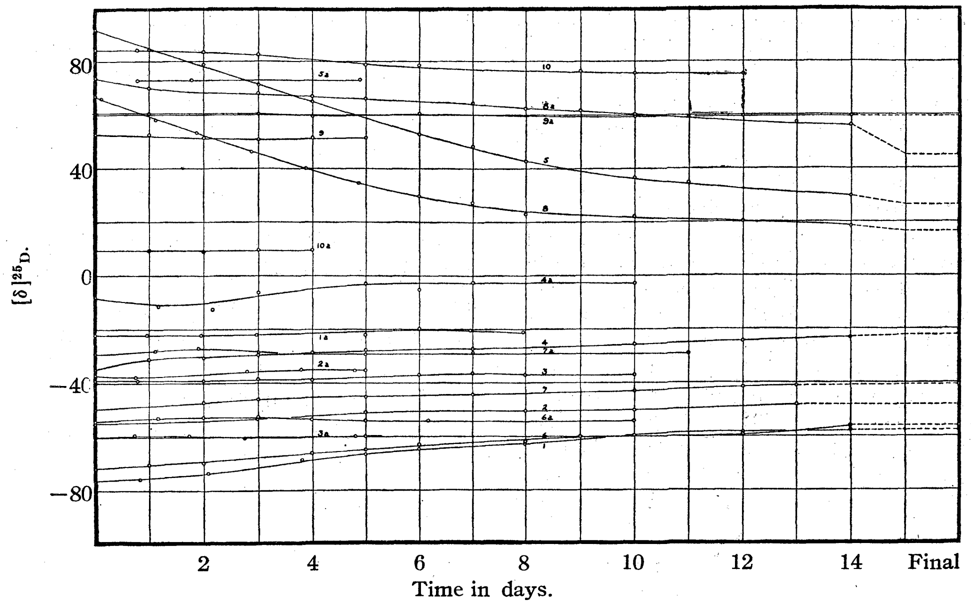

Fig. 1.—Gamma lactones and their acetyl derivatives: 1, 1a, *d*-galactonic; 2, 2a, *d*-gulonic; 3, 3a, *l*-rhamnonic; 4, 4a, *d*-talonic; 5, 5a, *l*-xylonic; 6, 6a, *l*-arabonic; 7, 7a, α-*d*-glucoheptonic; 8, 8a, *d*-gluconic; 9, 9a, *d*-mannonic; 10, 10a, α-*l*-rhamnohexonic.

of xylonic (5 and 5a), gluconic (8 and 8a) and mannonic (9 and 9a) the acetyl derivatives possess specific rotations somewhat higher than their lactones. In all cases there is a relatively slow change in rotation with time, the lactones and their acetyl derivatives showing a similar behavior. The only exceptions are found in the case of xylonic (5 and 5a) and gluconic (8 and 8a) where the rotation of the lactone changes somewhat more rapidly than that of the acetyl derivative. It is to be noted, however, that in all cases the mutarotation is relatively small in the first forty-eight to seventy-two hours.

In marked contrast is the behavior of the delta lactones and their acetyl derivatives as illustrated in Fig. 2. As has been noted in numerous investigations the specific rota-

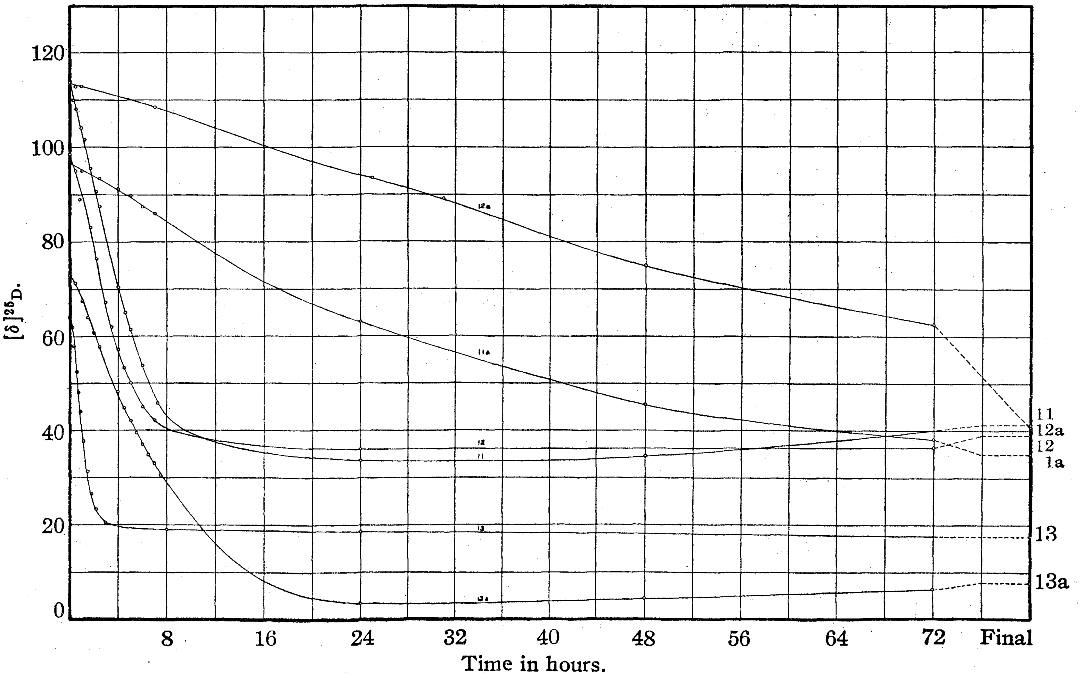

Fig. 2.—Delta lactones and their acetyl derivatives: 11, 11a, *d*-mannonic; 12, 12a, *l*-rhamnonic; 13, 13a, *d*-gluconic.

tions of the δ-lactones of gluconic (13), mannonic (11) and rhamnonic acids (12) are relatively high initial specific rotations which show rapid diminution in value during the first few hours after solution. In comparison with the parent lactones, the acetyl derivatives of mannonic (11a) and rhamnonic (12a) do not show as rapid diminution of specific rotation. The behavior of acetyl δ-gluconic lactone, however, parallels very closely that of the parent lactone. In comparison with the corresponding acetyl γ-lactone derivatives these acetylated δ-lactones all show a much more rapid rate of mutarotation and the initial rotations are all very close to those of the parent lactones. Thus the acetylated δ-mannonic lactone (2–11a) changes in rotation from +97 to +63° in twenty-four hours, whereas the corresponding gamma derivative (1–9a) has an initial specific rotation of +60° which shows no change even after ten days. In like manner the rotation of acetylated γ-rhamnonic lactone (2–12a) has an initial value of −114° which changes to −94° in twenty-four hours, while the acetyl derivative of the corresponding γ-lactone (1–3a) exhibits an initial specific rotation of −60° which shows no change even after five days. These acetylated δ-lactones are of special interest since they are the first derivatives to be prepared directly from the delta lactones themselves.

Summary

1. Thirteen acetylated monobasic sugar acid lactones have been prepared, ten of the γ-variety, and three of the δ-configuration.

2. The change in specific rotation with time at 25° has been determined.

3. It has been shown that the acetylated lactones parallel rather closely the parent lactones as regards change of rotations with time.

LINCOLN, NEB. RECEIVED OCTOBER 8, 1936

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Deuterium Abundance Ratios in Organic Compounds. III. Cholesterol

BY MALCOLM DOLE AND ROBERT B. GIBNEY

The interesting possibility of variations in the isotopic abundance ratios of deuterium in naturally occurring organic compounds as compared to the value of this ratio in normal water has been realized and investigated by a number of workers,[1] but there has not yet been published definite proof of an abnormal deuterium content in any organic compound. The hydrogen of benzene has been analyzed by one of us using a method presumably free of isotopic error[1] but its deuterium content is practically normal. In this paper we report data for the abundance of deuterium in cholesterol which appear to demonstrate the existence of a compound containing a slightly low abundance of deuterium although the observed effect is scarcely greater than the experimental error.[2] We chose cholesterol for this study because it is definitely an animal product,[3] and because its high molecular weight and complexity of structure led us to believe that if any animal product would be abnormal in its deuterium content, cholesterol would be that compound. Cholesterol is also interesting because of its apparently important relations to the hormones and other physiologically active substances. As compared to benzene cholesterol has a relatively high percentage of hydrogen; the small amount of oxygen present introduces a negligible error.

Experimental

Combustion of the Cholesterol.—The method of determining the deuterium content previously used was followed here. The source of the cholesterol was the Wilson Laboratories, Chicago, highest grade "Cholesterin" which comes 95% from the spinal fluid of cattle and 5% from the brains of pigs. The purity of this product was claimed by the manufacturers to be 99.9%, but Fieser states[3] (p. 113) that commercial cholesterol contains small amounts of closely related substances which cannot be eliminated by repeated crystallization, to the extent perhaps of 1 to 2%. Since these related compounds would probably contain similar isotopic proportions of deuterium, this small impurity can be neglected. The melting point temperature of the cholesterol was 149°. The combustion of the cholesterol was carried out using four different methods in order to make it fairly certain that the water obtained contained a representative sample of the hydrogen. Deuterium containing substances apparently burn more slowly than similar compounds made of protium, so that unless all or practically all the cholesterol suffers combustion, the

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(1) See M. Dole, THIS JOURNAL, **58**, 580 (1936), for a review of all previous work and a critical discussion of existing data.

(2) See M. Dole, *Science*, **83**, 31 (1936), for calculations showing that the work of Washburn and Smith apparently indicated a smaller than normal abundance of deuterium in dry wood of the willow tree after proper allowance had been made for the difference in atomic weights of oxygen of the air and of water. However, the isotopic composition of the oxygen in the willow tree water is still uncertain even after this correction has been made.

(3) L. F. Fieser, "The Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corporation, New York, 1936, states, p. 122: "Although the evidence is conclusive that the cholesterol present in higher animals is synthesized in the animal organism, the site and mechanism of cholesterol formation are unknown."

resulting water might not contain all the deuterium it should contain.

The first combustion of cholesterol was carried out by one of us in 1934 by heating the cholesterol to 350° in a Pyrex flask and leading the vapors over hot copper oxide by means of a stream of air which was passed over the surface of the hot cholesterol.[4] The cholesterol burned on the catalyst and tank oxygen of an unknown source (probably Linde oxygen) was added in relatively small amounts whenever the oxygen in the air was insufficient to keep the catalyst in the oxide form. The burning of the cholesterol was repeated by this method in 1936 using air to sweep the vapors of the cholesterol over the copper oxide. Air was also admitted to the middle portion of the combustion tube in just sufficient quantities to maintain the catalyst in the oxide form. An excess of air was avoided in order to prevent a separation of the isotopes of water by a fractional condensation of its vapors. In the case of this second combustion a large charred residue remaining in the cholesterol flask was removed, ground fine and burned in a modified apparatus using air. The yield of water was approximately 75% of the theoretical.

The third combustion of the cholesterol was carried out in a specially designed apparatus using instead of air Airco oxygen, whose isotopic composition in reference to that of atmospheric oxygen was known. The cholesterol burned at a jet made out of capillary tubing in a chamber 6.4 cm. in diameter, 10.2 cm. long which was sealed onto the combustion tube containing the copper oxide catalyst. Oxygen was supplied through a side arm. The cholesterol was kept in a liquid state in a flask by means of a cottonseed oil-bath heated to 180°. Nitrogen forced the cholesterol from the flask into the combustion system through a glass tube while more nitrogen entering into the tube halfway to the combustion chamber, broke the stream of cholesterol into bubbles and blew the cholesterol vapor which was now formed from the heat of the combustion furnace through the jet where the cholesterol burned in a flame steadily and brilliantly. Sometimes it was found unnecessary to add nitrogen at the half-way point. Oxygen was added just rapidly enough to keep the copper oxide catalyst in the oxide form. The yield of water was about 75%. Some of the cholesterol was occasionally blown through the apparatus unburnt due to slight explosions which occurred when the flame went out. Considerable attention was required to maintain a flame at the jet; the flame was lighted by explosions of the oxygen–cholesterol vapor mixture traveling back to the capillary tip.

The fourth method of burning the cholesterol (number III of Table I) consisted in dropping liquid cholesterol onto a copper oxide catalyst heated to about 500°. Air was admitted into the tube to keep the copper catalyst oxidized, and the water formed in the combustion was partially condensed in a water condenser, and the uncondensed residue completely frozen out in a dry ice–acetone trap. This trap was quite necessary as the condensing water was so warm due to the fact that the experiment was done in the summer that only 66% of the water was collected in the water condenser. This method of combustion produced about 75–80% of the theoretical yield.

Measurement of the Density.—The water was distilled from alkaline permanganate over hot copper oxide until all odor disappeared. It was then purified according to our previous method. The method of measuring the density was also the same as previously described except that the apparatus was rebuilt to accommodate smaller volumes of water, a smaller float was made and the motion of the float was observed with the aid of a cathetometer. The temperature measurements and corresponding values of γ are given in Table I where γ is the density of the water under investigation less the density of normal water at the same temperature, the difference expressed in parts per million.

TABLE I

DENSITY OF WATER OBTAINED IN THE COMBUSTION OF CHOLESTEROL

		Cholesterol + air Δt	γ
I		+0.007	
		+ .004	
	Av.	+ .005	+1.1
II		+ .005	
		+ .004	
	Av.	+ .004	+0.9
III		+ .005	
		+ .003	
	Av.	+ .004	+1.2
		Cholesterol + Airco oxygen Δt	γ
IV		(+0.019)	
		+ .008	
		+ .009	
	Av.	+ .008	+1.8
Corr. for oxy:		− .002	−0.5
Final result:		+ .006	+1.3

The method of measuring and the value for the correction to Airco oxygen to bring its atomic weight to that of atmospheric oxygen have already been published.[1] Oxygen from the same Airco tank was used in this experiment.

The density measurements for the combustion number III of Table I were made at 29.9° which accounts for the different relation between Δt and γ.

Interpretation of the Results

In interpreting the very slight difference between the density of the cholesterol–water and normal water calculated from the data of the first combustion, one of us[4] originally concluded that the deuterium content of cholesterol was normal, but at that time we were ignorant of the relatively large difference between the atomic weight of atmospheric oxygen and oxygen of water which has since been observed.[5] In order to correct for this effect 6.0 γ must be subtracted from 1.1 γ, the average of the four data from the three combustions, yielding -4.9 γ as the apparently correct value for the difference in density between

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(4) M. Dole, *J. Chem. Phys.*, **2**, 548 (1934).

(5) M. Dole, *ibid.*, **4**, 268 (1936).

water made from the hydrogen in cholesterol and normal water. However, there is the possibility that the oxygen isotopes may have separated during the combustion of the cholesterol as one of us has already pointed out.[1] We have investigated this source of error by electrolyzing the cholesterol water along with normal water, combining the liberated oxygen with the same tank hydrogen in both cases and comparing the density of these waters. Two independent experiments were carried out, the second series being the more reliable since more measurements were made in determining the density. Much to our surprise we found that the oxygen in the cholesterol which originally came from the air was not as heavy as we had suspected so that instead of subtracting 6.0 γ from the value of 1.1 γ given in Table I we should subtract only 2.5 γ (the average of the results given in Table II, giving double weight to the more accurate value of the second series) which is the extent in p. p. m. to which the density of water made from the oxygen in the cholesterol water exceeds the density of water made from the oxygen in normal water, the hydrogen in the two waters being identical. The result of this calculation is -1.4 γ which is the extent in p. p. m. to which the density of water made from the hydrogen in cholesterol is lighter than water made from normal hydrogen, the oxygen in the two waters being identical in isotopic composition. Considering all the corrections which must be made to the measured values in addition to the errors which are inherently present in the measurements themselves, we cannot consider this value of -1.4 γ as proving definitely that the isotopic abundance of deuterium in cholesterol is lower than normal. Indeed, when one considers the complicated nature of cholesterol, it is surprising that the hydrogen is not more abnormal.

TABLE II

DENSITY DATA OBTAINED IN THE ANALYSIS OF THE OXYGEN CONTAINED IN THE CHOLESTEROL WATER

Type of water		Δt	γ
First series (at 23.4°)			
Aqueous oxygen after electrolysis combined with tank hydrogen		-0.045	-10.4
Cholesterol water oxygen after electrolysis combined with tank hydrogen		$-$ .036	$-$ 8.3
Difference		$-$ .009	-2.1
Second series (at 29.9°)			
Aqueous oxygen after electrolysis		$-$ .040	-12.0
combined with tank hydrogen	I	$-$ .042	-12.6
		$-$ .0426	-12.8
	II	$-$ .040	-12.0
		$-$ .039	-11.7
Average		$-$ .0407	-12.2
Cholesterol water oxygen after electrolysis combined with tank hydrogen		($-$ .027)	
		$-$ .032	$-$ 9.6
		$-$ .0315	$-$ 9.5
Average		$-$ .032	$-$ 9.5
Difference		$-$ .009	$-$ 2.7
Average of both series			$-$ 2.5

We have also burned halibut liver oil residues in the same way that combustion III of Table I was carried out using Airco oxygen, however, instead of air. The water, after correcting for the Airco oxygen as in Table I, was 3.6 γ heavier than normal. The volume of the water obtained, however, was so small because of the limited amount of the oil at our disposal that we were unable to analyze the oxygen in the water with respect to its isotopic composition. Assuming that the oxygen behaved in this combustion similarly to the cholesterol combustion, and subtracting 2.5 γ for the excess density because of the different oxygen present, we obtain only $+1.1$ γ for the excess density of water made from the hydrogen in the halibut liver oil residues over normal water, the oxygen in each water being of identical isotopic composition. Once again we find the hydrogen to be surprisingly normal in its isotopic composition.

Since we have now analyzed benzene, a plant product, cholesterol, an animal product, and halibut liver oil residues, a fish product, without finding the hydrogen isotopic composition to be definitely abnormal, we are forced to the conclusion that the role of heavy hydrogen in nature cannot be very significant. There is definitely no indication here of the accumulation or rejection of deuterium in the building of these compounds utilizing hydrogen from the ultimate source of water.

In the combustion of the benzene one of us found no separation of the oxygen isotopes,[1] but the benzene burned in a blue flame at a much higher temperature than the temperature at which the cholesterol burned. The cholesterol burned at a catalyst about 500–600°, but even this temperature is so high that one would not expect an appreciable fractionation of the oxygen isotopes, at least from equilibrium theory, since the fractionation factor for the isotopic equilibrium reaction

$$CO_2^{16} + 2H_2O^{18}(g) \rightleftarrows CO_2^{18} + 2H_2O^{16}(g)$$

falls from 1.054 at 25° to 1.014 at 323°.[6] At 600° it would probably be even smaller. Perhaps an isotopic exchange takes place at lower temperatures before the carbon dioxide and steam are separated, but if such an exchange takes place, it would have to be catalyzed by products formed in the combustion since a simple mixing of carbon dioxide and steam for a short period of time produces no isotopic exchange.[1] The magnitude of the effect, about 4 p. p. m. in terms of water density, is small enough to be accounted for by such an exchange and it is in the direction expected.

Acknowledgments.—We are greatly indebted to Dr. D. L. Tabern of the Abbott Laboratories for supplying the halibut liver oil residues, to Mr. Stanley Cristol for carrying out the combustion of the oil, to Mr. J. L. Gabbard for the loan of the electrolysis cells, and to Mr. B. Z. Wiener for carrying out the second electrolysis mentioned in Table II.

Summary

Cholesterol has been examined for its deuterium content, but after all the necessary corrections have been applied to the data it appears that the deuterium content of cholesterol is normal. The measurements indicate a slight deficiency of heavy hydrogen, but the magnitude of the deficiency is hardly greater than the experimental error. Halibut liver oil residues have also been analyzed isotopically, but again the hydrogen appears to be normal in its deuterium content.

We have found, however, that there is a marked fractionation of the oxygen isotopes on combustion of the cholesterol.

EVANSTON, ILL. RECEIVED SEPTEMBER 21, 1936

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[6] H. C. Urey and Lotti J. Greiff, THIS JOURNAL, **57**, 321 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, THE UNIVERSITY OF LIVERPOOL]

The Reactivity of Hydrogen Peroxide in Bromine–Bromide Solutions

BY ROBERT OWEN GRIFFITH AND ANDREW MCKEOWN

A recent paper by Livingston and Schoeld[1] on the photochemical behavior of H_2O_2–HBr–Br_2 mixtures in aqueous solution prompts us to communicate briefly the results of some experiments which we carried out in 1933–34 on this same system, especially as (a) our conclusions regarding the photochemical reaction are diametrically opposed to those of Livingston and Schoeld, and (b) our observations on the thermal reaction differ in some respects from those of Bray and Livingston.[2]

Dealing first with the thermal reaction, we find that H_2O_2–HBr–Br_2 systems at constant temperature and in the dark never attain "steady state" conditions as defined by Bray and Livingston, that is, the concentration of bromine $[\Sigma Br_2]$, and correspondingly that of hydrobromic acid, never reach stationary values so long as any hydrogen peroxide remains undecomposed. According to our measurements, if no bromine is originally present in the system, $[\Sigma Br_2]$ at first rapidly increases toward a pseudo-stationary value, but instead of remaining at this value it then slowly but progressively increases with diminishing concentration of hydrogen peroxide. If excess of bromine is originally present, $[\Sigma Br_2]$ at first rapidly falls to a pseudo-stationary value, passes through a minimum, and then as before slowly increases. In either case, provided the sum $[HBr] + {}^1/_2[\Sigma Br_2]$ has the same value and provided enough hydrogen peroxide be present initially, the concentration of bromine becomes after a sufficient lapse of time the same function of the hydrogen peroxide concentration, independent of the previous history of the system.

For our experiments we have employed, with identical results, hydrogen peroxide from the following sources: (1) Merck 30% Perhydrol free from preservatives, (2) a preparation from sodium peroxide following the method of Rice, Rieff and Kirkpatrick,[3] and (3) a sample obtained from an A. R. hydrogen peroxide by distillation under reduced pressure. Our measurements of bromine concentration were carried out (α) analytically by the method described by Bray and Livingston,[2] and (β) spectrophotometrically.

Table I gives the results of four typical experiments. It will be noted that, after the attainment of pseudo-stationary conditions, the con-

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[1] Livingston and Schoeld, THIS JOURNAL, **58**, 1244 (1936).

[2] Bray and Livingston, *ibid.*, **45**, 1264 (1923).

[3] Rice, Rieff and Kirkpatrick, *ibid.*, **48**, 3019 (1926).

TABLE I

Temp. = 20°; $[HBr]_{init.} = 0.202$ *M*; $[\Sigma Br_2]_{init.} = 0.004$ *M*

Merck's $[H_2O_2]_{init.} = 0.40$ *M*

$[H_2O_2]$	$[\Sigma Br_2]_{anal.}$	$[\Sigma Br_2]_{phot.}$	$k_{uni.} \times 10^6$
0.337	0.00332	0.00323	695
.147	.00361	.00369	678
.054	.00406	.00416	663
.021	.00436	.00446	641
.008	.00446	.00456	

Synthetic $[H_2O_2]_{init.} = 0.54$ *M*

$[H_2O_2]$	$[\Sigma Br_2]_{anal.}$	$[\Sigma Br_2]_{phot.}$	$k_{uni.} \times 10^6$
0.239	0.00344	0.00341	682
.089	.00383	.00387	668
.033	.00420	.00432	660
.013	.00448	.00449	...
.002	.00465	.00472	

Temp. = 20°; $[HBr]_{init.} = 0.1616$ *M*; $[\Sigma Br_2]_{init.} = 0.0011$ *M*

Synthetic $[H_2O_2]_{init.} = 0.38$ *M*

$[H_2O_2]$	$[\Sigma Br_2]_{phot.}$	$k_{uni.} \times 10^6$
0.335	0.00091	456
.189	.00102	447
.092	.00119	442
.052	.00131	436
.026	.00145	...
.002	.00168	

Distilled $[H_2O_2]_{init.} = 0.4$ *M*

$[H_2O_2]$	$[\Sigma Br_2]_{phot.}$	$k_{uni.} \times 10^6$
0.360	0.00095	458
.213	.00103	449
.114	.00117	442
.028	.00144	431
.017	.00153	

centration of bromine steadily increases in every case; in some of our experiments the increase in $[\Sigma Br_2]$ amounts to more than 100%. The rate of increase of $[\Sigma Br_2]$ with time (beyond the pseudo-stationary state) is practically a constant in each experiment while the hydrogen peroxide concentration changes over the range $0.3 \longrightarrow 0.03$ *M*. When the hydrogen peroxide becomes very weak, however, $d[\Sigma Br_2]/dt$ falls off in each case. For the two concentrations of hydrobromic acid in Table I the constant rate $d[\Sigma Br_2]/dt$ equals 31 and 9.3×10^{-8} moles per minute, respectively, and from other experiments not listed this rate appears to be roughly proportional to the fifth power of [HBr].

Attention may also be directed to a further point. The last column for each experiment gives values of $k_{uni.}$ (natural logs; time in minutes) for the rate of disappearance of hydrogen peroxide, *viz.*, $-d[H_2O_2]/dt = k_{uni.}[H_2O_2]$. It will be seen that $k_{uni.}$ falls with time, that is, with diminishing $[H_2O_2]$. The fall is considerably greater than that which might be due to the slight decrease in the concentration of hydrobromic acid resulting from the increasing concentration of bromine. Thus in the first experiment [HBr] decreases about 1%, but $k_{uni.}$ falls by 8%. We have observed this fall in $k_{uni.}$ in all our experiments and we believe it to be real and of significance for the mechanism of the reaction.

We have also studied the photochemical behavior of H_2O_2–HBr–Br_2 systems from various aspects. One of the methods employed was to allow a H_2O_2–HBr–Br_2 mixture to attain, at constant temperature and in the dark, a pseudo-stationary state in which under our experimental conditions $[\Sigma Br_2]_d$ is changing but slowly, then illuminate with monochromatic light and measure by photometric means (thermopile–galvanometer) the *initial* rate of disappearance of bromine. The apparatus used was similar to that of Griffith, McKeown and Winn[4] the main difference being that e. m. fs. generated in the thermopile were balanced by a compensator, similar to that described by Goodeve and Nagai,[5] and recorded on a Weston precision millivoltmeter used in conjunction with a Zernicke *Zc* galvanometer. The thermopile was standardized by means of the uranyl oxalate reaction and checked with a carbon filament lamp standardized by the N. P. L. Table II gives the results (γ = quantum yield, molecules of bromine disappearing per quantum absorbed) of six experiments using blue light ($\lambda = 436$ mμ).

TABLE II

$[H_2O_2]$	$[\Sigma Br_2]_d$	Quanta absorbed per minute	Molecules of Br_2 disappearing per minute *initially*	γ
Temp. = 20°; $[HBr]_{init.} = 0.1437$; $[\Sigma Br_2]_{init.} = 0$; 2-cm. cell				
0.15	0.000523	2.04×10^{16}	1.61×10^{17}	7.9
.15	.000523	4.14×10^{15}	4.74×10^{16}	11.5
.042	.000714	2.17×10^{16}	4.42×10^{16}	2.0
.042	.000714	4.67×10^{15}	1.53×10^{16}	3.3
Temp. = 17°; $[HBr]_{init.} = 0.1071$; $[\Sigma Br]_{init.} = 2 \times 10^{-4}$; 10-cm. cell				
0.19	0.0001194	2.57×10^{16}	4.4×10^{17}	17
.19	.0001194	5.66×10^{15}	1.9×10^{17}	34

The data show that quantum yields considerably in excess of unity are obtained, and that γ is roughly proportional to $[H_2O_2]$ and increases with decreasing light intensity. On these grounds there appears therefore to be no doubt that the photochemical action between hydrogen peroxide and bromine is a chain reaction.

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(4) Griffith, McKeown and Winn, *Trans. Faraday Soc.*, **29**, 369 (1933).

(5) Goodeve and Nagai, *ibid.*, **27**, 508 (1931).

Results analogous to the above were also obtained by a method similar to that used by Livingston and Schoeld. A photostationary state (denoted by suffix l) was attained from a given pseudo-stationary state in the dark (suffix d) by illumination with monochromatic light of constant intensity. Both $[\Sigma Br_2]_d$ and $[\Sigma Br]_l$ were measured photometrically. On the basis of the Bray–Livingston mechanism for the thermal reaction, it can easily be shown, from the condition that the rate of formation of bromine equals its rate of disappearance both for the thermal and for the photostationary state, that the purely photochemical reaction of hydrogen peroxide and bromine is given by

$$\left\{-\frac{d[\Sigma Br_2]}{dt}\right\}_{\text{phot.}} = \frac{1}{2}k_{\text{uni.}}[H_2O_2]\left\{\frac{[H^+]_l[Br^-]_l}{[H^+]_d[Br^-]_d} - \frac{[H^+]_d[Br^-]_d[\Sigma Br_2]_l\{K_3 + [Br^-]_d\}}{[H^+]_l[Br^-]_l[\Sigma Br_2]_d\{K_3 + [Br^-]_l\}}\right\} \quad (1)$$

where K_3 is the equilibrium constant of tribromide formation. From a knowledge of the energy absorbed in the photo-stationary state the quantum yield can therefore be calculated. Table III gives the results of a few experiments of this type.

TABLE III

Temp. = 17°; λ = 436 mμ

$[\Sigma Br_2]_d$	$[\Sigma Br_2]_l$	Quanta absorbed per minute	Molecules of Br_2 disappearing per minute	γ
$[H_2O_2]$ = 0.167; $[HBr]_{\text{init.}}$ = 0.149; $k_{\text{uni.}} = 2.9 \times 10^{-4}$; 2-cm. cell				
0.000715	0.000088	5.41×10^{15}	4.33×10^{16}	8
.000715	.000231	2.81×10^{15}	3.36×10^{16}	12
$[H_2O_2]$ = 0.19; $[HBr]_{\text{init.}}$ = 0.1071; $[\Sigma Br_2]_{\text{init.}} = 2 \times 10^{-4}$; $k_{\text{uni.}} = 1.53 \times 10^{-4}$; 10 cm. cell				
0.0001194	0.0000179	4.59×10^{15}	1.18×10^{17}	26
.0001194	.0000414	2.25×10^{15}	0.91×10^{17}	40

It will be remarked that at the bromine concentrations and light intensities employed, the photostationary concentration of bromine has been reduced as much as eight-fold below the thermal value. This is in marked contrast with the much smaller relative changes in bromine concentration effected by Livingston and Schoeld, these authors using higher concentrations of bromine and green light which is less strongly absorbed than blue. However, the much smaller quantum yields recorded by them are not wholly to be ascribed to these differences. Our method of calculating the photochemical action at the photostationary state is quite different from that used by Livingston and Schoeld, who write

$$\{-d[\Sigma Br_2]/dt\}_{\text{phot.}} = (k_l - k_d)[H_2O_2] \quad (2)$$

where k_l and k_d are the (measured) unimolecular constants of decomposition of hydrogen peroxide in the light and dark, respectively. There appears, however, to be no theoretical justification for this relation even as an approximation, and indeed a closer scrutiny of their data shows that equation (2) must give far too low an estimate of the photochemical action. Thus, in their experiment 2 where $[\Sigma Br_2]$ has been reduced by the light from 0.0008 to 0.0005, that is, by 38%, it is obvious that approximately this same fraction of that reaction which uses up bromine in the thermal stationary state must now in the light be replaced by photochemical action. The reaction forming bromine in the dark is given by $^1/_2k_d[H_2O_2]$, hence the photochemical action is, at least as regards order of magnitude, about 19% of $k_d.[H_2O_2]$ and not 2% as taken by Livingston and Schoeld. Recalculation of their data for experiments 2, 4, 7, 10, 13 and 16 on the basis of equation (1) leads to γ = 5.1, 1.9, 1.8, 1.8, 2.4 and 0.46, respectively, in place of the recorded values 0.68, 0.34, 0.48, 0.26, 0.70 and 0.34. There seems little doubt therefore that, even with green light as used by Livingston and Schoeld, quantum yields greater than unity can be obtained, especially for low values of the energy absorbed.

The evidence presented above shows that under both thermal and photochemical conditions the kinetics of H_2O_2–HBr–Br_2 mixtures are likely to be of complex character. Photochemically, chain reactions must occur involving Br atoms and probably radicals such as HO_2 and OH. Under thermal conditions, while doubtless the excellent work of Bray and his co-workers has elucidated the main outlines of the kinetics, additional processes must be assumed to occur in order to explain the absence of a true stationary state. It seems likely that it is the reaction between hydrogen peroxide and bromine which—thermally as well as photochemically—is of complex nature. We do not wish, however, to discuss the mechanism further at present, as we are continuing our study of these reactions and hope to be able to publish a more detailed report in the near future.

Summary

1. Data are presented to show that for H_2O_2–HBr–Br_2 mixtures in aqueous solution, the "stationary state" characteristic of the Bray–Livingston mechanism for the thermal reaction does not in fact occur.

2. The photochemical reaction of hydrogen

peroxide and bromine under the influence of blue light gives quantum yields considerably in excess of unity. A recalculation of Livingston and Schoeld's data gives quantum yields greater than unity for green light also. A chain mechanism is indicated, contrary to the conclusion of Livingston and Schoeld.

LIVERPOOL, ENGLAND RECEIVED AUGUST 29, 1936

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Aqueous Solutions of Electrolytes as a Function of the Concentration. IV. Potassium Ferrocyanide

BY GRINNELL JONES AND ROBERT ELIOT STAUFFER

Introduction

This paper describes a continuation of the earlier researches[1] carried out in this Laboratory on the viscosity of solutions of electrolytes. An historical introduction and a discussion of the general objects of the investigation and the progress already made will be found in the earlier papers of this series and is therefore omitted here. In this paper the investigation is extended to a salt of a higher valence type and measurements are made at both 25 and 0° on the same solution in order to permit the study of the influence of temperature on the phenomena. Potassium ferrocyanide was selected as the most suitable uni-tetravalent salt since it is sufficiently soluble and stable and is only slightly hydrolyzed. Moreover, measurements on viscosity were needed for use in the interpretation of data on the conductance of this salt which were being obtained in this Laboratory (see the following paper).

Experimental

The apparatus and experimental procedure was the same as that described in the earlier papers with some modifications and improvements in detail. The most important innovation was the construction of an ice thermostat permitting the viscometer to be placed in succession in the 25 and 0° thermostats so that measurements could be made in succession on the same solution.

The ice thermostat consisted of a tank of about 180-liter capacity firmly supported on a three-point support of Monel metal and surrounded on all sides except the top with diatomaceous earth at least 8 cm. thick. The top had insulating covers built in sections permitting temporary removal in parts when necessary to insert the viscometers or to add fresh ice. The tank had small double windows of plate glass in front and rear to permit observation and operation of the optical system necessary for the automatic timing described in the earlier papers. The thermostat when in use was filled with a well-stirred mixture of ice and water. Wire screens of 14-mesh were arranged as near to the viscometer as possible to protect the fragile instrument from fracture by the moving ice and also to keep open narrow paths for the beam of light needed for operation of the automatic timing system and for inspection of the upper bulb of the viscometer. Water was kept circulating vigorously through the ice and around the viscometer by three motor-driven stirrers. A very good thermometer having an open scale 6 cm. long per degree was mounted totally immersed near the viscometer and read through the window to thousandths of a degree by a telescope. The readings of the thermometer and the consistency of the viscometric data prove that our thermostat can maintain a temperature safely within 0.003 of 0°. It requires about 50 pounds (25 kg.) of ice per day in hot summer weather.

Our old instrument has an inconveniently long period at 0° and therefore a new viscometer of vitreous silica was constructed with a slightly wider capillary (0.052 cm. diameter and 17.9 cm. long) and therefore a shorter period (428.7 sec. for water at 25° and 862.9 sec. for water at 0°). The ice thermostat had its own optical system, photoelectric cell and amplifiers but the same chronograph and clocks served both thermostats. Three different viscometers could be used interchangeably in either thermostat and measurements with different instruments could be going on simultaneously in both thermostats if desired.

The best potassium ferrocyanide available by purchase was twice recrystallized by dissolving in water at 60°, cooling and adding ethyl alcohol, followed by centrifugal drainage. It was dried by heating to 90° in nitrogen at low pressure for several hours. The solutions were made up by weight.

The experimental data at 25 and at 0° are recorded in Tables I and II, respectively. The values for the density given in parentheses were not actually measured but were computed by the formula given below. The third column gives the relative viscosity before applying the kinetic energy correction, which is shown in column 4. The relative viscosity after applying the kinetic energy correction is given in column 5. In some cases a small correction was necessary to bring the data to a round concentration. The results after applying this correction are shown in the last column.

Interpretation of the Data.—The experimental data given below on the density of potassium

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[1] Grinnell Jones and M. Dole, THIS JOURNAL, **51**, 2950 (1929); Grinnell Jones and S. K. Talley, *ibid.*, **55**, 624, 4124 (1933); *Physics*, **4**, 215 (1933); Grinnell Jones and H. J. Fornwalt, THIS JOURNAL, **57**, 2041 (1935); **58**, 619 (1936).

TABLE I

RELATIVE VISCOSITY AND DENSITY OF POTASSIUM FERROCYANIDE SOLUTIONS IN WATER AT 25°

Concn., c	Density, d^{25}_4	$d_c t_c/d_0 t_0$	K. E.	Relative η obsd.	η at round concn.
0.000200	(0.99712)	1.00053	0	1.00053	1.00053
		1.00053	0	1.00053	1.00053
.000350	(.99716)	1.00082	+1	1.00083	1.00083
.000349	(.99716)	1.00070	1	1.00071	1.00071
		1.00081	1	1.00082	1.00082
.000500	(.99720)	1.00102	1	1.00103	1.00103
		1.00102	1	1.00103	1.00103
.000749	(.99726)	1.00133	2	1.00135	1.00135
		1.00140	2	1.00142	1.00142
.000997	.997376	1.00161	2	1.00163	1.00163
		1.00161	2	1.00163	1.00163
.001995	.997562	1.00238	3	1.00241	1.00241
		1.00243	3	1.00246	1.00246
.004991	.998317	1.00455	4	1.00459	1.00459
.004963	.998304	1.00442	4	1.00446	1.00447
		1.00442	4	1.00446	1.00447
.009938	.999556	1.00736	6	1.00742	1.00744
		1.00736	6	1.00742	1.00744
.019768	1.001979	1.01231	10	1.01241	1.01252
.019975	1.002079	1.01249	10	1.01259	1.01259
.049935	1.009326	1.02615	18	1.02633	1.02634
.049916	1.009308	1.02610	18	1.02628	1.02630
.099212	1.021107	1.04778	30	1.04808	1.04839
.099822	1.021248	1.04804	30	1.04834	1.04840
.199543	1.044628	1.09339	58	1.09397	1.09412
.199588	1.044675	1.09353	58	1.09411	1.09416
.198806	1.044321	1.09272	58	1.09330	1.09414
		1.09272	58	1.09330	1.09414
.499582	1.112550	1.26143	178	1.26321	1.26350
		1.26138	178	1.26315	1.26344

TABLE II

RELATIVE VISCOSITY AND DENSITY OF POTASSIUM FERROCYANIDE SOLUTIONS AT 0°

Concn., c	Density, d^{0}_4	$d_c t_c/d_0 t_0$	K. E.	Relative η obsd.	η at round concn.
0.000200	(0.99992)	1.00054	0	1.00054	1.00054
		1.00052	0	1.00052	1.00052
.000351	(.99996)	1.00061	0	1.00061	1.00061
.000350	(.99996)	1.00056	0	1.00056	1.00056
		1.00062	0	1.00062	1.00062
.000502	(1.00000)	1.00091	0	1.00091	1.00091
		1.00089	0	1.00089	1.00089
.000751	(1.00007)	1.00098	0	1.00098	1.00098
.000751	(1.00007)	1.00092	0	1.00092	1.00092
.001000	1.000200	1.00120	0	1.00120	1.00120
		1.00120	0	1.00120	1.00120
.002002	1.000405	1.00165	0	1.00165	1.00165
		1.00163	0	1.00163	1.00163
.004978	1.001225	1.00260	0	1.00260	1.00260
		1.00245	0	1.00245	1.00245
.005005	1.001199	1.00255	0	1.00255	1.00255
.009968	1.002520	1.00374	0	1.00374	1.00375
		1.00376	0	1.00376	1.00377
.019830	1.005108	1.00554	0	1.00554	1.00557
.020037	1.005165	1.00550	0	1.00550	1.00550
.050110	1.012846	1.01018	−1	1.01017	1.01016
.050091	1.012846	1.01006	−1	1.01005	1.01004
.099610	1.025199	1.01800	−2	1.01798	1.01801
.100224	1.025353	1.01807	−2	1.01805	1.01804
.200532	1.049802	1.03918	−4	1.03914	1.03902
.200578	1.049856	1.03921	−4	1.03917	1.03904

ferrocyanide solutions may be expressed with an average deviation of 0.003% by the equations

$$d^{25}_4 = 0.99707 + 0.25074c - 0.02776c^{3/2}$$
$$d^{0}_4 = .99987 + .26836c - .04313c^{3/2}$$

The agreement with the Root equation is not quite so good as has been found for other salts of simpler valence type in previous work in this Laboratory. The deviations although small are apparently systematic in this case and greater than the experimental error.

Column 4 of Tables III and IV shows that the "Grüneisen Effect" is more pronounced than for the salts of lower valence type which have been studied in this Laboratory.

The results at 25° can be expressed in terms of relative fluidity by the equation having the form proposed by Jones and Dole, namely

$$\varphi = 1/\eta = 1 - 0.03995\sqrt{c} - 0.33518c$$

up to 0.1 molar (or 0.4 N) with an average deviation of only 0.004% as is shown in column 5 of Table III. The extended form of the equation $\varphi = 1/\eta = 1 - 0.03995\sqrt{c} - 0.32859c - 0.0639c^2$ fits the data over the entire range up to and including 0.5 molar (or 2 N) with an average deviation of only 0.006% as is shown in column 6

TABLE III

RELATIVE VISCOSITY AND RELATIVE FLUIDITY OF POTASSIUM FERROCYANIDE SOLUTIONS AT 25°

				Jones and Dole equation	
c	η	φ	$\frac{\eta - 1}{c}$	Simple $\Delta\varphi \times 10^5$	Extended $\Delta\varphi \times 10^5$
0.00020	1.00053	0.99947	2.65	+ 10	+10
.00035	1.00079	.99921	2.26	+ 7	+ 7
.00050	1.00103	.99897	2.06	+ 3	+ 2
.00075	1.00138	.99862	1.84	− 3	− 4
.001	1.00163	.99837	1.63	− 3	− 1
.002	1.00244	.99757	1.22	+ 3	+ 1
.005	1.00451	.99551	0.90	+ 1	− 2
.01	1.00744	.99261	.744	− 4	−10
.02	1.01255	.98761	.628	− 4	−14
.05	1.02632	.97435	.526	+ 4	−13
.1	1.04839	.95384	.484	− 1	− 3
.2	1.09414	.91396	.471	− 114	+10
.5	1.26347	.79147	.527	−1270	− 1

Jones and Dole equations	Range of validity	Average % deviation
$\varphi = 1 - 0.03995\sqrt{c} - 0.33518c$	0.1	0.004
$\varphi = 1 - .03995\sqrt{c} - .32859c - 0.0639c^2$	.5	.006
$\eta = 1 + .03695\sqrt{c} + .3660c$	.1	.008
$\eta = 1 + .03695\sqrt{c} + .33538c + 0.27832c^2$	.5	.023

of Table III. If the results are expressed in terms of relative viscosity instead of relative fluidity the agreement is not quite so good. The equation $\eta = 1 + 0.03695\sqrt{c} + 0.3660c$ fits the data up to 0.1 molar with an average deviation of 0.008% and the equation $\eta = 1 + 0.03695\sqrt{c} + 0.33538c + 0.27832c^2$ fits the data up to 0.5 molar with an average deviation of 0.023%.

After our experimental work was completed Hood and Williams[2] published measurements of the viscosity of solutions of potassium ferrocyanide at 18 and 25°. Their results for the viscosity at 25° are slightly lower than ours. They state that their results at 25° are in agreement with the equation $\varphi = 1 - 0.0245\sqrt{c} - 0.3720c$.

Our results show that as usual the relative viscosity at 0° is lower than at 25°, the difference being mainly in the effect responsible for the linear term. At 0° both the simple and extended forms of the Jones and Dole equation seem to be equally good whether expressed in terms of viscosity or of fluidity. At 0° the simple form only holds up to 0.02 molar, whereas at 25° the simple form holds up to 0.1 molar. These equations are given below Table IV.

TABLE IV

RELATIVE VISCOSITY AND RELATIVE FLUIDITY OF POTASSIUM FERROCYANIDE SOLUTIONS AT 0°

c	η	φ	$\frac{\eta - 1}{c}$	Jones and Dole equation Simple $\Delta\varphi \times 10^5$	Jones and Dole equation Extended $\Delta\varphi \times 10^5$
0.0002	1.00053	0.99947	2.6	− 3	− 3
.00035	1.00060	.99940	1.7	+ 6	+ 6
.0005	1.00090	.99910	1.8	− 10	−11
.00075	1.00096	.99904	1.28	+ 2	+ 2
.001	1.00120	.99880	1.20	− 7	− 7
.002	1.00164	.99836	0.82	− 2	− 3
.005	1.00255	.99746	.508	+ 7	+ 6
.01	1.00376	.99625	.375	+ 2	+ 2
.02	1.00554	.99449	.275	− 2	+ 7
.05	1.01010	.99000	.202	− 82	+ 5
.1	1.01803	.98229	.180	− 414	− 3
.2	1.03903	.96244	.195	−1651	+ 1

Jones and Dole equations	Range of validity	Average % deviation
$\varphi = 1 - 0.03502\sqrt{c} - 0.02679c$	0.02	0.005
$\varphi = 1 - .03502\sqrt{c} - .02266c - 0.4340c^2$	.2	.005
$\eta = 1 + .03508\sqrt{c} + .02768c$	.02	.005
$\eta = 1 + .03508\sqrt{c} + .02123c + 0.4778c^2$	.2	.004

An attempt was made to fit an equation of the form suggested by Onsager and Fuoss[3] to the data without success. In previous papers of this series it has been shown that the Onsager–Fuoss equation is useful for solutions of several salts in methanol but that it failed for aqueous solutions of potassium permanganate and of cesium iodide.

It now remains to compare the values of the coefficient of the square root term (A) determined by experiment with that computed by the Falkenhagen and Vernon equation.[4] Although we can probably estimate the equivalent conductance of the ferrocyanide ion at infinite dilution more accurately than that of any other tetravalent ion, nevertheless the difficulty of extrapolating the conductance of a 1–4 salt is so great that this equivalent conductance is not known as well as for ions of lower valence (see the following paper). If the equivalent conductance of the ferrocyanide ion at 25° is assumed to be 117, the value of A computed by Falkenhagen and Vernon's equation is 0.033. If the equivalent conductance is assumed to be 122 (which is probably too high), then the computed value comes out to be 0.032. The experimentally determined value is 0.037. At 0° the computed value of A (based on the equivalent conductance of the ferrocyanide ion of 64) is 0.030, whereas the experimental value is 0.035. Although the agreement is not perfect, nevertheless the experimental results do harmonize with the prediction of the theory that increasing the valence of the ions involved should increase greatly the value of A and that raising the temperature should cause a moderate increase in A.

Summary

1. The absolute density and relative viscosity of many solutions of potassium ferrocyanide have been determined at 0 and 25°, covering a range of concentration from extreme dilution nearly to saturation.

2. The "Grüneisen Effect" is especially pronounced in this salt of high valence type.

3. The Jones and Dole equation is found to fit our data.

4. The results confirm approximately the equation of Falkenhagen for the computation of the influence of interionic attraction on the viscosity.

CAMBRIDGE, MASS. RECEIVED AUGUST 12, 1936

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(2) G. R. Hood and J. C. Williams, *Ohio J. Sci.*, **35**, 415 (1935).

(3) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(4) H. Falkenhagen and E. L. Vernon, *Physik. Z.*, **33**, 140 (1932).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Conductance of Aqueous Solutions as a Function of the Concentration. II. Potassium Ferrocyanide

BY GRINNELL JONES AND FREDERIC C. JELEN

Introduction

The conductance of solutions is greatly influenced by the valence type of salt and therefore data on salts of a high valence type may serve as a severe and useful test of the validity and generality of the various equations which have been proposed for the conductance as a function of the concentration. For an historical review of the more important of these equations and the background of the problem the reader is referred to a recent paper by Jones and Bickford.[1] Potassium ferrocyanide seemed to be the most suitable salt of the 1–4 valence type because it is only very slightly hydrolyzed and is sufficiently soluble and stable and was therefore selected for this investigation.

Experimental

Potassium ferrocyanide was prepared for this investigation by two different methods. The best material available by purchase was twice recrystallized from conductivity water by dissolving at 60°, filtering through a sintered glass filter and cooling to 0°, followed by centrifugal drainage. Since there was a slight indication of instability of these solutions at 60°, we also prepared other samples by dissolving the salt in cold water and precipitating it by adding redistilled ethyl alcohol followed by centrifugal drainage. The entire process was then repeated. This method gave small crystals which were almost white in color. No difference in the conductivity could be detected between the salt prepared by the two methods of purification.

The salt was then placed in a platinum boat in a tube and heated at 90° in a stream of dry nitrogen for about two hours. The salt was cooled in nitrogen and the nitrogen replaced by dry air. The boat and salt was then bottled without exposure to the moist air of the laboratory in a Richards bottling apparatus. Repeated experiments demonstrated that a repetition of the heating and drying process did not change the weight by as much as 0.01%. The preparation of the solutions and the measurement of their conductivity at 25 and 0° were so similar to the procedure used by Jones and Bickford that no further description is needed. The cell constants were determined by the use of the values for the conductance of standard potassium chloride solutions determined by Jones and Bradshaw.[2] The density of each solution was determined by means of a large (65 cc.) pycnometer at both 25 and 0°. At each concentration at least two but sometimes three or four independent solutions were prepared. The actual concentrations were commonly slightly different from the round concentrations desired. Slight corrections were applied to bring the results for the conductivity to the round concentration. These corrections were rarely more than 0.01% and in only one case more than 0.05%. The detailed data on each solution and the corrections to round concentration are omitted to save space in printing.

No corrections have been applied for hydrolysis because tests made by indicators and a quinhydrone electrode on a 0.01 molar solution gave a pH of 7.5, from which it may be inferred that the effect of hydrolysis would be negligible. The results are shown in Tables I and II, in which c is the concentration in moles per liter and Λ is the molar conductance.

Interpretation of the Data

Figure 1 is a plot of the molar conductance against the square root of the concentration. The experimental data at 25° are represented by the centers of the circles. This gives a curve which is similar to the curves given by salts of lower valence types except that the slope and curvature in the dilute end are greater than has been found for salts of lower valence type. The curve is nearly straight at the dilute end but there is evidently some curvature even below 0.001 molar. Putting a straight line through the four lowest concentrations gives the equation $\Lambda = 741.9 - 4637\sqrt{c}$ (line K in Fig. 1). This method of extrapolation must give a value for the limiting conductance and limiting slope at infinite dilution which is too low unless there is a change in curvature at extreme dilution for which there is no experimental evidence or theoretical warrant. This equation, which has the form suggested by Kohlrausch, fails completely above 0.001 molar as is evident from the figure.

The coefficients of the Jones and Dole equation were determined by the method of least squares using all the experimental points including c = 0.5 molar or 2 N, giving the equation

$$\Lambda = 785.16 - \frac{9171.38\sqrt{c}}{1 + 17.106\sqrt{c}} - 12.84c.$$

The curve marked J in Fig. 1 is the plot of this equation and as will be seen it agrees with the experimental data so closely that the deviations are not apparent on the scale that can be printed.

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[1] Grinnell Jones and C. F. Bickford, THIS JOURNAL, **56**, 602 (1934).

[2] Grinnell Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

TABLE I

CONDUCTANCE OF POTASSIUM FERROCYANIDE SOLUTIONS AT 25°

1 c	2 Λ	3 J + D $\Delta\Lambda$	4 η	5 $\Lambda\eta$	6 J + D $\Delta\Lambda\eta$	7 Onsager Λ_0'	8 O + F $\Delta\Lambda$
0.00025	668.94	−2.08	1.00055	669.31	−2.07	724.45	+15.76
.00036	653.52	−0.26	1.00080	654.04	−0.33	719.95	−10.53
.0005	638.04	+1.22	1.00103	638.70	+1.08	716.14	+ 5.83
.00075	615.11	+1.00	1.00138	615.96	+0.81	710.40	− 1.83
.001	598.33	+1.40	1.00163	599.31	+1.15	708.21	− 6.25
.002	554.18	+1.43	1.00244	555.53	+1.11	709.70	+15.04
.005	491.29	−0.30	1.00451	493.52	−0.40	742.39	−18.10
.01	445.28	−1.40	1.00744	448.59	−1.18	817.10	−10.67
.02	403.72	−1.84	1.01255	408.79	−1.25	981	+ 2.56
.0475	360.45	−1.35	1.02525	369.55	−0.57	1507	+18.53
.05	(358.14)						
.1	332.01	+0.63	1.04839	348.08	+0.87		+12.09
.2	310.90	+2.48	1.09414	340.17	+1.41		−17.89
.5	282.63	−0.90	1.26347	357.09	−0.60		+ 2.63

Equations: Jones and Dole, column 3; $\Lambda = 785.16 - \dfrac{9171.38\sqrt{c}}{1 + 17.106\sqrt{c}} - 12.84c$

Jones and Dole, column 5; $\Lambda\eta = 783.75 - \dfrac{9000.35\sqrt{c}}{1 + 16.8424\sqrt{c}} + 133.9c$

Onsager and Fuoss, column 8; $\Lambda = 709.96 - 3954.98\sqrt{c} + 3063.41c - 5542.93c\log c$

TABLE II

CONDUCTANCE OF POTASSIUM FERROCYANIDE SOLUTIONS AT 0°

1 c	2 Λ	3 $\Delta\Lambda$ J + D	4 η	5 $\Lambda\eta$	6 $\Delta\Lambda\eta$ J + D	7 $\dfrac{\Lambda^{25}}{\Lambda^0}$
0.001	321.00	−0.25	1.00120	321.39	−0.19	1.8640
.002	298.01	+ .38	1.00164	298.50	+ .32	1.8596
.005	264.83	+ .10	1.00255	265.50	.00	1.8551
.01	240.34	− .17	1.00376	241.24	− .16	1.8527
.02	218.23	− .18	1.00554	219.44	− .07	1.8500
.0477	195.26	− .08	1.00981	197.17	+ .03	
.05	(194.19)					1.8443
.1	181.08	+ .33	1.01803	184.34	+ .22	1.8355
.2	171.96	− .13	1.03903	178.67	− .05	1.8080

Equations: Jones and Dole

$$\Lambda = 420.40 - \frac{4768.73\sqrt{c}}{1 + 16.4586\sqrt{c}} + 33.87c$$

Jones and Dole; column 6,

$$\Lambda\eta = 418.79 - \frac{4635.89\sqrt{c}}{1 + 16.0335\sqrt{c}} + 68.40c$$

Nevertheless, an examination of column 3 in Table I indicates that there are deviations which are probably greater than the experimental error. These deviations are substantially greater than were found for lanthanum chloride, and barium chloride and potassium bromide. This equation is clearly the best formula known to us for the more concentrated solutions of salts of all valence types but there are indications that it gives too great a curvature in the dilute end and too high a value of the limiting conductance and limiting slope.

Since the concentrated solutions of this salt are exceptionally viscous, the effect of applying a viscosity correction is of special interest. The viscosities of these solutions, η, have been determined for this and other purposes (see the preceding paper) as is shown in column 4 of Table I and the values of $\Lambda\eta$ are shown in column 5 and are plotted as the points within the triangle in Fig. 1. The Jones and Dole equation was then fitted to these values, giving

$$\Lambda\eta = 783.75 - \frac{9000.35\sqrt{c}}{1 + 16.8424\sqrt{c}} + 133.9c$$

The upper curve in Fig. 1 is the plot of this equation and, as will be seen, the deviations are so slight that they are not apparent on the scale that can be printed. Column 6 in Table I shows the computed deviations. The application of the viscosity correction substantially reduces the deviations in the more concentrated solutions but has little effect in the dilute range where the viscosity correction is small. It should be noticed that the curve depicting $\Lambda\eta$ has a flat minimum at about 0.2 molar.

It is next of interest to apply the Onsager–Shedlovsky method of extrapolation to the data. If the Onsager equation is transformed by using molar concentrations (gram molecules per liter) and molar conductances, and by introducing the appropriate numerical values for water at 25°, namely, $\eta = 0.008949$ and $D = 78.57$ and $T = 298.1$, the Onsager equation becomes

$$\Lambda = \Lambda_0 - [0.27446 w \Lambda_0 + 21.138 z_1 z_2 (z_1 + z_2)] \sqrt{z_1 z_2 (z_1 + z_2) c}$$

where $w = 2qz_1z_2/(1 + \sqrt{q})$

and $q = \dfrac{z_1 z_2 \Lambda_0}{(z_1 + z_2)\ \{\Lambda_0 + (z_2^2 - z_2)\Lambda_1^0 + (z_1^2 - z_1)\Lambda_2^0\}}$

for potassium ferrocyanide we substitute $z_1 = 1$ and $z_2 = 4$ giving $\Lambda = \Lambda_0 - (1.22742\ w\ \Lambda_0 + 1890.64)\sqrt{c}$

$$w = \frac{8q}{1 + \sqrt{q}}$$

$$q = \frac{4\Lambda_0}{5(\Lambda_0 + 12\Lambda_K^0)}$$

It is evident that the limiting slope cannot be computed from these equations without first assuming that the values of the limiting conductances of the two ions are known because the value of w depends on Λ_0 and Λ_K^0 in the complicated manner indicated by the equations. However, the value of w is rather insensitive to the value of Λ_0 so that we may proceed by a method of successive approximations and obtain a result if the equations are really valid.

If we take as a first approximation the value of $\Lambda_0 = 741.9$ obtained by putting a straight line through the four lowest points and assume that the limiting conductance of the potassium ion is 73.5 then $q = 0.36549$ and $w = 1.82226$ and the Onsager equation becomes $\Lambda = \Lambda_0 - (2.23668\ \Lambda_0 + 1890.64)\sqrt{c}$ or $\Lambda_0 = (\Lambda + 1890.64\sqrt{c})/(1 - 2.23668\sqrt{c})$.

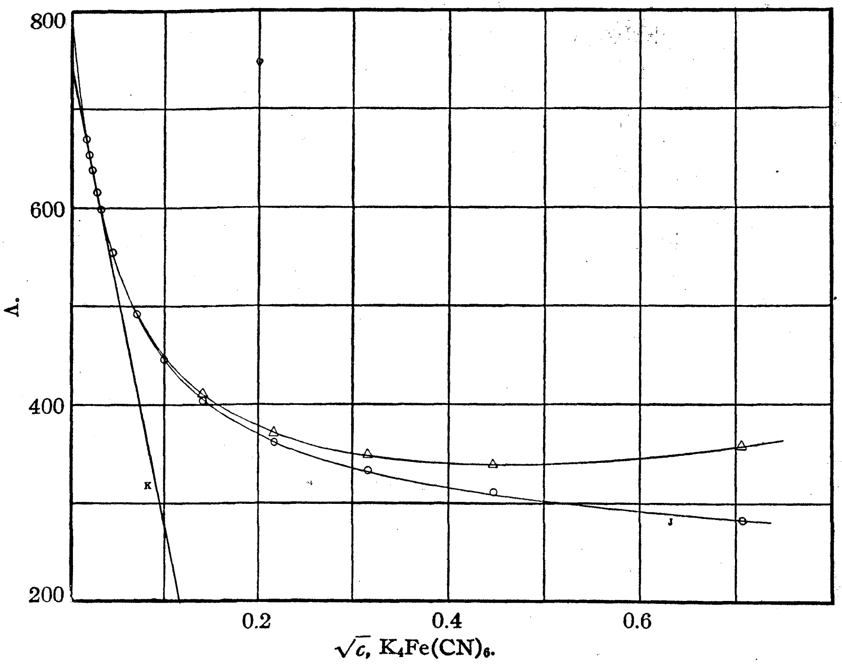

Fig. 1.

If the Onsager equation were valid over any range accessible to experimentation, the values of Λ_0 computed from this equation should be a constant over the range of validity of the equation. The values of Λ_0 computed by this equation are given in column 7 of Table I. As will be evident from the table, the values of Λ_0 are far from being constant. Attempts were made to obtain constancy by varying the value of Λ_0 assumed in the computation of w but no appreciable improvement could be obtained in this manner. This proves that Onsager's equation is not valid for potassium ferrocyanide even up to 0.001 molar.

It has been demonstrated previously that the values of Λ_0 computed by this method are not constant for salts of any valence type. Shedlovsky[3] found for many uni-univalent salts that if the values of Λ_0 computed by the Onsager formula were plotted against c a straight line was obtained up to about 0.1 molar and he proposed to use this method to obtain Λ_0 by extrapolation and also suggested a modified Onsager equation $\Lambda_0 = \dfrac{\Lambda + \beta\sqrt{c}}{1 - \alpha c} + Bc$ which fitted the data up to about 0.1 N. In this Shedlovsky equation definite numerical values can be assigned to α and β from the Onsager theory and only Λ_0 and B are arbitrary parameters selected to fit the data for each salt. Some uni-univalent salts did not obey this equation. Shedlovsky suggests that this exceptional behavior is due to association.

Jones and Bickford applied Shedlovsky's method to lanthanum chloride, obtaining a curve which was approximately straight between 0.0025 and 0.01 molar but had a definite positive curvature in the more dilute range and a negative curvature between 0.01 and 0.1 molar. At the dilute end the plot appeared to be curving so as to enter the axis horizontally, which is the behavior to be expected if Onsager's law is valid as a limiting law. However, Shedlovsky's method

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[3] T. Shedlovsky, THIS JOURNAL, **54**, 1405, 1411 (1932).

of straight line extrapolation could not be applied to this tri-univalent salt.

Shortly afterward Shedlovsky and Brown[4] reported measurements on the chlorides of four divalent metals which when plotted gave a similar curvature at the dilute end. They, therefore, abandoned extrapolation along a straight line and recommended extrapolation along a curve and thus in effect for divalent salts abandoned the Shedlovsky equation, although they are not clear as to whether or not this curve is assumed to enter the axis horizontally. They propose a modification of the original Shedlovsky equation by the addition of two more terms each containing an arbitrary parameter giving the equation

$$\Lambda_0 = \frac{\Lambda + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} + Bc + Dc \log c - Ec^2$$

This equation, of course, can be made to fit the data better than the original Shedlovsky equation because it contains two more parameters selected to fit the data for their four divalent salts. But they do not give a detailed comparison of the data for the four divalent salts with the results computed by their equation.

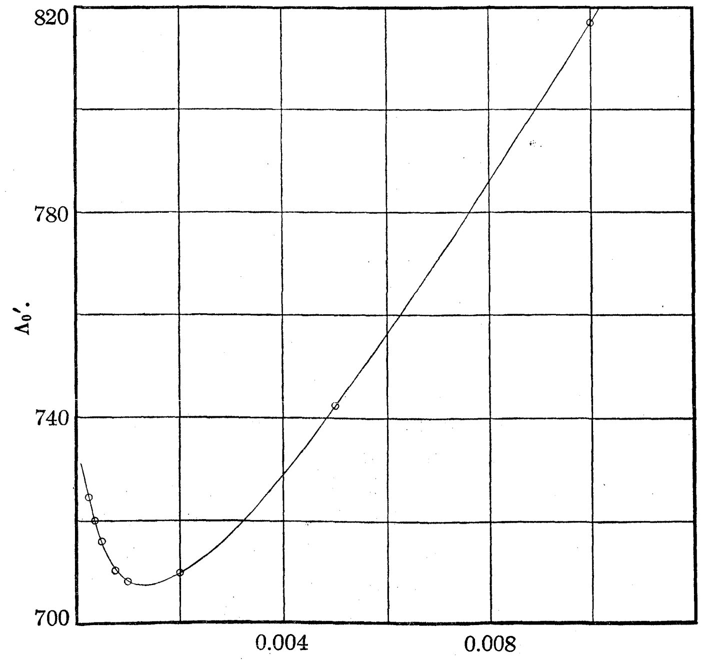

Fig. 2.

Shedlovsky, Brown and MacInnes[5] have shown that this equation may be applied successfully to potassium chloride up to 0.12 *N*.

The results of an attempt to apply the Shedlovsky method of extrapolation to obtain Λ_0 by plotting $\Lambda_0' = \frac{\Lambda + \beta\sqrt{c}}{1 - \alpha\sqrt{c}}$ against c with our data on potassium ferrocyanide are shown in Fig. 2. In this case the plot has a very definite minimum and the portion of the curve which must be extended for extrapolation has a pronounced curvature. Any attempt to extrapolate such a curve depends too much on a guess as to the curvature to have much value. The influence of making other assumptions as to the value of Λ_0 in the computation of w and hence of Λ_0' was tried but there was no change in the character of the curves. These curves are so close together that only one can be shown without confusion on the scale which can be printed and, therefore, only one curve is shown in Fig. 2.

Onsager and Fuoss[6] have suggested a generalized equation for the properties of solutions of the form $F(c) = F(o) - A\sqrt{c} + Bc - Dc \log c + \ldots$. It seemed worthwhile, therefore, to attempt to apply this generalized equation to conductance in the form $\Lambda = \Lambda_0 - A\sqrt{c} + Bc - Dc \log c$. Although in principle the value of A might be computed theoretically if the value of Λ_0 were known, yet since Λ_0 is not known and the results depend so greatly on the value of A, it seemed best to treat A as a parameter and evaluate it from the data by the method of least squares. The result is $\Lambda = 709.96 - 3954.98\sqrt{c} + 3063.41\,c - 5542.92\,c \log c$. The values computed by this equation and the deviations between the experimental and computed results are shown in column 8 of Table I. As will be seen, the results are disappointing. The average deviation is more than eight times as great as for the Jones and Dole equation, although both are four parameter equations. The value of Λ_0 is substantially below that given by Kohlrausch's method of extrapolation (741.9), although there is strong reason for believing that the Kohlrausch method gives too low a result. Moreover, the equation gives a curve having a minimum at about 0.1 molar and a maximum at about 0.25 molar whereas

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[4] T. Shedlovsky and A. S. Brown, THIS JOURNAL, **56**, 1066 (1934).

[5] T. Shedlovsky, A. S. Brown and D. A. MacInnes, *Trans. Am. Electrochem. Soc.*, 165 (1934).

[6] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

the experimental data show no such minimum and maximum in this or other cases.

The data for 0° are given in Table II. These data cover a smaller range of concentration than for 25°, and therefore give a less severe test of the equations. The solubility is not great enough at 0° to make it possible to work with 0.5 molar solutions and the data below 0.001 molar were not obtained. These data are probably not quite so reliable as the data at 25°, because it is harder to control the temperature inside an oil bath at 0 than at 25°. The Kohlrausch method of extrapolating to infinite dilution using the data from 0.001 to 0.01 molar gives $\Lambda_0 = 353$ but this figure is undoubtedly much too low. The Jones and Dole equation for this case is $\Lambda = 420.40 - 4768.7\sqrt{c}/(1 + 16.459\sqrt{c}) + 33.87c$. The differences between the observed results and the results computed by this equation are given in column 3 of Table II. The deviations are much less than were found at 25°, but this is probably due to the fact that the data cover a smaller range of concentration and are therefore easier to fit to an equation. The deviations are probably somewhat greater than the experimental error.

By the use of the values of the relative viscosity given in the preceding paper we have computed the values of $\Lambda\eta$ given in column 5 of Table II. With the viscosity correction applied the Jones and Dole equation becomes $\Lambda\eta = 418.79 - 4635.89\sqrt{c}/(1 + 16.0335\sqrt{c}) + 68.40c$. As will be seen by a comparison of columns 3 and 6 the deviations are substantially reduced by the application of the viscosity correction especially in the more concentrated solutions.

The last column in Table II gives the ratio between the conductance at 25 and at 0°. As will be seen the temperature coefficient of the conductance decreases with increasing concentration.

Summary

1. The conductance of potassium ferrocyanide solutions has been determined at 25 and at 0° from great dilution up to nearly saturation.

2. The data have been used to test various equations which have been proposed to express the conductance as a function of the concentration.

CAMBRIDGE, MASS. RECEIVED AUGUST 12, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 375]

The Palladium–Hydrogen Equilibrium and New Palladium Hydrides[1]

BY LOUIS J. GILLESPIE AND LIONEL S. GALSTAUN

The early work of Troost and Hautefeuille, Hoitsema, Sieverts, Lambert and Gates and others was reviewed in the paper of Gillespie and Hall. It may be remembered that Troost and Hautefeuille[2] claimed the existence of Pd_2H on the basis of evidence just short of that demanded by the phase rule, which was about to be announced by Gibbs, and that this claim was usually disallowed after the paper of Hoitsema,[3] although Lambert and Gates[4] pointed out that their descending isotherms show "breaks" at approximately the same composition (about $Pd_{1.9}H$) at 75, 103 and 120°. Gillespie and Hall[5] worked with finely-divided palladium, allowed much time —often one to three days or longer—to elapse before recording pressures, and obtained for the first time a phase diagram for the system in obvious conformity with the phase rule. This diagram indicates the existence of Pd_2H capable of formation in definite proportions from about 80 to 180° or higher; at lower temperatures the phase contains a progressively greater excess of hydrogen.

In their first work at 0° they established the first break between the first rising isotherm and the relatively horizontal one as a sharp angle, which could be demonstrated reversibly at constant temperature. Large additions of hydrogen produced hysteresis effects. They discovered that if some hydrogen were withdrawn and the

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[1] Part of this article is taken from the thesis presented by L. S. Galstaun in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology. The work at 270, 280 and 285°, upon which the finding of new hydrides mainly rests, was done since presentation of the thesis.

[2] Troost and Hautefeuille, *Compt. rend.*, **78**, 686 (1874); *Ann. chim. phys.*, [5] **2**, 273 (1874).

[3] Hoitsema, *Z. physik. Chem.*, **17**, 25 (1895).

[4] Lambert and Gates, *Proc. Roy. Soc.* (London), **108A**, 456 (1925).

[5] Gillespie and Hall, THIS JOURNAL, **48**, 1207 (1926).

system heated for a short time to 360° and exposed again to 0°, the pressure returned to the same level as that of the first break. They were able by the use of this "heat treatment" to follow along a truly horizontal isotherm. Now the pressure at the first break was proved by the classical method, and the results of the heat treatment must be correct—so long at least as the isotherm remains horizontal—as they maintained in an extended discussion. This method was then used for other temperatures, and for the second rising isotherms.

Some writers have since felt misgivings because of this use of heat treatment, yet no one has tried unsuccessfully to reproduce the results. No theoretical objection to the heating has been presented, except that Gillespie and Hall pointed out that the results refer palladium that has recently been heated and that this must in any case be so, as heating *in vacuo* is a necessary preliminary to the experimentation. This being granted, it cannot be admitted further that there is any theoretical advantage in conducting the additions of hydrogen isothermally. A practical advantage is that of greater consistency of data at a given temperature.

Since the work of Brüning and Sieverts,[6] who established the existence of a critical solution temperature at about 300° and found that equilibrium is very quickly reached above this even in the case of wire, it is possible to understand why the heat treatment was beneficial in the case of large additions of hydrogen.[7] The heating to 360° must have brought about uniformity of composition throughout the mass. On cooling, the mass had to separate into two phases, but these phases could form equally well at all points in the mass, whereas a crust may form on direct isothermal addition. There is still of course a difficulty due to the necessary exchange of gas between solid and dead space, which would make the treatment nearly or quite useless for small additions.

Linde and Borelius[8] obtained very exact X-ray data that show at 100, 150 and 200° the presence of two mutually saturated solid solutions. The lattice constant of that richer in hydrogen is about the same at all three temperatures, and they suggested without further evidence that perhaps Gillespie and Hall were mistaken in supposing the richer phase to contain, at temperatures below 80°, an excess of hydrogen over the composition of Pd_2H. This appears impossible, however, as the proof of the excess seems to be perfect, according to the discussion above. Linde and Borelius found the lattice constant practically the same at the two higher temperatures for the hydrogen-weak phase. This is quite consistent with the original data plotted in the Fig. 3 of Gillespie and Hall (though not consistent with the broken line that interprets the compositions of this phase). This fact indicates the existence of Pd_8H, which will be discussed later in connection with new data.

Brüning and Sieverts[6] have studied the pressures, compositions and electrical resistance of palladium wire containing hydrogen. In their work at 210 to 310° the compositions were estimated from the resistances with the aid of extrapolated relations determined at lower temperatures. Thus no great accuracy can be claimed for the calculated compositions, particularly in some cases where the relations involved an angle whose magnitude must change with the degree of hysteresis (see their Fig. 9), since the hysteresis vanishes at the highest temperatures. Nevertheless they found with certainty that there is a cirtical solution temperature between 290 and 310°, estimated at about 300°.

In their work at 160, 180 and 200° they measured the compositions directly. Hysteresis was very marked when two solid phases were obviously present. They forebore to compare their results with those of Gillespie and Hall at the two lower temperatures on the grounds that the latter used finely divided palladium heated to 400° in a vacuum and did not carry out the measurements isothermally. But along the first rising isotherm there was no hysteresis; their results with wire should not differ from the results in this Laboratory. Figure 1 shows one of their two series at 180°, their points being joined with broken lines, and the final results of Gillespie and Hall being shown by a solid line. The agreement along the first rising isotherm is not bad; in the case of their other series at 180° it is better; at 160°, as also shown in Fig. 1, it is very good; and at 200° the agreement is equally good, when in this case the data presented below are used for comparison. Although Gillespie and Hall believed they reached the second rising isotherm, it is doubtful whether Brüning and Sieverts did so, except prob-

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(6) Brüning and Sieverts, *Z. physik. Chem.*, **163A**, 409 (1933).

(7) We cannot say it was really beneficial for small additions.

(8) Linde and Borelius, *Ann. Physik*, [4] **84,** 747 (1927).

ably at 160°. Only in this case is there a hint of agreement along the second rising isotherm, and here their break is estimated at the atomic ratio H:Pd = 0.49—nearly at Pd_2H. Figure 1 indicates very clearly that the experiments at 180° were not carried along with sufficient addition of hydrogen to convert the whole of the wire into the second solid phase. For, if from the point A hydrogen had been subtracted instead of added a false break at a ratio of 0.4 or less would probably have been obtained; whereas if from B hydrogen had been added again instead of withdrawn it appears entirely possible that another hysteresis loop might have been observed, followed by a break at a ratio greater than 0.49. Figure 1 shows that at 160° the rising and falling isotherms at the top of the figure nearly coincide, and therefore complete conversion, or nearly so, may have been obtained at the point D. Even here, all that can be concluded is that the second break lies somewhere within the area of hysteresis, probably at a level higher than the line EC. In short, Fig. 1 indicates a complete confirmation of the 160° isotherm of Gillespie and Hall within the error of hysteresis. In the other three cases not enough hydrogen was ever added to produce rising and falling isotherms at the top of the diagrams in approximate coincidence and the results do not really speak against the existence of Pd_2H.

This matter has been discussed at length because, interpreting the phase relationships for this system, Brüning and Sieverts allow the picture in their Fig. 13 to be obscured by the inclusion of the unexplained early results of Hoitsema and some irrelevant data[9] concerning palladium charged with hydrogen by electrolysis and draw their temperature–composition line in disregard to data of Lambert and Gates and of Gillespie and Hall (particularly at 80°) and of the existence of Pd_2H.

It seems significant that when they draw the locus of the resistance of mutually saturated solid phases as function of the pressure in their Fig. 11 they avoid the second break-points plotted at 180 and 200° to prevent an unnatural change of curvature. We think the corresponding points should be similarly avoided in the composition–pressure locus of their Figs. 12 and 13.[10]

Ipatieff and Tronow[11] have measured some rising isotherms at various temperatures and at pressures up to about 25 atm. Hysteresis was not discussed but was evidently great. Thus at 150° the pressure could be reduced from 3.5 atm. (at the atomic ratio 0.79) to 1 atm. without changing the amount of hydrogen absorbed by more than about 1 part in 250. The object of the authors was not to study the phase diagram and they do not refer to recent work on it.

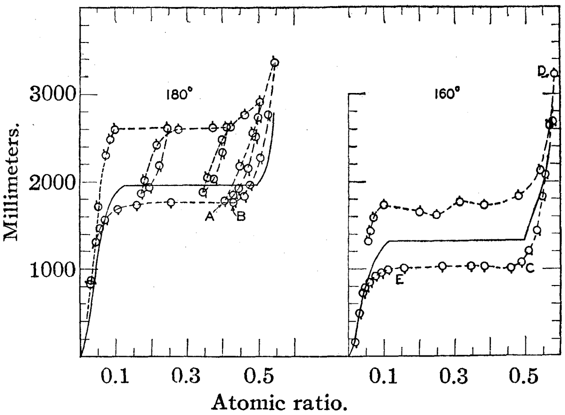

Fig. 1.—Comparison of previous data.

Tromp and De Loor[12] criticize the interpretation of Gillespie and Hall, but the criticism is really not specially directed against them, being a general attack on orthodox interpretations of phase diagrams, and is based on a misunderstanding of the mass action law.[13]

Hüttig[14] has given a general review of hydrides.

Valensi[15] has given a general discussion of the action of gases on metals and has pointed out the similarity of the chromium–nitrogen diagram studied by him—with its compound CrN and critical solution temperature—to the palladium–hydrogen system.

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(9) We do not call these data irrelevant simply because hydrogen was added by a special method (electrolysis), but because the line in question is supposed by phase theory to be the locus of compositions of mutually saturated solid phases There appears not the slightest reason to suppose that the substance prepared by electrolysis is a pure phase in equilibrium with the so-called first, hydrogen-poor phase. It is probably not even in internal equilibrium.

(10) Their reference to the material of Gillespie and Hall as *gesinterter Mohr* is not understood by us. Our palladium black will undergo great volume contraction and sinter when heated in air or oxygen, but nothing like this happens when it is heated much over 400° *in vacuo*, in carbon dioxide or in hydrogen, and sintered material has not been used by us for absorption experiments.

(11) Ipatieff and Tronow, *J. Phys. Chem.*, **38**, 623 (1934).

(12) Tromp and De Loor, *J. Chem. Met. Mining Soc. S. Africa*, **35**, 169 (1934).

(13) The mass action law for *homogeneous* systems admits of no discontinuities. This is taken to deny certain orthodox discontinuities in the diagrams representing *heterogeneous* systems.

(14) Hüttig, *Z. angew. Chem.*, **39**, 67 (1926).

(15) Gabriel Valensi, Thesis, Paris, 1929.

Experimental

Apparatus.—The apparatus for the generation, measurement and confinement of hydrogen is shown schematically, not to scale, in Fig. 2. Hydrogen is made by electrolysis of 10% NaOH containing some barium hydroxide between nickel electrodes, the generator being run continually to keep out air. It can be passed through a heated platinized-asbestos tube M, but in the present experiments it has been passed through a thin palladium tube, L heated to about 300°. Some is rejected through H, the rest is passed through two phosphorus pentoxide tubes, one of which is shown at J, and hence to the storage bulb K or the gas buret E. From this a measured portion can be passed into the steel-protected glass bulb B by means of a mercury compressor G. By closing the stopcock 2 and opening 1 the gas can then be compressed into the heavy Pyrex reaction bulb A until the mercury stands in the glass capillary tube at the level of the dotted line above B.

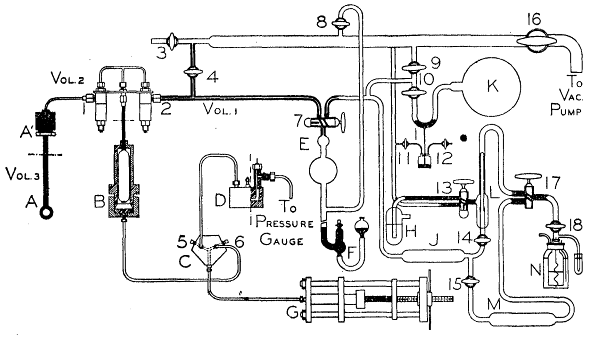

Fig. 2.—Apparatus.

The stopcocks 1 and 2 are of steel, worked from below, and are provided with mercury seals to keep gas from the waxed packing gland. The volumes 1, 2 and 3 were determined by expanding dry hydrogen from the gas buret in a series of experiments, volume 3, extending to the dotted line, having first been determined by weighing water. Stopcock 1, when opened, is open always to the same extent, likewise stopcock 2. In this case the change of volume on closing is 0.02 cc. The volumes 1, 2 and 3 contain 2.4383, 1.5834 and 0.8906 cc., respectively, the last without palladium. 0.96670 g. of palladium was added to the bulb and the capillary resealed without appreciable change of volume. Assuming the density of palladium to be 11.78, we find the free volume 3 to be 0.8085 cc. This is assumed to be at the temperature of the palladium in the thermostat, as the level of demarcation was suitably chosen after exploration with a thermocouple.

The riser block D contains the junction between mercury on the left and oil on the right. The oil line leads to a dead-weight pressure gage. The junction can be maintained at a known level at the end of a steel needle, by means of a vacuum tube circuit which requires only a grid current across the junction. Corrections were made for all oil and mercury columns and the barometric pressure exerted on the gage and the pressures are reported in international atmospheres.

The glass-to-steel joint A′ is shown in detail in Fig. 3. A small steel baffle A, slightly greased, is used to catch and detect any chance droplet of mercury from the stopcocks, but none was found at the end of the experiments.

The thermostat is of steel, provided with an efficient stirrer and wells of steel for the reception of two platinum thermometers, a knife-blade heater and the reaction bulb. Steady heating is provided by an external coil, operated through a Raytheon voltage regulator of 250 watts, working at full load by means of an adjustable shunt load. One of the platinum thermometers is used for measuring the temperature, having been carefully calibrated and compared with other good thermometers. The other is part of a bridge circuit, the galvanometer in which actuates a selenium cell controlling, in a "phase-shift" circuit, a thyratron tube which furnishes the auxiliary current for the knife-blade heater. The thyratron furnishes about 15 to 20% of the total heat. The bath is a mixture of sodium, lithium and potassium nitrates. Under favorable circumstances of room temperature, regulation to better than 0.001° is obtained at the experimental temperatures.

The dead space at room temperatures is protected by the use of aluminum foil and the temperature measured.

Materials.—The hydrogen was purified by diffusion through a hot palladium tube as described above. In some preliminary work at 310° such hydrogen was found to give the same isotherm as hydrogen passed over platinized asbestos (and in either case, over phosphorus pentoxide).

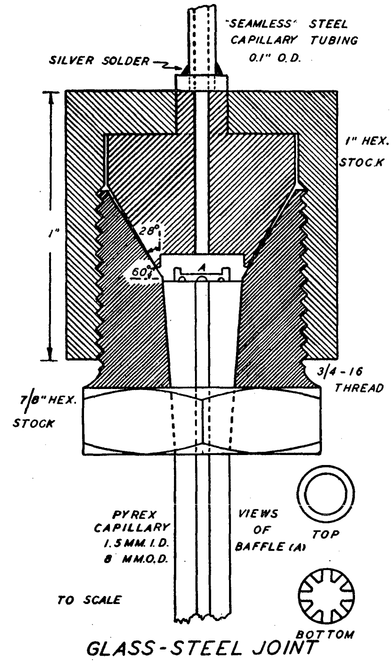

Fig. 3.—Detail of glass to metal joint.

Ammonium chloropalladate was obtained through the kindness of the National Bureau of Standards. It was stated to be free of other metals, particularly platinum-like metals, though not of alkali metals. From this the yellow palladosammine chloride was prepared, reprecipitated twice from ammoniacal solution with hydrochloric acid, thoroughly washed in conductivity water and dried at 100°. A weighed sample was reduced in a stream of hydrogen at 150°, the temperature then slowly raised to a maximum of 500° and a stream of carbon dioxide substituted for the hydrogen. After ten minutes at 500° it was then slowly cooled in the stream of carbon dioxide and weighed. Vacuum corrections were applied. Palladium found, 50.353 and 50.344%; calculated by 1935 atomic weights 50.407%.

Palladium reduced in this way was placed in a Pyrex bulb, and the bulb was evacuated and heated with a hand torch until it partly collapsed. This was an effort to remove any trace of ammonium chloride. The material was allowed to cool in a vacuum, weighed and transferred to the reaction bulb.

In this type of experiment the palladium is easily contaminated with mercury through accident. Furthermore, mercury may be transferred with hydrogen to the palladium, or may distil to it during evacuation. We have not introduced a liquid air-bath to prevent this because of the damaging increase of dead-space corrections and increased liability of accident to the glass apparatus. A palladium mercuride occurs naturally in British Guiana, containing 54.4 to 65.2% Hg.[16] An excess of mercury can react with palladium, especially readily if the palladium contains hydrogen and if heated. After driving off mercury with a fairly strong Bunsen flame we have found to remain 58.2 and 59.1%, most of which could be removed by the strongest Bunsen flame on a small crucible. The formula Pd_4Hg_3 corresponds to 58.5% Hg. Our preparation was hard, sank in the excess of mercury and appeared to have a very low solubility in it. The natural mercuride is hard and denser than its elements.

If the hydrogen which actually entered the palladium during our experiments had been saturated with mercury at 1 atmosphere total pressure, the palladium would have contained about 0.01% of mercury at the end of the experiments. Even ten times as much would not—we have reason to suppose—influence the pressures seriously, though it might hinder equilibrium.

After the last pressure measurement the palladium was exhausted at 290°, cooled in a vacuum and exposed to air. It was then weighed in a porcelain boat with a suitable tare. Then it was conditioned at about 370° in hydrogen, followed by carbon dioxide for half an hour and finally cooled in carbon dioxide, conditioned in the balance case and weighed again with undisturbed weights and rider. The loss of weight was only 0.03 mg. on 942 mg. of sample. Such heating will not remove small amounts of mercury. The boat was placed in a narrow quartz tube and strongly heated with a Meker burner to bright red heat in a current of carbon dioxide, the palladium conditioned with hydrogen and carbon dioxide, cooled in carbon dioxide and weighed as before. The loss of weight was about 2 mg. The palladium was then heated again in the quartz tube in a current of oxygen, followed by hydrogen and carbon dioxide as before. The further loss of weight was about 0.3 mg. The total loss of weight was 0.26% of the weight of the palladium. Previous experience with the elimination of known quantities of mercury showed that this procedure is sufficient.

The loss in weight in this case cannot be due mainly to mercury, as this should have been collected in a narrow water-cooled part of the quartz tube, and none could be found by inspection with the low-power microscope. As the tube at this place appeared etched, about 2 mg. of mercury was intentionally distilled and collected in this part, without cleaning it. Under the low power, the mercury made a striking display, no substantial fraction of which could have been missed in the analysis. In the analysis the gas was passed into a test-tube of water for cooling, and this gave a test with Nessler's reagent.

We conclude that part of the loss of weight was due to elimination of ammonium chloride, and that the amount of mercury in the palladium was much less than 0.2%.

Measurements of Equilibrium Pressure.—We considered the pressure worthy of record as equilibrium pressure when it remained constant for one-half hour. Weighings of the pressure were made to 1 g., corresponding to about 1 mm., though in most cases not reported so precisely in the table. At the higher temperatures equilibrium was evidently reached very quickly, and this was confirmed by coincidence of the rising and falling isotherms. In the two-solid-phase region hysteresis was increasingly evident as the temperature was lowered, until it was very serious at 200°. The "heat treatment" of Gillespie and Hall was not used at all in this work, as it was very inconvenient with the new apparatus. The mercury compressor allowed of a withdrawal of hydrogen followed by return of the same amount to the palladium plus dead space. This seems to be of some assistance in gaining proper equilibrium, but proof of this is lacking, and in the interpretation of the measurements no particular weight has been given to data secured in this way. Such points are shown in the diagrams by circles without tails—they should in most cases be regarded as additions. Additions are shown by tails pointing upward; subtractions, by tails pointing downward.

Calculation of Concentrations.—The hydrogen admitted to the apparatus during an experiment is partly in the palladium and partly in the dead space. Frequently only one-fourth of it was in the palladium. The dead space is in two parts, one at bath temperature and one at room temperature. The density of palladium with adsorbed hydrogen is not well known, and perhaps cannot be. Measurements of Wolf[17] on palladium wire show marked hysteresis and lack of reproducibility. However, they lead us to believe that the error we make in assuming constant density is not serious. We have given above enough apparatus constants to allow of easy correction of our concentrations, if better density data become available. The error of neglecting the thermal and pressure expansion of the glass reaction bulb should be much smaller. At the higher pressures it is necessary to correct for the non-ideality of hydrogen and this correction has been made throughout. It amounted to an increase of 0.0086 in the atomic ratio at 32 atm. and 310° and was a strong function of the pressure and a weak function of the temperature.

The concentration is reported throughout as the atomic ratio: atoms hydrogen per atom palladium.

Experimental Results.—The data are presented in Table I in the order in which they were taken, except for some measurements at 0°, made

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(16) Harrison and Bourne, *Off. Gazette, Brit. Guiana*, No. 71, Feb. 27, 1925; *C. A.*, **19**, 3075 (1925).

(17) Wolf, *Z. physik. Chem.*, **87**, 575 (1914).

between those at 200° and those at 280°. When the mercury compressor was used as described above to withdraw and return hydrogen the ratio is followed by an asterisk. In the last few cases the entries do not begin with zero pressure. This means that the preceding experiment was continued at a new temperature without exhaustion.

TABLE I

Equilibrium Pressures in Atmospheres and Corresponding Atomic Ratios (*r*)

p	*r*
313.02°	
0	0
5.78	0.0398
10.86	.0621
15.60	.0914
19.59	.1253
22.44	.1690
24.43	.2179
25.16	.2818
25.85	.3303
27.01	.3669
30.44	.4196
27.65	.3814
25.91	.3362
24.98	.2719
23.67	.1946
22.54	.1679
19.41	.1253
16.63	.1031
13.47	.0833
10.69	.0679
8.39	.0576
6.32	.0500
310°	
0	0
0.296	0.0078
.538	.0106
.740	.0125
.891	.0138
0	0
0.30	0.0078
3.72	.0306
7.89	.0511
11.81	.0706
16.77	.1020
20.67	.1409
23.02	.1925
24.06	.2720
25.29	.3506
28.58	.4146
31.87	.4449
28.43	.4129
25.94	.3724
24.83	.3341
24.25	.2955
23.79	.2426
22.98	.1942
21.46	.1561
19.43	.1280
14.44	.0879
310°	
9.47	0.0606
5.51	.0417
300°	
0	0
0.31	0.0123
4.76	.0384
10.08	.0660
15.05	.0993
18.84	.1427
20.51	.1804
21.01	.2316
21.20	.2845
21.62	.3391
22.83	.3863
0	0
4.23	0.0359
9.33	.0614
14.15	.0960
18.45	.1368
20.84	.2121
21.12	.2617
21.15	.2738
21.15	.2740
21.18	.2850
21.23	.2967
21.25	.3001
21.31	.3105
21.38	.3185
21.44	.3244
21.62	.3379
22.71	.3822
24.12	.4116
22.65	.3822
22.03	.3619
21.61	.3400
21.21	.2961
20.86	.2162
18.18	.1370
14.01	.0926
295°	
0	0
0.514	0.0108
6.54	.0484
10.20	.0719
14.33	.0991
17.72	.1393
19.647	.2199
19.739	.2368
19.787	.2609
295°	
19.805	0.2856
19.818	.2961
19.811	.2934
19.846	.3101
19.95	.3308
20.20	.3532
22.42	.4194
27.90	.4721
25.10	.4526
22.69	.4243
20.75	.3804
19.868	.3214
19.867	.3179
19.805	.2978
19.792	.2793
19.794	.2716
19.791	.2746
19.767	.2627
19.777	.2629
19.753	.2503
19.455	.2034
290°	
0	0
0.464	0.0105
5.96	.0466
11.22	.0777
15.57	.1217
17.10	.1477
18.18	.1873
18.20	.1915
18.39	.2092
18.38	.2096
18.45	.2256
18.49	.2444
18.51	.2609
18.53	.2790
18.53	.2933
18.54	.3198
18.57	.3363
18.57	.3376
18.79	.3594
19.03	.3739
19.61	.3995
21.89	.4415
21.80	.4392
26.30	.4792
30.58	.5040
25.23	.4749
21.86	.4434
290°	
19.32	0.3894
18.76	.3605
18.75	.3570
18.57	.3390
18.52	.3247
18.52	.3180
18.51	.2983
18.52	.2960
18.50	.2765
18.52	.2771*
18.51	.2699
18.51	.2639
18.50	.2586
18.49	.2538
18.49	.2527
18.45	.2328
250°	
0	0
8.88	0.0958
10.27	.1446
10.36	.1555
10.39	.1624
10.41	.1778
10.36	.1793
10.44	.1965
10.48	.2377
10.38	.2002*
10.44	.2127
10.40	.2140*
10.49	.2891
10.38	.2915*
10.55	.3580
10.49	.3591*
10.55	.4257
12.61	.4805
12.58	.4835
15.97	.5138
20.62	.5385
20.51	.5396
16.83	.5215
16.82	.5214*
14.27	.5031
14.23	.5031
11.72	.4686
11.75	.4691*
10.78	.4435
11.06	.4513
10.19	.4171
10.44	.4128*
10.44	.4294
10.62	.4383
10.56	.4356
10.44	.4306
10.39	.3684
10.27	.2756
10.39	.2737*
10.25	.1869
10.28	.1852*
10.07	.1675
10.27	.1650*
8.63	.0996
250°	
8.63	0.0992*
6.27	.0615
200°	
0	0
0.35	0.0140
3.22	.0608
4.40	.1068
4.36	.1074
4.44	.1286
4.47	.1549
4.52	.2583
4.53	.3465
4.58	.4299
4.55	.4553
4.40	.4723
4.51	.4706*
4.58	.4773
4.66	.4955
4.89	.5150
6.06	.5399
8.02	.5626
12.55	.5794
11.33	.5820
8.43	.5648
5.76	.5357
5.04	.5206
4.67	.5119
4.41	.5032
4.31	.4992
4.49	.4962*
3.95	.4434
4.46	.4338*
3.81	.3116
4.43	.3003*
3.76	.2344
4.39	.2229*
4.35	.1456
3.80	.0782
280°	
0	0
3.05	0.0327
6.42	.0552
8.19	.0684
11.06	.0931
13.75	.1271
15.61	.1784
15.87	.1985
15.98	.2127
16.02	.2191
16.01	.2263
16.09	.2435
16.13	.2597
16.13	.2748
16.20	.3489
0	0
5.18	0.0458
9.94	.0803
13.62	.1223
16.05	.2178
16.04	.2340
16.11	.2503
280°	
16.30	0.3625
16.38	.3646*
16.72	.3853
18.82	.4379
21.84	.4704
26.44	.5024
20.35	.4586
16.89	.3961
16.36	.3702
16.36	.3700
16.12	.3406
16.11	.3312
16.10	.3261
16.14	.3269*
270°	
14.01	0.3633
13.93	.3540
13.88	.3299
13.94	.3379
13.95	.3438
14.04	.3604
13.96	.3537
14.00	.3536*
13.93	.3209
13.88	.2852
13.93	.2838*
13.97	.2746
13.93	.2713
13.93	.2711*
13.93	.2590
13.88	.2490
13.88	.2413
13.91	.2415*
13.89	.2344*
13.88	.2256*
13.78	.2005*
285°	
16.02	0.1651
16.94	.2110
17.07	.2252
17.19	.2420
17.21	.2478
17.25	.2585
17.29	.2828
17.74	.3689
19.63	.4284
17.53	.3562
17.54	.3563*
17.46	.3489
17.39	.3404
17.32	.3252
17.30	.3137
17.29	.3021
17.28	.2922
17.22	.2638
17.23	.2606
290°	
18.33	0.2436
18.33	.2436*

At 0° no attempt was made to investigate the whole curve, or to find again the first break, but we have tried to find the pressure of the horizontal isotherm more accurately than did Gillespie and Hall, who found the average 3.95 mm. by the use of capillary tubes and a meter stick. In this case we have used wide tubes and a good cathetometer. We find that the equilibrium pressure cannot be greater than about 3.56 mm. "Heat treatment" was not used, but the palladium was heated *in vacuo* at 360° before the experiments. The material absorbed hydrogen over a wide range of composition at much lower pressures than in the former investigation, as did the material used by Gillespie and Ambrose.[18] For instance, when the atomic ratio was increased from 0.047 to 0.408 the pressure fell in twelve and a half hours to only 4.03 mm. This is probably a result of the better elimination of ammonium chloride. On withdrawing hydrogen, however, even from the ratio 0.07, the material showed hysteresis, the pressure falling to 3.0 mm. with a decrease of only 0.002 in the ratio.

The last entry of Table I is for a check on the condition of the palladium in comparison with the earlier 290° isotherm. It is not plotted in the diagrams. This result is about 1% lower than the curve at 290°. If plotted in Fig. 5 the center of its circle would lie on the circumference of one of the circles shown. This result points to some small change in the material. The palladium was found to be packed together after the experiments. The mass could be broken up almost entirely by shaking the container so that most of it was removed through the capillary tube. Care was taken to include all of the packed material for the test for mercury.

Discussion

The data cannot be properly judged by a single diagram of constant scale. Hence the experimental points in the neighborhood of the heterogeneous region are plotted in Fig. 4 with different pressure scales for the different isotherms. Even here, the magnification is not quite sufficient to make evident the horizontal portion at 295°, and one must examine the numbers. The scale at 300° is the same as at 295°, though displaced, and the difference between these isotherms, one above the critical point, and one just below it, is very clear. The isotherm at 285° is the last one obtained. It is not so consistent as the others—indeed, taken by itself, it suggests a continuous curve. In order to locate the breaks as well as possible in this and some other cases, we have sought to take advantage of the fact that the pressure level of the horizontal portion is very well defined at some temperatures. A plot was made of log p against $1/T$ for the horizontal portions, and the doubtful levels were chosen so that all the pressures lie within 0.2% of the pressure given by the equation

$$\log p = 4.6018 - 1877.82/T$$

At the seven temperatures increasing from 200 to 295° the pressures chosen differ from those given by this equation by the respective percentages: 0, +0.24, −0.11, 0, −0.06, 0, 0. This equation prescribes a pressure of 4.05 mm. at 0°, which is too high. It agrees with the experimental value 3.56 mm. about as well as any linear equation can, the true equation being that of a curve. On this

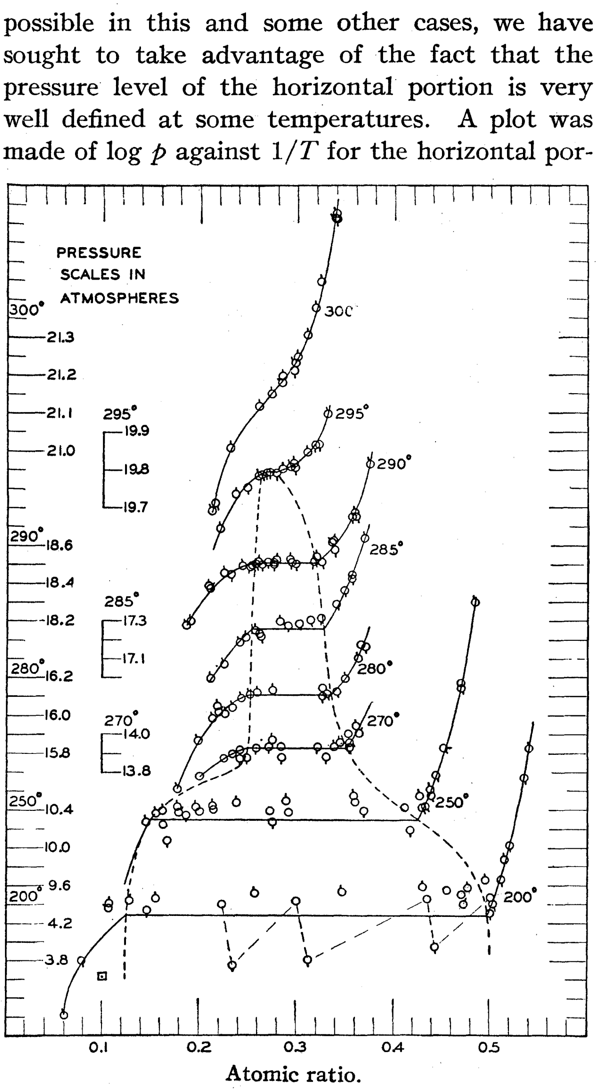

Fig. 4.—Detail of breaks. The square denotes a point in the 250° isotherm. All other points belong on the nearest curve.

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(18) Gillespie and Ambrose, *J. Phys. Chem.*, **35**, 3105 (1931).

plot the results of Gillespie and Hall at the higher temperatures, particularly 180°, appear too low.

The breaks may be sharper than we have drawn them, but it would seem that the heat of absorption per mole of hydrogen is nearly the same at a given temperature, whether the palladium is nearly saturated or whether it is already a two-phase mixture and hydrogen is being used for compound formation. One would therefore expect it legitimate to use a continuous function for smoothing in the manner just described.

The main results of the measurements are shown in summary in Fig. 5, a diagram of uniform scale. Although the exact location of the breaks is very difficult, requiring a smoothing in two variables, yet we think it certain that the boundary of the two-solid-phase region is substantially as shown in Figs. 4 and 5 and that the boundary has steep tangents at ratios 0.125, 0.250, 0.333 and 0.5, corresponding to the compounds Pd_8H, Pd_4H, Pd_3H and Pd_2H. The existence of the first and last of these depends in part on the results of Gillespie and Hall, which are likewise shown in Fig. 5, and is supported in both cases by the X-ray diagram of Linde and Borelius.[8] The short vertical lines across the isotherms at 160 and 180° show the limits allowed by the original data.

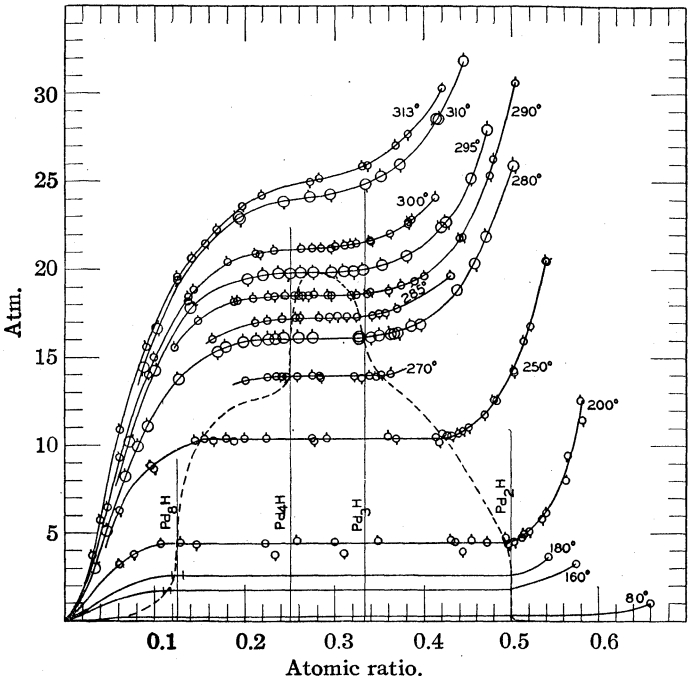

Fig. 5.—Pressure–concentration diagram of palladium–hydrogen system.

We have drawn the tangent much steeper at Pd_4H than at Pd_3H, but such comparisons depend upon the smoothing and are perhaps not fully justified. We think it possible that the tangents are vertical in all cases except Pd_3H, which would mean that the corresponding compounds follow the law of definite proportions. In such a case as shown for Pd_3H there is evidence of chemical individuality, even if the law of definite proportions seems to hold only at a point—*i. e.*, not at all from a practical standpoint. The curve for it is like the curve for FeO in the Fe–H–O system shown by Eastman and Evans,[19] and Pd_3H seems to have as great a claim for existence as FeO.

It may be noted that the tangent cannot be assumed vertical at Pd_7H or Pd_9H. The next compound in the obvious series would be $Pd_{16}H$. This was not observed by Gillespie and Hall, and their data in the neighborhood of 80° are not sufficient to give any information about its possible existence.

The critical solution temperature is estimated by us to be 295.3°, the corresponding pressure 19.87 atm. and the atomic ratio, 0.270.

No compound PdH has ever been shown, nor any phase diagram presented that gives evidence of it. Palladium has been heavily loaded with hydrogen by electrolysis by Fischer[20] to an atomic ratio of 0.84. On standing, hydrogen was lost until the ratio was 0.81. Paal and Gerum[21] report a single experiment in which hydrogen was absorbed by palladium black suspended in water and shaken until the ratio reached 0.98, indicating PdH. But when their absorptions are plotted against the time, a curve is obtained which suggests that further absorption might have been observed in a longer time. Thus there is no evidence here of the existence of PdH even if one grants the enormous absorption, which appears quite inconsistent with the results of electrolysis. This process ought to be capable of saturating palladium under virtually very great pressure—indeed, von Samson-

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(19) Eastman and Evans, THIS JOURNAL, **46**, 888 (1924). In this case the temperature is replaced with per cent. of H_2 in the gas phase as variable, the temperature and partial pressure of water being held constant in the 3-component system, but the curves are analogous.

(20) Fischer, *Ann. phys.*, [4] **20**, 503 (1906).

(21) Paal and Gerum, *Ber.*, **41**, 818 (1908).

Himmelstern[22] has found an increase of pressure from 1 to 968 atm. to increase the atomic ratio found on electrolysis by a negligible amount (from 0.7 to not more than 0.707).

Summary

Seven isotherms, from 200 to 313°, have been traced on the pressure–composition diagram for palladium and hydrogen, in most cases from zero pressure through the heterogeneous region and well into the second homogeneous solid phase. The diagram, including the previous results at lower temperatures of Gillespie and Hall, indicates that the compounds Pd_2H, Pd_3H, Pd_4H and Pd_8H have chemical individuality, even though in the second case, and possibly others, the tangent to the boundary curve is not vertical, the curve then resembling the analogous curve for FeO in the Fe–H–O system. In all cases the compound is to be regarded as a solid solution that has a stoichiometrical composition over a limited range of temperature. The finding of Brüning and Sieverts of a critical solution temperature for the solid phases near 300° is confirmed, and the critical constants are found to be: temperature, 295.3°; pressure, 19.87 atm. and atomic ratio H:Pd, 0.270.

In the discussion the validity is denied of (1) certain evidence against the existence of Pd_2H, and (2) certain evidence in favor of the existence of PdH.

Mention is made of palladium mercuride, probably Pd_4Hg_3, of very low decomposition pressure. The palladium investigated was found at the conclusion of the experiments to contain a presumably harmless amount of mercury, much less than 0.2%.

CAMBRIDGE, MASS. RECEIVED AUGUST 14, 1936

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[22] Von Samson-Himmelstern, *Z. anorg. Chem.*, **186**, 337 (1930).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 548]

The Extraction of Ferric Chloride from Hydrochloric Acid Solutions by Isopropyl Ether

BY RICHARD W. DODSON, GERARD J. FORNEY AND ERNEST H. SWIFT

Introduction

The extraction of ferric chloride from solutions approximately 6 formal in hydrochloric acid by ethyl ether has been studied repeatedly,[1–5] but, although such an extraction process offers obvious advantages over precipitation methods, this separation has not been used as widely in general qualitative and quantitative procedures as would seem justified. This has been due to several factors: the efficiency of the extraction process is critically dependent on the hydrochloric acid concentration; the solubility of ether in the acid is of such magnitude that the volume of the aqueous phase is increased by as much as 25%, making the concentration of the acid after an extraction uncertain or requiring the use of acid previously saturated with the ether; it has been feared that peroxide or alcohol which are frequently present in ether would reduce the iron to the ferrous state, in which form it is not extracted; finally, the volatility of ethyl ether makes the quantitative technique of the extraction somewhat difficult at room temperatures, and especially for student use, involves a serious fire hazard. Because of these facts, it has seemed worth while to investigate the use of other, less volatile ethers for this separation, and this paper presents the results of experiments with isopropyl ether. This ether is readily available, and the present cost of the best technical grade is somewhat less than that of ethyl ether of a comparable grade.

The Experimental Method

Materials.—Concentrated hydrochloric acid, C. P. grade, was standardized against sodium carbonate. Ferric chloride solutions were prepared and standardized, by permanganate, using the Zimmermann–Reinhardt method, or by thiosulfate, using the iodometric method.[6] In every case the ferric chloride used was shown to be free from ferrous salt by testing with ferricyanide. Except when testing the suitability of the technical product for routine analyses, the isopropyl ether used was prepared from a technical grade by fractional distillation, the fraction

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[1] Skey, *Chem. News*, **36**, 48 (1880).

[2] Rothe, *Mitt. königｇ. tech. Ver.*, **10**, 32 (1892); *Chem. News*, **66**, 182 (1892); *Stahl und Eisen*, **12**, 1052 (1892).

[3] Langmuir, THIS JOURNAL, **22**, 102 (1900).

[4] Kern, *ibid.*, **23**, 689 (1901).

[5] Speller, *Chem. News*, **83**, 124 (1901).

[6] E. H. Swift, THIS JOURNAL, **51**, 2682 (1929).

taken distilling over a temperature range of 0.1°. The ethyl ether used had been distilled over sodium, and before use was shaken with mercury to remove peroxide. Solutions of the chlorides of copper, cobalt, manganese, nickel, aluminum, chromium and zinc were prepared by dissolving appropriate amounts of these substances in distilled water, and adding such amounts of concentrated hydrochloric acid and water that the final acid concentration was 7.75 *f*, and the metal ion was present in the desired concentration. Hydrochloric acid solutions were prepared similarly of technical titanic sulfate solution, vanadol and vanadyl ions (from ammonium vanadate), sodium molybdate, sodium hydrogen sulfate and sodium dihydrogen phosphate.

Extraction Technique.—Twenty-five ml. of a solution of hydrochloric acid and ferric chloride in definite concentrations was introduced into a 50-ml., glass-stoppered, graduated cylinder, 25.0 ml. of ether added and the mixture shaken vigorously 500–1000 times. After a separation of the layers was obtained, the phase volumes were read and the mixture transferred to a dry separatory funnel. Portions for analysis were withdrawn from each phase. Except where otherwise stated, the extractions were performed at room temperatures. The same technique was used in the extractions of the other substances tested.

Analytical Procedure.—Small amounts of iron were determined colorimetrically with thiocyanate, larger amounts either by the Zimmermann–Reinhardt method or by the iodometric method. The peroxide content of the ethers used was estimated colorimetrically by means of titanium sulfate. In studying the reducing effect of peroxide and alcohol, ferrous iron was estimated by adding ferricyanide to the solution to be tested and comparing the precipitate so obtained with the precipitate obtained under similar conditions with known amounts of ferrous iron, also by the difference between thiocyanate determinations of ferric iron and, after permanganate oxidation, of total iron.

The Experimental Results

Effect of Varying the Acid Concentration.—Since the efficiency of the extraction with ethyl ether is known to be very dependent on the acid concentration, extractions using isopropyl ether were performed with 125 and 250 mg. of ferric iron over a wide range of acid concentrations. The results of these extractions are recorded in Table I. As noted, with these amounts of iron, three phases appear at hydrochloric acid concentrations above 7.5 formal. In these cases, the two upper layers are considered as ether phases, and the sum of their volumes is recorded. The volumes of these two phases at acid concentrations of 7.5–8.0 formal are approximately equal and the distribution ratio for iron between them varies from about 2.5 to 7.5, the ratio favoring the bottom layer of the two and increasing with increase in hydrochloric acid concentration.

For purposes of comparison there are recorded in Table II values obtained under similar conditions for the distribution of ferric iron between aqueous hydrochloric acid solutions and ethyl ether.

TABLE I

THE DISTRIBUTION OF FERRIC IRON BETWEEN ISOPROPYL ETHER AND AQUEOUS HYDROCHLORIC ACID SOLUTIONS

Initial HCl concn., moles per liter	Volume after shaking, ml. Ether layer	Water layer	Iron found, mg. Ether layer	Water layer	% extracted	Distribution ratio $(Fe_{ether})/(Fe_{water})$
2.0	24.8	25.3	0	252.0	0	
3.0	24.5	25.4	1.1	250.9	0.44	0.0045
4.0	24.6	25.3	30.5	221.6	12.1	.142
5.0	24.8	24.9	203.9	48.1	80.9	4.25
5.5	24.7	24.9	235.2	16.8	93.3	14.1
6.0	24.7	25.0	247.3	4.7	98.1	53.3
6.5	23.9	25.9	124.7	1.1	99.1	123
6.6	24.5	25.2	250.4	1.6	99.4	161
7.0	24.2	25.5	251.1	0.92	99.6	287
7.0	23.7	26.0	123.7	0.65	99.5	208
7.5	23.7[a]	25.8	248.4	0.39	99.8	690
7.5	23.7	26.2	123.6	0.79	99.4	173
7.75	23.4[a]	26.2	248.6	0.24	99.9	1160
8.0	23.3[a]	26.2	251.9	0.16	99.9	1770
8.0	23.2[a]	26.6	124.2	0.19	99.8	750
8.25	22.5[a]	26.9	248.5	0.30	99.9	990
8.5	22.0[a]	27.4	247.9	0.88	99.6	351
8.5	22.4[a]	27.2	123.8	0.61	99.5	246
9.0	19.1[a]	30.1	238.5	13.5	94.6	27.8
9.0	18.5[a]	30.8	116.1	8.3	93.3	23.3

[a] Two ether phases. The sum of the volumes is recorded.

TABLE II

THE DISTRIBUTION OF FERRIC IRON BETWEEN ETHYL ETHER AND AQUEOUS HYDROCHLORIC ACID SOLUTIONS

Initial HCl concn., moles per liter	Volume after shaking, ml. Ether layer	Water layer	Iron found, mg. Ether layer	Water layer	% extracted	Distribution ratio $(Fe_{ether})/(Fe_{water})$
0.0	23.3	26.5	Trace	250	0.0	0.0
2.0	23.2	26.7	2.4	248	.96	.011
3.0	22.9	26.8	44.5	205	17.8	.25
4.0	22.7	26.7	204	46.4	81.5	5.18
5.25	21.2	28.0	246	4.4	98.2	74
6.2	19.6	29.4	247	2.6	99.0	143
7.0	17.3	31.7	244	5.5	97.8	81
7.1	17.1	31.8	244	5.9	97.6	72
8.0	11.8	36.6	218	32.4	87.0	20.9
8.6[a]	8.0	40.4	169	80.6	67.7	10.6
9.3[a]	5.3	43.2	35.0	215	14.0	1.33

[a] Separate ether phase metastable.

Values for the phase volumes and extraction percentages with ethyl ether at acid concentrations of 8.6 and 9.3 formal are recorded in Table II. In subsequent experiments it was found that at these concentrations the ether phase very slowly but completely dissolves in the other phase on continued shaking. The values given for these concentrations represent, therefore, extraction under metastable conditions.

In Fig. 1 are plotted the extraction percentages given in Tables I and II.

In order to determine the suitability of the technical grade of isopropyl ether for this extraction, experiments similar to those previously described were made using commercial isopropyl ether. The results of these experiments are given in Table III.

TABLE III

THE DISTRIBUTION OF FERRIC IRON BETWEEN TECHNICAL ISOPROPYL ETHER AND AQUEOUS HYDROCHLORIC ACID SOLUTIONS

Initial HCl concn., moles per liter	Volume after shaking, ml. Ether layer	Water layer	Iron found, mg. Ether layer	Water layer	% extracted	Distribution ratio $(\mathrm{Fe}_{ether})/(\mathrm{Fe}_{water})$
6.0	24.7	25.0	244.0	7.76	96.9	31.8
8.0	23.5	26.1	251.5	0.52	99.8	540

Effect of Varying the Iron Concentration.—In order to determine the effect on the distribution of varying the iron concentration, a series of extractions were made with isopropyl ether in which the acid concentration was kept constant and the amount of iron was varied. In these experiments the solutions were kept at 25° during the extraction process. A hydrochloric acid concentration (5.0 formal) below that for optimum extraction was selected in order that more accurate values for the distribution ratio might be obtained. The results of these experiments are given in Table IV. The isopropyl ether used in obtaining the data presented in Table IV was found to be 0.03 *N* in peroxide.

Because it was seen from the data recorded in Table IV that the distribution varies with the total amount of iron, extractions were performed with one milligram of iron with both ethyl and isopropyl ethers. The results are given in Table V.

The Effects of Peroxide and Alcohol.—To determine the reducing effects of peroxide and alcohol, extractions were made with ethers containing known amounts of these impurities. A thirty-minute extraction of 250 mg. of ferric iron was performed with ethyl ether from hydrochloric

TABLE V

THE EXTRACTION OF ONE MILLIGRAM OF FERRIC IRON FROM AQUEOUS HYDROCHLORIC ACID SOLUTIONS BY ETHYL AND ISOPROPYL ETHERS

Ether used	Initial HCl concn., moles per liter	Volume after shaking, ml. Ether layer	Water layer	Iron found in water layer, mg.	% extracted
Ethyl	4.0	22.1	27.4	0.6	40
Ethyl	6.0	17.9	31.2	.2	80
Isopropyl	7.0	23.5	26.3	.1	90
Isopropyl	7.5	22.9	26.9	.04	96
Isopropyl	8.0	21.8	27.8	.04	96
Isopropyl	8.5	20.4	29.2	.1	90

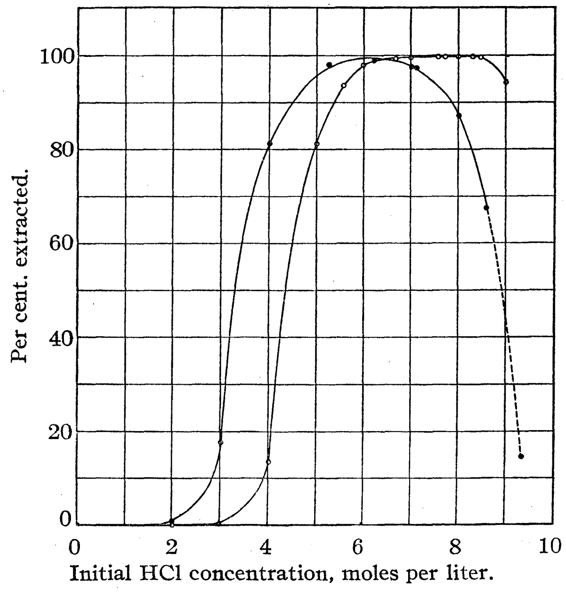

Fig. 1.—Extraction of ferric chloride from aqueous hydrochloric acid solutions by ethyl and isopropyl ethers: -●-, ethyl ether; -○-, isopropyl ether.

TABLE IV

THE DISTRIBUTION OF VARYING AMOUNTS OF FERRIC IRON BETWEEN ISOPROPYL ETHER AND 5.0 FORMAL HYDROCHLORIC ACID SOLUTIONS[a]

Initial HCl concn., moles per liter	Amount of iron taken, mg.	Volume after shaking, ml. Ether layer	Water layer	Iron found, mg. Ether layer	Water layer	% extracted	Distribution ratio $(\mathrm{Fe}_{ether})/(\mathrm{Fe}_{water})$
5.0	500	25.4	24.1	451	49	90.2	8.7
5.0	243	24.8	24.9	200	43	82.4	4.7
5.0	203	24.8	25.0	161	42	79.5	4.0
5.0	102	24.6	25.2	69	33	67.5	2.1
5.0	41	24.5	25.4	16	25	39	0.7
5.0	22	24.4	25.5	8	14	36	0.6

[a] It is to be emphasized that these data do not represent extraction under the most favorable conditions of acid concentration (see Table I).

acid 6.0 *f* and with isopropyl ether from hydrochloric acid 8.0 *f*. A small amount of ferrous iron was found in the aqueous layer after the ethyl ether extraction, less than 0.3 mg. when the ether was 0.003 *N* in peroxide and contained ethyl alcohol 4% by volume, and a like amount when no alcohol was present. With isopropyl ether, 0.1 *N* in peroxide, both with and without isopropyl alcohol present 4% by volume, no test for ferrous iron was obtained, or less than 0.0 mg. was formed.

The Behavior of Elements Other than Iron.—In order to determine the behavior of other elements with isopropyl ether, extraction experiments were performed with copper, cobalt, nickel, manganese, aluminum, chromium, zinc, molybdenum, vanadium, titanium, sulfur and phosphorus.

TABLE VI

THE EXTRACTION OF ELEMENTS OTHER THAN IRON FROM 7.75 *f* HYDROCHLORIC ACID SOLUTIONS BY AN EQUAL VOLUME OF ISOPROPYL ETHER

Element taken	Amount, mg.	Amount found in ether, mg.	% extracted
Cu^{II}	500	0.0	0.0
Co^{II}	500	.0	.0
Mn^{II}	500	.00	.00
Ni^{II}	500	.00	.00
Al^{III}	500	.00	.00
Cr^{III}	500	<.03	<.01
Zn^{II}	500	.0	.0
V^{V}	250	54	22
V^{V}	48.5	21	43
Fe^{III}	500		
V^{IV}	258	<0.2	<0.08
V^{IV}	51.5	.2	.4
Fe^{III}	500		
Mo^{VI}	250	53	21
Mo^{VI}	125	56	45
Fe^{III}	250		
Ti^{IV}	125	0.00	0.00
S (as H_2SO_4)	62.5	.2	.3
Fe^{III}	250		
P (as H_3PO_4)	125	.1	.1
P (as H_3PO_4)	62.5	39	62
Fe^{III}	250		

These extractions were performed at an initial hydrochloric acid concentration of 7.75 formal. The results are given in Table VI.

Discussion

It is to be seen from Tables I and II and from Fig. 1 that with 250 mg. of iron the extraction with ethyl ether reaches an efficiency of 99% or slightly greater at an initial hydrochloric acid concentration of 5.5–6.5 formal. Above 6.5 formal the efficiency of extraction falls off quite rapidly. With isopropyl ether the efficiency of extraction reaches 99% at an initial acid concentration of 6.5 formal, rises above the curve for ethyl ether, and does not fall off appreciably until an acid concentration of 8.5 formal is reached. Under optimum conditions (acid 7.75–8.0 formal) the extraction is 99.9% complete. From the standpoints both of maximum efficiency of extraction and of range of acid concentration over which a favorable extraction is obtained, isopropyl ether is seen to be markedly superior to ethyl ether.

Technical isopropyl ether was found to give an extraction almost as efficient as that obtained with the redistilled ether.

Tables IV and V show that, with both ethers, the percentage extraction decreases with decrease in total iron. However, as for the extraction of large quantities, isopropyl ether is also found to be superior for the extraction of small quantities of iron, the extraction of one milligram under optimum conditions being 96% with isopropyl ether as compared with 80% with ethyl ether. In view of the completeness of extraction of quantities of iron as small as one milligram it can be said that with isopropyl ether a very satisfactory separation of iron is possible. Shaking with three successive portions of isopropyl ether should give a separation that is practically quantitative.

Under conditions of maximum extraction the volume changes of the ether and aqueous layers are considerably less with isopropyl than with ethyl ether. This is an advantage in analytical separations in which it is desired to know the approximate acid concentration after an extraction. An optimum final acid concentration corresponding to an initial concentration of 8.0 *f* is calculated to be 7.4 *f*. (The assumption is made that the formula of the extracted complex is approximately $HFeCl_4$; the concentration of hydrochloric acid in isopropyl ether saturated from aqueous 7.5 *f* solution has been determined by us to be 0.0246 mole per liter at 25°.)

The reduction of ferric iron in the ether layer does not occur even when isopropyl alcohol and peroxide are both present in moderate amounts. With ethyl ether, reduction is slight.

The data recorded in Table VI indicate that a very satisfactory separation of iron from copper, cobalt, manganese, nickel, aluminum, chromium, zinc, quadrivalent vanadium, titanium and sulfur is to be obtained. Large amounts of pentavalent vanadium are extracted; phosphoric acid and molybdenum pass into the ether layer with ferric iron.

Experiments are in progress to determine the formula of the iron compound in the ether phase, and to study the factors affecting the distribution between phases and the formation of two ether phases under certain conditions. Experiments are planned to determine the efficiency of isopropyl ether in the separation of other elements, such as gallium and thallium.

Summary

It has been shown that isopropyl ether offers marked advantages over ethyl ether for the extraction of ferric iron from aqueous hydrochloric acid solutions, giving a more efficient extraction over a wider range of acid concentrations than does ethyl ether. Data are given which show the effect of varying the hydrochloric acid concentration, the amount of ferric iron, the effect of the presence of alcohol and peroxide and the behavior of other elements commonly occurring with or alloyed with iron.

PASADENA, CALIF. RECEIVED SEPTEMBER 22, 1936

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY INSTITUTE OF THE UNIVERSITY OF COPENHAGEN]

The Strength of Acids in Formamide

BY FRANK H. VERHOEK

As a part of the study of the behavior of acids and bases in various solvents being carried on in this Institute, it was undertaken to investigate the strengths of acids in formamide. This substance is particularly interesting in that it is reported by Walden[1] to have a dielectric constant greater than that of water. It is a colorless, odorless, hygroscopic liquid, denser and more viscous than water, freezing at +2.55°, and it is a good solvent for both inorganic and organic salts. The study is concerned with the determination of the strength constants of representative groups of acids in formamide, from measurements of the conductivity of acid–base mixtures in that solvent, and from measurements of the potential differences set up between a standard buffer solution and buffer solutions made up with the different acids.

Purification of the Solvent.—Formamide obtained commercially is frequently acid and contains ammonium formate. The latter is volatile enough so that it is not readily removed by distillation at reduced pressure; further, it is so largely solvolyzed that the ammonia is pumped off in the distillation, leaving formic acid, which then appears in the acid distillate. Any water present in the solvent during the distillation reacts with the formamide to form ammonium formate. Formamide reacts with strong bases and with phosphorus pentoxide. The method adopted finally for the purification was to add solid brom thymol blue directly to the formamide, and neutralize with sodium hydroxide, avoiding an excess. The neutral liquid is heated at 80–90° under an oil pump vacuum until distillation is about to begin, ammonia and some of the water formed by the neutralization being pumped off. During this time the formamide has turned acid again, by loss of ammonia both from the ammonium formate originally present and from that formed by reaction with the water from the neutralization. The neutralization with sodium hydroxide is repeated, and the liquid heated in a vacuum to incipient distillation. This time less water is formed by the neutralization, and consequently less acid from the reaction *water* ⟶ *ammonium formate* ⟶ *formic acid.* With a repetition of the process four or five times, even quite impure samples will remain neutral when distillation begins. The whole of the formamide is now distilled from the sodium formate by evaporation from the surface at 80–90° in a vacuum, neutralized again with sodium hydroxide and redistilled in the same fashion, collecting the last four-fifths. This material is neutral, melts at about 2.2°, and has a specific conductance of about 5×10^{-5}. The neutral distillate is now further purified by fractional crystallization in a water- and carbon dioxide-free atmosphere. From 400–500 cc. five or six fractions are removed, giving a final 100 cc. with a specific conductance of 1 or 2×10^{-6}. The fractions removed, together with the first portion from the distillation, are returned again for treatment with sodium hydroxide, distillation, and recrystallization.

Residues were recovered by the same method as that for the purification of the original substance.

The pure material is not stable; the conductance increases by a factor of eight or ten in ten days or two weeks. It was found, however, that if a stream of air, purified by passing through a train containing soda lime, calcium chloride, phosphorus pentoxide and cotton, was bubbled rapidly through the liquid, the conductance would remain low for a longer period. With certain samples a decrease of conductance occurred at first on bubbling air through the formamide, followed by an increase. The solvent was considered still sufficiently pure for use when the specific conductance was less than 3.5×10^{-6}; the large majority of the experiments, however, were made on material having

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[1] Walden, *Z. physik. Chem.*, **46**, 175 (1903).

a conductance between 1.0×10^{-6} and 2.0×10^{-6}. The lowest value found for the conductance in the course of the work was 6.2×10^{-7}; already the next day, however, the conductance of this sample had risen to 1.17×10^{-6}. The best previously reported value[2] is 1.58×10^{-6}. Data reported below indicate that the specific conductance of pure formamide is in the neighborhood of 10^{-10}.

The hygroscopic nature of formamide was tested by exposing 5.6 g. in a small beaker to the room atmosphere, the liquid having a free surface of about 9 sq. cm. There was a gain in weight of 0.2% in one hour, 1% in five and one-half hours, and 10% in one hundred and forty-one hours. It was found, however, that amounts of water even up to 1% had no large effect in either the conductance or potentiometric experiments, so no special precautions, beyond a reasonable care in preventing unnecessary exposure to air on transferring and pipetting, were taken to prevent contamination with moisture.

Conductance Experiments.—By measuring the conductivity of a solution containing an acid and a base, and knowing the equivalent conductance at various concentrations of the salt formed by the reaction between the acid and the base, the amount of salt present in the acid–base mixture can be calculated. Using the same base and several different acids, the amount of salt formed with the several acids will depend upon the strengths of the acids, so that the relative strengths of the acids with respect to that base may be obtained. With the help of suitable transition systems the strengths of another group of acids with respect to another base may be referred back to the first group and a continuous scale of acid strengths set up over the whole range. If the solvent is itself basic or acidic, a detectable part of the conductivity of the acid–base mixture may be due to the free acid or base still present, so that the measured value must be corrected for this in order to get the true value for the salt.

In the case of formamide the bases used were the solvent itself, pyridine, and α-picoline, covering a range of acids from the strongest down to *p*-nitrophenol. To study still weaker acids, stronger bases would be required; piperidine and benzylamine, however, were found to react with formamide, forming ammonia and a substituted formamide, while the strong tertiary amines, which would not be expected to react, were too insoluble, except for triethylamine, which volatilized so rapidly from the solution that the data were not reliable. The equivalent conductances in formamide of the salts formed by the acid–base reaction are not known; since the formamide could not be obtained in a really pure state, these values could not be obtained accurately. Extrapolation to infinite dilution of the equivalent conductances of potassium dichloroacetate, potassium benzenesulfonate and potassium picrate solutions, using the Onsager equation with an assumed dielectric constant of 90 and making no corrections for the self-conductance of the solvent, gave the values 22.1, 20.7 and 19.8. Davis, Putnam and Jones[3] report for the equivalent conductance at infinite dilution for tetramethylammonium iodide 24.3, and for sodium iodide 24, the lowest concentration observed being only 0.1 *M* in the first case and 0.02 *M* in the second. The value 22 has then been chosen as reasonable for the equivalent conductance; it has been taken the same for all the salts, and it has been assumed to be unchanged with change in concentration. The protolysis constants are increased by a factor of two by changing the value of the equivalent conductance used in calculating them from 25 to 20; no accuracy greater than, say, 0.2 *pK* unit can therefore be claimed for the results.

Since formamide is itself both an acid and a base, an acid or a base alone dissolved in formamide gives an appreciable increase in conductivity, so that the measured conductance of the acid–base mixture is not that due to the presence of the salt alone. To get the true value the increase in the conductance of the solvent due to the addition of acid alone was added to the increase in conductance due to the addition of base alone, and the sum subtracted from the increase in conductance when both acid and base were present at the same concentrations as in the first two cases. From these values of the conductance at the various concentrations, and the assumed value for the equivalent conductance, the concentration of the ions may be obtained; subtraction of this value from the stoichiometric concentrations of the acid and base added gives the concentration of the free acid and base present, so that the protolysis constant for the reaction

$$A_1 + B_2 \longrightarrow A_2 + B_1$$
$$K_{A_1B_2} = \frac{[A_2][B_1]}{[A_1][B_2]}$$

may be calculated. If the extent of salt formation is large, as with strong acids, the value obtained in this manner is a first approximation, since in correcting for the conductance due to the addition of acid alone and base alone, values have been used corresponding to concentrations of acid and base higher than those actually present in the final solution. A second approximation using values for the acid and base concentrations found in the first approximation could be made, but the difference between the first and second approximations amounts at the most to 0.03 *pK* unit; the error introduced by virtue of the uncertainty in the value for the equivalent conductance is greater than this, and such a second approximation has been omitted. In general, equivalent amounts of acid and base were used; in representative cases, an excess of one of the components was introduced. The protolysis constants for those experiments containing an excess checked with those in which equivalent amounts were present. The detailed data for an experiment with benzoic acid and picoline are given in

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(2) G. F. Smith, *J. Chem. Soc.*, 3257 (1931).

(3) Davis, Putnam and Jones, *J. Franklin Inst.*, **180**, 567 (1915).

TABLE I

PROTOLYSIS CONSTANT OF BENZOIC ACID AND α-PICOLINE

Concn.	Sp. cond. $\times 10^6$			Increase $\times 10^6$			Corr. cond. of salt	Concn of ions	$K \times 10^2$
	Salt	Acid	Base	Salt	Acid	Base			
0.0	1.82	1.88	1.90	0.00	0.00	0.00	0.00		
.001	5.55	1.94	2.03	3.73	.06	.13	3.54	0.000161	3.68
.002	9.36	2.08	2.10	7.54	.20	.20	7.14	.0003246	3.76
.005	21.10	2.50	2.25	19.28	.62	.35	18.31	.0008324	3.99
.01	40.57	3.09	2.44	38.75	1.21	.54	37.00	.001686	4.11
.02	78.8	4.07	2.66	77.0	2.19	.76	74.0	.003364	4.08
.05	189.5	6.54	3.61	187.7	4.66	1.71	181.3	.008242	3.90
.1	361.0	10.17	4.51	359.2	8.29	2.61	348.3	.01583	3.53

Table I. It is evident that a possible increase in the protolysis constant with increasing salt concentration is not greater than the experimental error.

For the strong acids, where formamide itself acts as the base, a conventional dissociation constant was calculated, using Ostwald's dilution law and the value 22 for the equivalent conductance. There was some indication, from a comparison of the equivalent conductance–concentration curves for the strong acids benzenesulfonic and picric with those for the corresponding potassium salts, that the equivalent conductance at infinite dilution of an acid is two units less than that of its potassium salt, but no account has been taken of this difference. Table II gives the data for *o*-nitrobenzoic acid dissolved in formamide. The constants at lower concentrations are inaccurate, since the solvent itself has such a high conductivity that it amounts to a large fraction of the total.

TABLE II

THE DISSOCIATION CONSTANT OF *o*-NITROBENZOIC ACID IN FORMAMIDE

Sp. cond. of solvent: 1.54×10^{-6}

Concn.	Equiv. cond.	100α	$K \times 10^5$
0.000831	5.59	25.22	7.07
.001689	3.84	17.45	6.23
.002602	3.08	14.00	5.93
.00539	2.13	9.69	5.60
.01147	1.47	6.66	5.45
.02349	1.04	4.71	5.46
.04899	.73	3.31	5.55
.0929	.54	2.45	5.72
.1030	.51	2.34	5.76

$pK_{0.05} = 4.26$

The conductivity experiments were carried out at 20° in a small narrow cell of 15-cc. capacity with platinized electrodes, and a constant of 0.3827. To 5 cc. of solvent was added from a weight buret a solution roughly 0.2 *M* in acid and base, giving concentrations in the cell from slightly less than 0.001 up to 0.1 *M*. In the particular case of trichlorophenol a saturated solution of the acid is only 0.06 *M*, putting an upper limit to the concentration at which the experiments could be carried out. The density of the final solution in the cell was measured at the end of the experiment, and the density assumed to vary linearly with the concentration in calculating the concentrations from the weight data. Values at round concentrations for correcting for the conductances of the free acid and base were obtained from these original data by straight line interpolation. The three experiments required for the determination of the protolysis constant of an acid–base pair, namely, an experiment with both acid and base, one with acid alone and one with base alone, were always made on the same day, so as to have the solvent as nearly identical for the three as possible.

The negative logarithms of the strength constants determined from the conductance measurements are given in the second, third and fourth columns in Table V. The values given are those for the arbitrarily chosen stoichiometric concentration of acid or of acid and base 0.05 *M*. Picric acid and trichloroacetic acid are so strongly dissociated in formamide that the values given for them are uncertain; benzenesulfonic acid appears to be dissociated completely at all concentrations up to 0.1 *M*. The values in the third column have been obtained from the protolysis constants of the acids reacting with pyridine by the relation

$$pK_{\mathrm{AM}} = pK_{\mathrm{AP}} - pK_{\mathrm{SP}} + pK_{\mathrm{SM}}$$

where pK_{AM} is the negative logarithm of the conventional dissociation constant given in that column, K_{AP} is the protolysis constant for acid A reacting with the base pyridine, K_{SP} is the constant for salicylic acid and pyridine, and K_{SM} is the constant for salicylic acid and the pure solvent. An extension of this equation through benzoic acid chosen as a standard connects the data for pyridine with that for α-picoline, and so back to the pure solvent.

Potentiometric Experiments.—The potentiometric experiments were carried out with hydrogen electrodes in each of two compartments connected through stopcocks to a narrow U-tube filled with saturated potassium chloride (0.88 *M*) as a bridge. The potential was found to depend in part upon the rate at which the hydrogen was bubbled through the solutions in the two compartments. If the rate of bubbling was the same in the two compartments, a value of the potential difference constant over several hours was obtained; if the rate at which the hydrogen passed through one solution was greater than that in the other the potential difference rose or fell at a constant rate, but would return to a value near to the original value when the rate of bubbling was made equal in the two compartments again. The experiments were made using the same constant and equal rate for all. The substitution of quinhydrone for the hydrogen electrode proved to be of no advantage, since quinhydrone gradually darkens on standing with formamide, and there is a slow change in the potential difference. It is possible, however, to extrapolate back to an initial value, and a dissociation constant determined with the quinhydrone electrode in a case where hydrogen would have been unsuitable is included in the data reported. Junction potentials were neglected in all cases.

The standard buffer was a solution 0.05 *M* in potassium chloride, 0.05 *M* in anhydrous potassium salicylate and 0.05 *M* in salicylic acid. The *p*H of the salicylic acid–salicylate buffer was determined by measuring against benzenesulfonic acid, assuming complete dissociation of the latter. With this strong acid there was a slow decrease in potential with time, and the value used in calculating the *p*H is that obtained by extrapolating to zero time. The average of three experiments for which the maximum difference was 0.071 unit gave 4.358 for the *p*H of the standard buffer. The standard salicylate solution was made up anew for each experiment at the same time as the test solution, so as to have the two solutions as nearly comparable as possible. The test buffers in the case of the carboxylic acids were 0.05 *M* in potassium chloride, and 0.05 *M* in the potassium salt of the particular acid; they were made 0.02, 0.05 and 0.1 *M* in the acid by adding weighed amounts of acid to 5 cc. of salt solutions in the apparatus. The hydrogen ion concentrations in the test solutions were calculated from

$$\log [\mathrm{H}^+] = E/0.05814 + \log [\mathrm{H}^+]_{\text{salicylic–salicylate}}$$

where $\log [\mathrm{H}^+]_{\text{salicylic–salicylate}}$ is -4.358. The *pK* for the acid is then found from

$$pK = -\log K = -\log [\mathrm{H}^+] - \log [\text{base}] + \log [\text{acid}]$$

the stoichiometric concentrations of the acid and base present being corrected where necessary for the dissociation of the acid. The constants calculated for the three buffer ratios checked to about 0.1 logarithmic unit, and duplicate experiments checked with the same accuracy. An experiment with salicylic and benzoic acid buffers in which the buffer ratio was changed by adding salt to a 0.05 *M* acid solution showed that the effect of changing ionic strength on the dissociation constant is not greater than the experimental error. Table III gives the results for measurements on salicylic acid–benzoic acid buffer pairs under various conditions.

For the anilinium acids, the test solutions were made 0.05 *M* in potassium chloride, and 0.1 *M* in the anilinium chloride or benzenesulfonate; to a known volume of this solution in the electrode compartment was added one, two, or three drops of piperidine from a weight pipet, forming free base by the reaction

$$\mathrm{RNH_3^+ + C_5H_{11}NH \longrightarrow C_5H_{11}NH_2^+ + RNH_2}$$

This reaction is complete with the strong acids and piperidine, and the piperidinium ion plays no part in determining the hydrogen ion concentration of the solution in the presence of the strong acids. Addition of piperidine in excess of 0.1 *M* gave a buffer solution in piperidine–piperidinium ion, from which the acid strength of piperidinium ion could be obtained. For benzylamine, triethylamine, and pyridine, the pure bases were added from a weight buret to solutions 0.05 *M* in potassium chloride and 0.05 *M* in the amine salt. With the amine bases present there is a change in potential difference with time due to the reaction with formamide. This change is not great; even with the strongest base piperidine it amounts only to one and one-half or two millivolts an hour, so that an extrapolation to the initial time is carried out easily. Readings were taken at fifteen-minute intervals until the rate of change remained constant for an hour, and the value obtained by extrapolating to zero time used in the calculations. About one-half hour was usually required for the system to come to equilibrium. With triethylamine, the triethylamine was bubbled out by the hydrogen so rapidly that the potential difference decreased by 10 mv. an hour. The correctness of the value reported for this substance, however, is indicated by the fact that the addition of further triethylamine to the solution, and extrapolation back to the moment of addition, gave values for the dissociation

TABLE III

DISSOCIATION CONSTANT OF BENZOIC ACID

Salicylic acid, m./l.	Potassium salicylate, m./l.	Benzoic acid, m./l.	Potassium benzoate, m./l.	E. m. f., mv.	$pK_{\text{benzoic acid}}$
0.05	0.05	0.02	0.05	131.4	6.220
		.05		108.8	6.229
		.1		90.6	6.217
.05	.05	.02	.05	135.6	6.292
		.05		112.1	6.286
		.1		92.4	6.248
.02	.05	.05	.05	88.8	6.283
.05				112.6	6.294
.1				130.8	6.307
.05	.02	.05	.05	133.7	6.260
	.05			111.9	6.282
	.1			96.7	6.288

TABLE IV

DISSOCIATION CONSTANT OF *o*-CHLOROANILINIUM ION

Time, min.	0.04371 *M* piperidine E. m. f., mv.	0.07638 *M* piperidine E. m. f., mv.
10		125.1
15	151.4	124.7
20	150.8	
30	150.4	124.8
45	150.6	124.6
60	150.5	124.4
75	150.4	124.2
90	150.2	124.0
105	150.1	123.8
120	149.9	
E. m. f. at zero time	151.0	125.2
pK	1.566	1.527

constant of the triethylammonium ion which agreed with the first, when the concentration of triethylamine added the first time was corrected for the amount which had bubbled away. Table IV gives the data for an experiment in which the dissociation of *o*-chloroanilinium ion was studied. To a solution 0.1 *M* in *o*-chloroanilinium chloride was added in the first half of the experiment piperidine corresponding to 0.04371 *M* per liter; to this solution was later added piperidine corresponding to 0.03267 *M* per liter. No correction was applied for the reaction of the amine with the formamide during the first half of the experiment in calculating the concentrations in the second half.

The *pK* values from the electrometric measurements are included in Table V. The values given for the carboxylic acids in the table are those for buffer solutions containing equal quantities of acid and salt; for the cation acids the values are those obtained from the first addition of piperidine or other amine.

TABLE V

THE DISSOCIATION CONSTANTS OF ACIDS IN FORMAMIDE

Acid	*pK* in H_2O	*pK* in formamide Solvent			
		Solvent	Pyridine	Picoline	Potentiometric
Picric acid	0.3^a	(1.20)			
Trichloroacetic acid	0.7^a	1.46			
Dichloroacetic acid	1.3	2.85			2.60
2,4-Dichloroanilinium ion	2.14				1.08
α,β-Dibromopropionic acid	2.17	4.08			
o-Nitrobenzoic acid	2.19	4.28			
o-Chloroanilinium ion	2.68				1.57
Monochloroacetic acid	2.86	4.56	4.50		4.74
Salicylic acid	2.98	4.46	4.46^e		4.36
m-Nitrobenzoic acid	3.45		5.30	5.41	
m-Chloroanilinium ion	3.54				2.75
2,6-Dinitrophenol	3.58	4.17			
m-Chlorobenzoic acid	3.81		5.75	5.72	5.70
2,4-Dinitrophenol	4.02	4.50	4.54		
p-Chloroanilinium ion	4.03				3.26
Benzoic acid	4.19		6.21	6.21^f	6.27
Succinic acid I	4.20^h				5.90
Anilinium ion	4.69				4.10
Propionic acid	4.87		7.02	6.98	7.18
Trimethylacetic acid	5.01		7.39	7.33	7.43
2,5-Dinitrophenol	5.12		6.00	5.94	
Pyridinium ion	5.26^b				4.48
Succinic acid II	5.57^h				7.89
2,4,6-Trichlorophenol	6.41		7.28	7.28	
p-Nitrophenol	7.15			8.53	8.51^g
Benzylammonium ion	9.37^c				9.77
Triethylammonium ion	10.97^d				9.99
Piperidinium ion	11.13^b				11.08

[a] Hall, *Chem. Rev.*, **8**, 191 (1931). [b] Hall and Sprinkle, THIS JOURNAL, **54**, 3478 (1932). [c] Carothers, Bickford and Hurwitz, *ibid.*, **49**, 2408 (1927). [d] Åkerlöf, *ibid.*, **50**, 739 (1929). [e] Standard value for transposing from base pyridine to base formamide. [f] Standard value for transposing from base picoline to base pyridine. [g] Measured with quinhydrone electrode. [h] Simms, *J. Phys. Chem.*, **32**, 1128 (1928).

The Ion Product of Formamide.—The ion product of the solvent, $K_M = [M^+] [M^-]$, was determined directly by measuring the potential difference between a solution of potassium hydroxide and the standard salicylate buffer, and combining these data with those for benzenesulfonic acid measured against the standard buffer. The reaction between potassium hydroxide and formamide does not have such a great effect on the potential difference as might be expected; the potential dropped at a steady rate of about 8 mv. an hour, and a value extrapolated back to the moment at which the solution was made was easily obtained. The potential difference between 0.0976 *M* KOH and the salicylate buffer was 669.7 mv.; between 0.0303 *M* KOH and the buffer 632.2 mv. For 0.02498 *M* benzenesulfonic acid against the buffer the potential difference was 157.6 mv.; for 0.06956 *M* benzenesulfonic acid 187.0 mv. These data make possible two independent calculations of the ion product. Even combining them to pairs in such a way that the difference between the two values of the ion product is greatest, the values obtained for pK_M

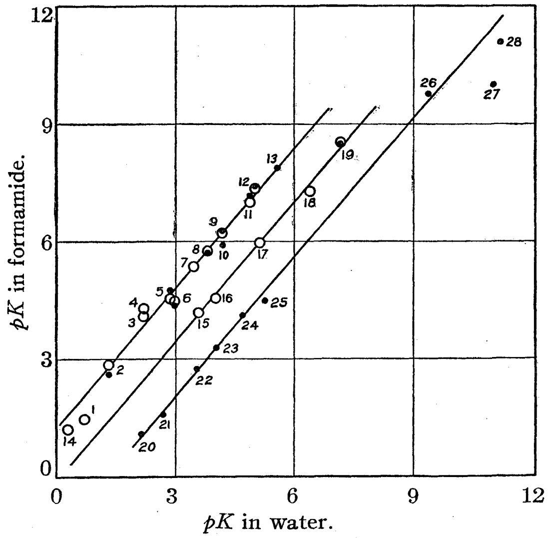

Fig. 1.—Logarithmic dissociation constants in formamide and water.

Circles, average of conductimetric values; dots, potentiometric values.

1, Trichloroacetic acid
2, Dichloroacetic acid
3, α,β-Dibromopropionic acid
4, *o*-Nitrobenzoic acid
5, Monochloroacetic acid
6, Salicylic acid
7, *m*-Nitrobenzoic acid
8, *m*-Chlorobenzoic acid
9, Benzoic acid
10, Succinic acid I
11, Propionic acid
12, Trimethylacetic acid
13, Succinic acid II
14, Picric acid
15, 2,6-Dinitrophenol
16, 2,4-Dinitrophenol
17, 2,5-Dinitrophenol
18, 2,4,6-Trichlorophenol
19, *p*-Nitrophenol
20, 2,4-Dichloroanilinium ion
21, *o*-Chloroanilinium ion
22, *m*-Chloroanilinium ion
23, *p*-Chloroanilinium ion
24, Anilinium ion
25, Pyridinium ion
26, Benzylammonium ion
27, Triethylammonium ion
28, Piperidinium ion

are: for 0.0303 M KOH and 0.02498 M $C_6H_5SO_3H$: 16.70; for 0.0976 M KOH and 0.06956 M $C_6H_5SO_3H$: 16.90. The agreement is good.

If $pK_M = 16.8$, and the equivalent conductance of a mixture of M^+ and M^- ions is 22, the value calculated for the specific conductance of the pure solvent is 9×10^{-11}.

Discussion

The data of Table V are plotted against the corresponding pK values for water in Fig. 1. Except as otherwise noted, the pK values for water for the carboxylic and cation acids are taken from the paper of Brønsted, Delbanco and Tovborg-Jensen;[4] the values for the phenols are from the Landolt–Börnstein "Tables." Some of the values for acids not included in the paper cited are for temperatures other than 20°. The slope of the curves as drawn is 1.19, *i. e.*, greater than unity. The slope usually found on plotting the logarithm of acid or basic dissociation constants in a non-aqueous solvent against the corresponding values in water is unity, and the latter slope is also predicted theoretically if the assumption is made that the effect of changing the medium is only to change the activity coefficients of the ions by virtue of the change in dielectric constant. It has been difficult to decide whether the unusual slope found in the formamide–water diagram is the result of experimental error. For the carboxylic acids, the only point which is greatly in doubt is that for trichloroacetic acid. The pK value for trichloroacetic acid in water is not too well known. The value given for formamide is probably too high rather than too low, since the change in the equivalent conductance with concentration has not been considered; consideration of this change would give the acid a larger dissociation constant. A determination of the potential difference between a trichloroacetic acid solution and the standard salicylate buffer using quinhydrone indicated that trichloroacetic acid is completely dissociated at 0.02 M, but as stated previously, the potential values with quinhydrone are not dependable. Consideration only of the pK values of the carboxylic acids obtained by potentiometric measurements would definitely give a curve with a slope greater than unity. For the phenols, the data are perhaps not numerous enough to serve as a basis for discussion; a curve drawn through the points with the same slope as for the other two acid types is at least not inconsistent with the positions of the points, with the exception of the point plotted for picric acid. A valid dissociation constant for picric acid cannot be calculated from conductivity data, since the degree of dissociation is too large. Direct comparison of the equivalent conductances at various concentrations of the three acids picric, trichloroacetic and benzenesulfonic given in Table VI shows picric acid to be much stronger than trichloroacetic acid, and nearly completely dissociated. In comparing the data it should be noted that the equivalent conductance at infinite dilution is evidently greater for trichloroacetic acid than for picric and benzenesulfonic acids. The value of pK actually calculated from the data for picric acid is given in Table V and plotted in the figure, but it is evident that it should be much less. In the curve for the cation acids, only the points for the primary amines can properly be compared, that is, the curve must be drawn through the points for the substituted anilines and benzylamine. One would of course expect a difference in slope if primary are compared with secondary or tertiary amines. A curve drawn through the points for the anilines and benzylamine must have a slope greater than unity.

TABLE VI

CONDUCTANCE OF STRONG ACIDS IN FORMAMIDE

Benzenesulfonic acid Sp. cond. of solvent 1.62×10^{-6}		Picric acid Sp. cond. of solvent 2.31×10^{-6}		Trichloroacetic acid Sp. cond. of solvent 2.87×10^{-6}	
Concn.	Equiv. cond.	Concn.	Equiv. cond.	Concn.	Equiv. cond.
0.000938	18.93	0.000789	18.58	0.000880	19.67
.001979	18.23	.001360	18.04	.001742	18.86
.002928	18.00	.002114	17.60	.002603	18.43
.006031	17.69	.004509	17.12	.005235	17.57
.01298	17.20	.009988	16.33	.01127	16.25
.02658	16.52	.02137	15.85	.02240	14.64
.05935	15.59	.04205	14.98	.04828	12.35
.1170	14.52	.09118	13.60	.1026	9.90

One is inclined to believe, then, that the anomalous slope of the curves is real. The curves have been drawn in such a way as to give all three the same slope; the possibility of some variation in slope in the three cases is not, however, excluded. The literature records another case in which the slope of a curve in a plot similar to that in Fig. 1 differs from unity, namely, the case of the singly charged cation acids in acetonitrile,[5] where the slope is only 0.47. The reason for this deviation is probably to be sought in a consti-

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[4] Brønsted, Delbanco and Tovborg-Jensen, *Z. physik. Chem.*, **A169**, 361 (1934).

[5] Kilpatrick and Kilpatrick, *Chem. Rev.*, **13**, 131 (1933).

tutional effect on the activity coefficients of the components of the solution. Such effects of structural differences in changing from one solvent to another are quite common, and must in any case be adduced to explain the difference between the carboxylic acids and the phenols. The unexpected in the case of formamide and acetonitrile is that such an effect should be operative over such a large range, and so consistently parallel to the acid strength. One usually finds a scattering of points on both sides of a line of the predicted unit slope, rather than a single line of a different slope. It is possible, of course, that the inclusion of more acids would give such a chance scattering about curves of unit slope.

The figure shows that if a carboxylic acid, a phenol, and a singly charged positive acid have the same strength in water, the phenol will be twenty-five times stronger than the carboxylic acid in formamide, and the cation acid five hundred times stronger. The difference between the carboxylic acids and the phenols must be due, according to the equation of Brønsted[6] $K_A = K_a f_A/f_B$ where K_a is a thermodynamic dissociation constant independent of the medium, K_A is the dissociation constant in the solvent concerned, and f_A and f_B are activity coefficients of the acid and the base in that solvent, to a change in the ratio of the activity coefficient of the acid to that of the base to a different extent for the two sorts of acids on passing from water to formamide. This change must be due to influences other than those of electric charge and dielectric constant, since, as far as the latter forces are concerned, the system is the same for carboxylic acids and phenols. An increase in the strength of certain phenols relative to carboxylic acids has been found for several other solvents—ethyl and methyl alcohols, *n*-butyl alcohol, acetonitrile—and has been attributed by Wynne-Jones[7] in the case of picric acid to the greater effective radius of the picrate ion compared to a carboxylate ion. The same treatment applied to the data in formamide, however, would require the phenolate ions to be smaller than the carboxylate ions.

In passing from an uncharged to a charged acid, the effect of the electric charge and dielectric constant should ordinarily become noticeable. In the particular case of a change from water to formamide, however, comparatively little effect resulting from the change in the dielectric constant should be observed. If the dielectric constant of formamide is taken as 100, the strength of a cation acid relative to an uncharged acid should be decreased by 0.125 logarithmic unit on passing from water to formamide, the calculation being made according to the equations developed by Brønsted,[6] using 5×10^{-8} cm. as the ionic radius. The actual difference found between the anilinium ions and the carboxylic acids is an increase of 2.7 units, which would correspond to a value of 15 for the dielectric constant of formamide. The dielectric constant of formamide has not been measured in this investigation, but it is hardly likely that it can be as low as this. Salts are, in general, easily soluble in formamide—simple salts such as potassium and sodium chloride are about one-fifth to one-sixth as soluble in formamide as in water, while the cobaltammines are either as soluble or often much more soluble in formamide than in water—which would indicate that it has a high dielectric constant. Experiments on the change of solubility with ionic strength of the 2–1 salts chloropentammine cobalt chloride, bromopentammine cobalt bromide and *trans*-dinitrotetrammine cobalt sulfate in solutions of potassium thiocyanate and sodium formate gave limiting slopes at infinite dilution of 0.7, 0.6 and 0.9. The results are obscured by the initial contamination of the solvent with salt, as observable in its high conductivity, but the slopes are in all three cases less than the value 1.0 calculated for a 2–1 salt in water, indicating that the dielectric constant is higher than that of water. At concentrations above 0.005 *M*, where the conductivity of the solvent is no longer such a disturbing factor, the change of conductance with concentration of the three salts potassium dichloroacetate, potassium benzenesulfonate and potassium picrate is in fair agreement with that to be expected from the Onsager equation, assuming the dielectric constant to be 90. From cryoscopic measurements Walden[8] concluded that potassium iodide, tetramethylammonium iodide, and other alkyl ammonium salts are as highly ionized in formamide as in water, indicating a high dielectric constant. The dielectric constant of formamide's nearest homolog, acetamide, is 60 in the liquid phase, and it is reasonable to expect that that of formamide should be at least as great. The increase in the strength of a cation

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[6] Brønsted, *Z. physik. Chem.*, **A169**, 52 (1934).

[7] Wynne-Jones, *Proc. Roy. Soc.* (London), **A140**, 440 (1933).

[8] Walden, *J. Chem. Soc.*, **102**, II, 26 (1912).

acid with respect to a carboxylic acid in passing from water to formamide must then be attributed to a more marked effect of the same influence which causes the increase in strength of a phenol as compared to a carboxylic acid, and to be not at all the result of a change in the dielectric constant. If the change in structure represented by a change from benzoic acid to 2,4-dinitrophenol, which have nearly the same strength in water, causes the strength to change by a factor of 25, it is evident that one cannot exclude the possibility of a further change by a factor of 20 on passing from 2,4-dinitrophenol to *p*-chloroanilinium ion.

Further light on this question would be given by a study of negatively charged acids such as acid salts of dicarboxylic acids. The theoretically predicted effect of the change in dielectric constant on the relative strengths of monocarboxylic acids and the acid salts of dicarboxylic acids is of the same (small) magnitude but opposite in sign to that predicted for a change to a cation acid. Further, one would not expect any enormous change in activity coefficient ratios in going from a mono- to a dicarboxylic acid, since these two are in any case more nearly similar than a carboxylic acid and a phenol or a carboxylic acid and an amine ion. The prediction would be, then, that a group of acids including both monocarboxylic acids and acid salts of dicarboxylic acids would show nearly the same relative strengths in formamide as in water. Unfortunately, of the normal salts of dibasic acids which were available—sodium and potassium oxalate, sodium tartrate, sodium malonate and sodium succinate—only the last named was sufficiently soluble for use in an acid salt–normal salt buffer, and the short time left did not permit the preparation of other salts. Values for the somewhat "overlapping" strength constants for succinic acid were calculated by the method of Simms[9] from the potential difference between sodium succinate–succinic acid mixtures and the standard buffer, and are given in Table V. On plotting the value for the second dissociation constant of succinic acid, the point is found to lie directly upon the curve for the other carboxylic acids, in agreement with the above prediction.

The observed difference between the carboxylic acids, the phenols and the cation acids in formamide shows that extreme care is necessary when attributing solely to a difference in charge type effects which may be due to the change in chemical type which is inextricably connected with the change in charge type.

The author wishes to express his gratitude to Professor J. N. Brønsted for help and criticism in the course of the work.

Summary

1. A simple method for the preparation of formamide having a specific conductance of 10^{-6} has been described. It consists in the distillation of formamide treated with sodium hydroxide, followed by a fractional crystallization.

2. From measurements of the conductivity of formamide solutions of free carboxylic acids and of mixtures of acids with pyridine and α-picoline, and the assumption of certain values for the equivalent conductances of the salts formed in the solutions, dissociation constants of the acids in formamide have been calculated.

3. Dissociation constants of a group of phenols in formamide have been obtained by the same procedure.

4. From measurements of the potential difference between buffer solutions of various carboxylic acids and a standard potassium salicylate–salicylic acid buffer, which was in turn compared with a benzenesulfonic acid solution, a scale of acid strengths in formamide independent of the conductivity measurements has been obtained. The dissociation constants obtained by the two methods are in agreement within the experimental error.

5. Dissociation constants of a group of singly charged cation acids have been obtained by the potentiometric method.

6. The value 10^{-17} has been found for the ion product of formamide by measurements of the potential difference between solutions of potassium hydroxide and benzenesulfonic acid and the standard buffer.

7. On plotting the negative logarithms of the dissociation constants of acids in formamide against the corresponding values in water, three straight lines of slope greater than unity, corresponding to the carboxylic acids, the phenols and the cation acids, have been obtained. The relative positions of the lines indicate that if a carboxylic acid, a phenol and a singly charged cation acid have the same strength in water, the phenol will be 25 times stronger than the carboxylic acid in formamide, and the cation acid 500 times stronger.

COPENHAGEN, DENMARK RECEIVED OCTOBER 14, 1936

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[9] Simms, THIS JOURNAL, **48**, 1245 (1926).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Molecular State of the Vapor of Acetic Acid at Low Pressures at 25, 30, 35 and 40°

BY F. H. MACDOUGALL[1]

Introduction

In a previous publication[2] it was pointed out that our knowledge of the equilibrium between single and double molecules of acetic acid in the vapor phase at room temperatures was far from being exact. The published data were discordant and could lead to only a very rough estimate of the equilibrium constants. It seemed desirable to undertake an accurate investigation of the behavior of acetic acid vapor at room temperatures and under pressures ranging from that of the saturated vapor to three or four millimeters of mercury.

The Preparation of Acetic Acid

The method of Chandlee and Hutchison[3] was employed in the purification of glacial acetic acid. A tail fraction from the final distillation was further purified by fractional crystallization until an acid melting at 16.60 ± 0.01° was obtained. Two samples prepared by Dr. Fuller had melting points of 16.612° (sample A) and 16.616° (sample B), respectively. These were used in the final measurements. The "International Critical Tables"[4] give 16.60° as the melting point of the pure acid.

In order to free the acid from dissolved gases, a 200-ml. sample was introduced into a small flask, which had been cleaned previously, dried and filled with dry nitrogen. The flask was fitted with two glass break-off seals. After the introduction of the acid, the flask was sealed and was then attached to the distillation system shown in Fig. 1 by means of one of the break-off joints. The flask in question is shown at A, Fig. 1. When the entire system had been evacuated and flamed out, so that over a period of twenty-four hours it was able to maintain a vacuum of the order of 10^{-5} mm. of mercury as read on the McLeod gage G, the break-off seal was broken, and the acid was distilled into one of the bulbs B. The distillation was accomplished by freezing the acid into B by means of a bath of ether and solid carbon dioxide. After the residual nitrogen had been pumped off, the acid was sublimed repeatedly in the evacuated system back and forth between the two bulbs B. After each sublimation the residual pressure due to permanent gases was read on the McLeod gage, and the system was again exhausted to 10^{-4} mm. This procedure was repeated until the residual pressure after a sublimation did not exceed 10^{-5} mm. Finally about one-half of the sample was collected in the original flask and sealed off from the distillation system. It was then ready to be connected by means of the second break-off joint to the apparatus for determining the pressure-volume data, Fig. 2.

The Experimental Apparatus for Obtaining the Density Data

The Specific Information to be Obtained.—By a suitable manipulation of this apparatus and by means of certain auxiliary operations it was possible to obtain the following three pieces of information about each sample of acetic acid employed in these experiments: (1) the pressure and (2) the volume at three different pressures at a given constant temperature and (3) the absolute quantity of acetic acid in the sample.

General Plan of the Apparatus.—In Fig. 2 there is a diagrammatic sketch of the apparatus used in making the density measurements. The three glass bulbs, A, B, C, of known volume, part of one of which, A_1, also served as one arm of a U-type differential mercury manometer, were connected to each other in series by mercury Y-seals of the usual type. Thus if B were evacuated and if A contained a sample of gas, the opening of the seal between A and B would allow free expansion of the gas from A into B. These bulbs were set into a water-bath in which the temperature could be controlled to within 0.05° between 25 and 40°. The water-bath, which was 36″ × 18″ × 18″ (91 × 46 × 46 cm.) and was made of galvanized iron, contained a large glass window on one side, through which the operation of the mercury seals could be observed. Holes were punched in the bottom of the bath for the tubes for the control of the mercury seals and for the manometer, the other arm of which was outside of the bath, and the cracks about these holes were sealed with picein wax. The metal walls of the bath were insulated with heavy felt.

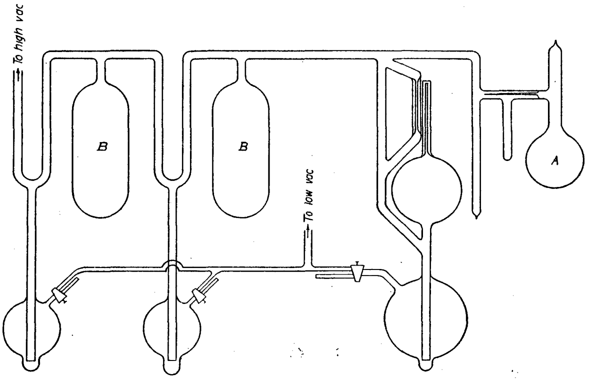

Fig. 1.—Distillation system.

The manometer used to obtain the pressure data was of the differential U type. One arm, A_1, was inside the bath,

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(1) This research has been made possible by grants from the Research Fund of the Graduate School of the University of Minnesota. Credit for the devising, constructing and testing of the apparatus should go chiefly to Dr. C. P. Roe. Dr. Donald Fuller prepared several samples of very pure acetic acid. Mr. Herbert Sargent carried out the final series of measurements.

(2) MacDougall and Blumer, THIS JOURNAL, **55**, 2242 (1933).

(3) Chandlee and Hutchison, *ibid.*, **53**, 2881 (1931).

(4) "International Critical Tables," Vol. IV, p. 6.

and the other arm, M, was outside. The inside arm was considerably larger than the outside one, so that most of the movement took place in the outside arm. The reading of the mercury level in the latter was accomplished by means of a traveling microscope which could be focused alternately on the meniscus or on a steel meter bar which was graduated in 0.5-mm. divisions and which was rigidly fixed with respect to the manometer. The microscope also contained a scale on which it was found that 13.3 divisions were equal to 0.5 mm. on the steel meter bar. Thus the position of the meniscus could be estimated to 0.004 mm., but in practice it was found that results which were reproducible to 0.01 mm. were the best that could be obtained. In order to obtain consistent results with the manometer it was found necessary to surround the greater part of the outside arm with a wooden jacket lined with wax, through which a stream of water from the bath was kept moving by means of a circulating pump. In this way the temperature of the manometer was kept constant. The manometer was calibrated for the reading of absolute pressures against the McLeod gage, G, with help of pure nitrogen as a permanent gas.

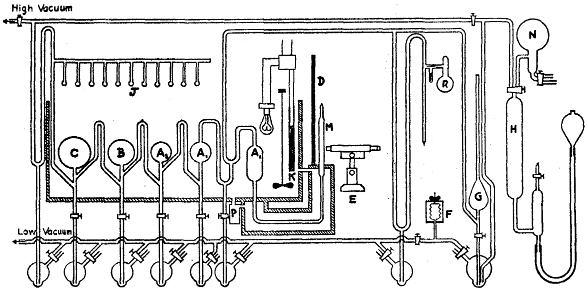

Fig. 2.

Between the bulb C and the pumps there was inserted a line of small sample bulbs of 1 to 2 ml. each. These bulbs were blown on the ends of stubs of heavy-walled Pyrex tubing of about 4 mm. inside diameter. A sample of acetic acid, following the taking of pressure readings on it, was frozen into one of the sample bulbs, sealed off from the line and subsequently analyzed for its acetic acid content by titrating with a standard barium hydroxide solution.

The remainder of the apparatus consisted of a mercury condensation pump, an oil pump, a glass reservoir *N* for nitrogen and the necessary mercury traps for the control of the McLeod gage and the mercury seals.

Details of the McLeod Gage.—This instrument, shown at G in Fig. 2, served the two-fold purpose, (1) of testing the state of evacuation of the entire density apparatus, and (2) of calibrating the differential manometer so that readings taken directly from the manometer could be converted to absolute pressure. In order to gain the necessary precision for the latter purpose, two unusual features in the construction of the gage were introduced.

The first was that the capillary tube of the ordinary McLeod gage was replaced by a tube some 30 cm. long and of approximately 6 mm. inside diameter. By means of hydrofluoric acid three fine scratches were etched on this tube, and the volume from each scratch to the sealed-off end of the tube was determined by finding its mercury capacity. The total volume of the gage was also determined with mercury. The scratches were so located that when the instrument was in use for the measurement of pressures lying in the range from 1–15 mm., the meniscus in the gage could always be set on one of the scratches and the pressure could then be read on the special comparison barometer for the gage, which was taken from the same piece of stock as the etched tube. A cathetometer with scale and vernier attached was used for this purpose. It should be noted that the special barometer, although drawing on the same mercury well as the gage, had no connection with the gage. The necessity for this arrangement is obvious when one considers the magnitude of the pressures to be measured. The high pressure readings on the gage always lay in the range from 8 to 45 cm., and it is to be noted that the precision of the gage was always much greater than that of the manometer.

The second unusual feature of the gage was an arrangement for making fine adjustments of the meniscus near the scratches. Credit is due to Dr. George Glockler for suggesting the method of doing this. The essential part of this arrangement was a short length, 13 cm., of semi-collapsible corrugated brass tubing about 2.5 cm. in diameter which was mounted between two rigidly connected brass plates. One end of the tube was soldered to one of the plates, while the other end was closed up and attached to a screw which operated in the other plate as a base. A small outlet tube, which was cemented to a suitable glass connection, was inserted in the brass plate which was fixed to the collapsible tube. This arrangement was sealed to the low vacuum side of the mercury well controlling the gage. By suitable operation of the screw, the brass tubing could be expanded or collapsed within certain limits, and corresponding changes could thus be produced in the menisci of the gage and its barometer.

In the calibration of the etched tube on the gage it was necessary to hold the tube in a position which was just inverted from that which it occupied when in use. Thus each of the volumes determined from the mercury calibration had to be given a positive correction of twice the volume of the meniscus. The data on this point were obtained in the "International Critical Tables."[5]

Details of Calibration and Use of Manometer.—The manometer, the arms of which are shown at A_1 and M in Fig. 2, was of the differential U-type; but it was unusual in that the two arms were of different diameters. This had the effect of confining the movement resulting from changes in pressure on the meniscus in the larger arm, A_1, largely to the meniscus in the smaller arm, M. The diameter of the larger arm was approximately 6 cm., while that of the smaller arm was 16 mm. The considerable size of the larger arm had the advantage of reducing the relative importance of edge effects, which presumably varied with varying conditions, to a negligible order of magnitude. The manometer was prepared by evacuation and suitable flaming out of the glassware, and subsequent vacuum distillation of the mercury into the U. When the distillation had proceeded far enough, the arm M was sealed off permanently from the still and from the high vacuum system.

Since the position of the meniscus in the smaller arm had to be read with an accuracy of 0.01 mm., if possible, a

(5) "International Critical Tables," Vol. I, p. 72.

small traveling microscope which magnified to the extent of about twenty-five diameters was mounted on a wooden frame at a convenient place in front of M. The immediate standard of comparison in the reading of heights with microscope was a steel meter bar prepared by the Gaertner Scientific Corporation of Chicago, and graduated in 0.5-mm. divisions. This was mounted rigidly just behind the smaller manometer arm as referred to the microscope. The microscope could be focused either on the meniscus or on the steel meter bar by means of a screw adjustment, and the vertical motion was controlled by a similar device.

The calibration of the manometer between 1 and 15 mm. was accomplished by admitting pure nitrogen to the system up to the desired pressure and then reading both the rise in the manometer column and the absolute pressure as indicated by the McLeod gage. The upper reaches of the manometer were calibrated after the volumes of the density bulbs had all been determined. When these volumes were known, it was necessary only to allow a sample of nitrogen to expand from one bulb to another and measure the change in the manometer and repeat the process as often as it seemed desirable in order to complete the calibration.

In the manipulation of the manometer the following procedure was used. The microscope was first set at approximately the level of the meniscus and was then focused on the steel scale. A given mark on the microscope scale, in practice 6.00, was set on the nearest scratch on the steel scale. The microscope was then focused on the meniscus. In order to get a sharp image of the latter the aid of a strip of black paper with a slit in it was required. The paper was wrapped and pasted about the tube M so that the slit was in a horizontal position and so that the whole strip could be moved up and down the tube at will. When the meniscus was under observation, the slit, which was about 2 mm. in width, was so placed with respect to the meniscus that the band of light between the meniscus and the upper edge of the slit as seen in the field of the microscope always had the same width. The position of the meniscus could then be read, and its displacement from the zero position, which was determined in the same manner, could be calculated from a direct count of the number of scratches on the steel scale past which the reference mark on the microscope scale had been moved and from the displacements of the meniscus from the reference mark. It should be mentioned that the vertical carriage of the microscope carried a small light, so that optical effects in the microscope were always the same.

Details of Temperature Control.—The temperature of the water thermostat was controlled by the suitable turning on and off of a bank of several 100-watt light bulbs, connected in parallel and immersed in the water. A small telephone relay was used to open and close the tilting mercury switch which controlled the power circuit upon which the heater lamps drew. The relay was in turn operated by the grid circuit of a Commander 71a power vacuum tube, the circuit being opened and closed by the thermal contraction and expansion of a standard mercury control placed in the bath.

Calibration of the Density Bulbs.—The final calibrations of the bulbs A_2, B, C, were made during a period when the apparatus was temporarily dismantled, but after it had once been set in place. Hence the validity of the various water and mercury calibrations was only negligibly affected by subsequent glass blowing operations which were necessary to make the seals between the various parts of the apparatus. The explanatory material in connection with the presentation of the data is sufficient to indicate the details of these calibrations.

Since the volume of A_1 or of A taken as a whole could be found only after the whole system was in place (this was on account of the impossibility of controlling precisely the amount of mercury distilled into the manometer) it was necessary to resort to the use of the expansion of pure nitrogen for this purpose. The procedure was as follows. A sample of nitrogen was admitted to A_1, the seal between A_1 and the nitrogen reservoir was closed and the pressure was read by means of the manometer. Then the seal between A_1 and A_2 was opened, and the pressure was again read. It was necessary in making calculations to take account of the change in capacity of A with pressure. This change was due to the vertical movement of the large meniscus in the manometer, and could be found directly from the movement in the small one, the diameter of which was known to be 16 mm. Now let R_1 and R_2 be the rises observed on the manometer when the gas occupies A_1 and the whole of A, respectively. From the known diameter of the outside manometer tube, a 1-mm. rise produces an increase in the volume of A of 0.2 ml. Let V_{A_2} and V_A be the zero pressure volumes of A_2 and A, respectively. Then

$$V_A = V_{A_2}\left(\frac{R_1}{R_1 - R_2}\right) - 0.2(R_1 + R_2)$$

The Experimental Procedure

The entire system was exhausted to a point where no pressure could be detected on the McLeod gage. A sample of acetic acid vapor from the reservoir of liquid acid at R was then admitted to the bulb A, and when the desired pressure was approximately reached, the mercury seal between A and R was closed. The mercury levels in the seals confining the vapor to the bulb A were adjusted to their proper marks, and after sufficient time had elapsed to ensure that the vapor had come to the temperature of the bath, the change in the manometer meniscus from its zero position was read and recorded. The seal between bulbs A and B was then opened, so that the vapor occupied the combined volumes of these two bulbs. The manometer was again read and recorded. When this procedure had been repeated for the bulb C, the seal leading to the line of sample bulbs was opened, and the vapor in the apparatus was condensed into one of them by means of liquid air. The liquid air was allowed to remain on the sample bulb for at least fifteen minutes after the meniscus in the manometer had returned to its zero position. The sample bulb was then sealed off and detached from the line. The bulb was broken while submerged in a weighed amount of barium hydroxide solution. The broken bulb was then rinsed with distilled water and the acid yet unneutralized was titrated with standard base using phenol red as indicator. The solution was boiled when near the end-point and was then cooled to room temperature under a soda–lime tube. The titration was completed under a stream of nitrogen.

Barium acetate, purified by recrystallization, was dissolved in carbon dioxide-free water, phenol red was added and the volume and concentration were adjusted to the conditions obtaining at the end-point of the titrations. This solution was stored under carbon dioxide-free air and was used in estimating end-points.

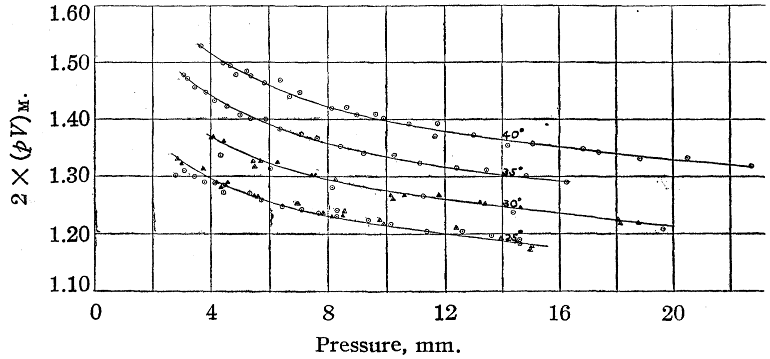

Fig. 3.—Isothermals of acetic acid vapor.

Calibration of the McLeod Gage

V_4 = total volume

V_1 = volume from uppermost scratch to the top

V_2 = volume from middle scratch to the top

V_3 = volume from lowest scratch to the top

These volumes were determined with mercury at 25°. The values obtained (corrected for inversion of meniscus by adding 0.023 ml.) were $V_4 = 326.4$, $V_1 = 3.804$, $V_2 = 7.700$, $V_3 = 11.734$ ml. The factors, $V_1/V_2 = 0.01165$, $V_2/V_4 = 0.02359$ and $V_3/V_4 = 0.03595$ are needed. These factors are represented by the symbol F.

Calibration of Manometer by Means of the McLeod Gage at 25° Using Nitrogen

R = manometer rise in millimeters

P' = pressure observed on McLeod gage in millimeters of mercury at 25° after the nitrogen in the gage had been compressed from the volume V_4 to the volume V_3 or V_2

F = V_3/V_4 or V_2/V_4 (see preceding section)

P = pressure of the gas in the system in mm. at 0° before being compressed in the gage. $P = P' \times F \times 0.9955$

f = P/R = factor used to convert manometer rise to pressure in mm. at 0°

From seventeen determinations of the value of the factor f at 25°, we obtain an average value of 1.0956. The average value of the deviations was ±0.0014. The accepted value of f at 25° was 1.096. The values of f at 30, 35 and 40° are calculated to be 1.095, 1.094 and 1.093, respectively.

Experimental Data

In the following tables, R is the rise in the manometer, p is the pressure in mm., V is the volume in ml. of the bulb or bulbs containing the acetic acid vapor, g is the weight in grams of barium hydroxide solution (0.007925 equivalent per kilogram of solution) required to neutralize the sample of acetic acid, and $(pV)_M$ is the pressure–volume product for 60.03 g. of acetic acid when 760 mm. × 22,414 ml. is taken as unity. It will be evident that

$$2(pV)_M = (1 + \alpha)T/273.1 \quad (1)$$

where α is the degree of dissociation of $(HOAc)_2$ into HOAc.

In Table I are given the complete data for two runs, one at 25° and the second at 35°. In the presentation of the rest of the experimental results we give the number of the run, the temperature, the pressure and the value of $2(pV)_M$. The work at 25 and at 35° was carried out with sample A, that at 30 and 40° with sample B of the acid prepared by Dr. Fuller.

Table I

Run	t, °C.	R	p	V	g	$2(pV)_M$
I	25	10.38	11.38	652.5	91.32	1.204
		5.88	6.44	1194		1.248
		3.16	3.46	2315		1.300
VIII	35	11.32	12.39	652.8	91.14	1.314
		6.47	7.08	1194		1.374
		3.52	3.85	2315		1.448

In Fig. 3 we have plotted the experimental values of $2(pV)_M$ against p for each of the four temperatures, 25, 30, 35 and 40°. Included in the figure are values (indicated by triangles) obtained by Dr. Roe at 25 and 30°. From curves drawn on a large scale plot, we have read off the "best" values of $2(pV)_M$ for integral values of the pressure. These values are given in Table IV.

From the chemical equation $(HOAc)_2 = 2HOAc$ we find for the dissociation constant, K_p

$$K_p = 4\alpha^2 p/(1 - \alpha^2) \qquad (2)$$

where α, the degree of dissociation, is given by the equation

$$\alpha = 2(pV)_M \times (273.1/T) - 1 \qquad (3)$$

In Table V are given values of α corresponding to the data of Table IV and the values of X_p calculated by means of equation 2.

TABLE II

Runs I to VII at 25°; VIII to XIV at 35°

Run	p	$2(pV)_M$	Run	p	$2(pV)_M$
II	10.15	1.216	IX	16.25	1.289
	5.73	1.258		9.24	1.340
	3.08	1.310		5.01	1.408
III	12.56	1.204	X	13.43	1.311
	7.09	1.242		7.65	1.366
	3.80	1.290		4.14	1.433
IV	13.59	1.196	XI	14.83	1.300
	7.68	1.236		8.44	1.353
	4.13	1.288		4.58	1.423
V	9.38	1.224	XII	11.16	1.324
	5.32	1.270		6.37	1.383
	2.81	1.302		3.46	1.456
VI	14.59	1.182	XIII	10.28	1.337
	8.31	1.230		5.88	1.400
	4.44	1.272		3.19	1.473
VII	14.61	1.190	XIV	5.33	1.401
	8.33	1.240		3.07	1.478
	4.45	1.284		1.68	1.568

TABLE III

Runs I and II at 30°; III to XI at 40°

Run	p	$2(pV)_M$	Run	p	$2(pV)_M$
I	19.63	1.208	VII	16.85	1.348
	11.25	1.265		9.63	1.409
	6.03	1.313		5.24	1.485
II	14.38	1.237	VIII	15.08	1.357
	8.14	1.280		8.63	1.402
	4.37	1.333		4.69	1.495
III	20.52	1.332	IX	14.19	1.355
	11.74	1.392		8.13	1.419
	6.39	1.468		4.43	1.499
IV	22.74	1.318	X	11.66	1.370
	12.97	1.372		6.70	1.440
	7.06	1.447		3.67	1.429
V	18.85	1.331	XI	8.50	1.407
	10.78	1.391		4.88	1.479
	5.85	1.463		2.66	1.563
VI	17.37	1.343			
	9.92	1.402			
	5.39	1.476			

TABLE IV

Values of $2(pV)_M$ Obtained from Graphs

p	25°	30°	35°	40°
3	1.319		1.471	
4	1.295	1.369	1.442	1.516
5	1.272	1.342	1.413	1.484
6	1.255	1.321	1.390	1.458
7	1.242	1.306	1.372	1.438
8	1.231	1.294	1.357	1.421
9	1.222	1.284	1.345	1.407
10	1.214	1.275	1.334	1.396
11	1.208	1.267	1.325	1.386
12	1.201	1.260	1.317	1.378
13	1.194	1.253	1.310	1.370
14	1.188	1.248	1.303	1.364
15	1.182	1.242	1.297	1.358
16		1.236	1.292	1.351
17		1.230		1.346
18		1.225		1.340
19		1.219		1.335
20		1.213		1.330
21				1.325
22				1.320
23				1.316

Since the saturated vapor pressures of acetic acid (see a later section of this paper) are 15.5 at 25°, 20.6 at 30°, 27.0 at 35° and 35.2 at 40°, it will be observed that the pressures recorded in Tables II and III for 25 and 30° approach quite closely the saturation pressures whereas for 35 and 40° the highest pressures measured are approximately 60% of the saturation pressures. It will be noticed that at 25 and 30° the calculated values of K_p fall off rapidly as the saturated pressure is approached. This may be due to an increasing deviation from ideal behavior, but whatever the reason may be, it seems plausible to derive the best value of K_p for 25° from the values for pressures in the range 3 to 9 mm. and the best value of K_p for 30° from the values for pressures in the range 4 to 11 mm. For 40° the best value of K_p was taken to be the average of the values corresponding to pressures from 10 to 23 mm. On this basis, we obtain

K_p at 25° = 0.547 mm. K_p at 35° = 1.37 mm.
K_p at 30° = 0.909 mm. K_p at 40° = 2.08 mm.

When $\log_{10} K_p$ is plotted against $1/T$, the points obtained fall, within the experimental error, on a straight line given by the equation

$$\log_{10} K_p = 11.789 - (3590/T) \qquad (4)$$

The values of K_p calculated by means of equation (4) for 25, 30, 35 and 40° are, respectively, 0.557, 0.881, 1.37 and 2.10 mm.

The Measurement of the Saturated Vapor Pressure of Acetic Acid

The density bulbs and the line leading to the mercury seal separating the reservoir R from the density bulbs were exhausted as completely as possible. After the temperature of the bath had been constant for fifteen minutes, the height of the mercury meniscus in the manometer was read. With the pump going, the mercury seals separating

Table V

Degree of Dissociation and Dissociation Constant

P, mm.	25° α	25° K_p	30° α	30° K_p	35° α	35° K_p	40° α	40° K_p
3	0.208	0.543			0.304	1.22		
4	.186	.573	0.233	0.919	.278	1.34	0.322	1.85
5	.165	.560	.209	.914	.252	1.36	.294	1.89
6	.150	.552	.190	.899	.232	1.37	.272	1.92
7	.138	.544	.177	.906	.216	1.37	.254	1.93
8	.128	.533	.166	.907	.203	1.38	.239	1.94
9	.120	.526	.157	.910	.192	1.38	.227	1.96
10	.112	.508	.149	.908	.182	1.37	.218	2.00
11	.107	.510	.142	.906	.174	1.37	.209	2.01
12	.100	.485	.135	.891	.167	1.38	.202	2.04
13	.094	.464	.129	.880	.161	1.38	.195	2.06
14	.088	.437	.124	.875	.155	1.38	.190	2.10
15	.083	.416	.119	.862	.150	1.38	.185	2.13
16			.114	.843	.145	1.37	.178	2.09
17			.108	.802			.174	2.12
18			.104	.787			.169	2.12
19			.098	.737			.164	2.10
20			.093	.696			.160	2.16
21							.156	2.10
22							.151	2.05
23							.148	2.06

(1) the line of sample bulbs from the high vacuum line, and (2) the line of sample bulbs from density bulb C, were closed. Acetic acid vapor from the reservoir R was admitted to the bulbs by opening the seal between the reservoir and the line leading to the density bulbs. Cold water was allowed to run over bulb C until a sufficient amount of acetic acid had condensed and collected above the mercury surface of the seal separating bulb C from the line of sample bulbs. The seal between the line leading to the reservoir and the bulb A_1 was then closed. The bath was again brought to the original temperature, and, after thirty minutes had elapsed to allow the system to become uniform and constant in temperature, the height of the manometer meniscus was read.

The seal separating the line of sample bulbs from the bulb C was opened and the acetic acid in the bulb system was frozen into one of the sample bulbs by means of liquid air. After the sample bulb had been cooled for fifteen minutes the height of the manometer meniscus was again read as a check on the original reading.

Subsequent runs were made using this same sample of acid. The acid was frozen into a sample bulb and, while it remained cooled by the liquid air, the seal separating the system from the high vacuum line was opened and the entire sample bulb and density bulb system was subjected to evacuation for thirty minutes, although the manometer readings taken during this time showed negligible changes. The seal separating the system from the vacuum line was closed, and the sample of acid was transferred from the sample bulb to the density bulbs by removing the liquid air and running cold water over one of the density bulbs. The seal between the density bulb system and the sample bulbs was then closed, confining the vapor to the bulbs inside the water bath.

In each run enough acid was condensed into the system so that a visible amount of liquid was present after equilibrium had been established. In practice it was found that liquid acetic acid collected on the surface of the mercury in the inner manometer arm, causing an indeterminate error in the manometer reading. It was impossible to avoid this entirely, although it was minimized by using as little excess acid as possible. The maximum thickness of this layer of liquid on the surface of the mercury was estimated to be 1 mm. and the usual thickness much less than 1 mm.

The thermometer used in these experiments was compared with thermometer 40316 in Bureau of Standards set 19691, marked C343, and was found to require a correction of −0.06° at 25 and 30°, of −0.03° at 35° and of −0.07° at 40°.

Table VI

Data on Vapor Pressure of Acetic Acid

t = 24.94

Manometer rise	Vapor pressure
14.20	15.56
14.13	15.48
14.09	15.44
Average	15.49

t = 34.97

Manometer rise	Vapor pressure
24.75	27.08
24.72	27.04
24.56	26.87
24.58	26.89
24.50	26.80
24.60	26.91
24.65	26.97
Average	26.94

t = 29.94

Manometer rise	Vapor pressure
18.90	20.70
18.84	20.63
18.76	20.54
18.71	20.49
18.70	20.48
Average	20.57

t = 39.93

Manometer rise	Vapor pressure
32.20	35.19
32.19	35.18
31.95	34.92
31.95	34.92
Average	35.05

In Table VI are given the results obtained for the vapor pressure of acetic acid at 24.94, 29.94, 34.97 and 38.93°. We readily obtain for 25.00°, 15.54 mm., for 30.00°, 20.64 mm., for 35.00°, 26.98 mm. and for 40.00°, 35.18 mm. The "International Critical Tables"[6] give for these temperatures 15.6, 20.6, 26.9, 34.8. The equation

$$\log_{10} p_s(\text{in mm.}) = 8.5723 - (2200/T) \qquad (5)$$

reproduces our results very accurately, the average deviation corresponding to ±0.04 mm., which is well within the experimental error.

Thermochemical Calculations

Heat of Dissociation.—Representing by ΔH the heat absorbed in the dissociation of a mole of $(HOAc)_2$ into two moles of HOAc, we find from equation (4) for a temperature between 25 and 40°

$$\Delta H = 16{,}400 \text{ cal.} \qquad (6)$$

We judge that this value may be in error by as much as 800 cal.

Heat of Vaporization.—If we assume that the saturated vapor of acetic acid does not deviate much from an ideal gas, we can calculate the latent heat of vaporization of one mole (120 g.) of acid by means of the equation

$$L = -(1 + \alpha)R\frac{\mathrm{d}\log_e p_s}{\mathrm{d}\,(1/T)} \qquad (7)$$

In view of equation (5), we obtain

$$L = 10{,}060(1 + \alpha) \qquad (8)$$

Inserting in equation (2) the measured values of K_p and of p_s, we find for 25°, $\alpha = 0.093$; for 30°, $\alpha = 0.104$; for 35°, $\alpha = 0.112$ and for 40°, $\alpha = 0.121$. From equation (8) we obtain

L at 25° = 11,000 cal.
L at 30° = 11,110 cal.
L at 35° = 11,190 cal.
L at 40° = 11,270 cal.

Brown[7] obtained by direct measurement at 117.4° a value of 97.05 calories per gram, equivalent to 11,650 calories per 120 g. of the acid.

From Ramsay and Young's[8] measurements of the saturated vapor pressure, p_s, at 100, 110, 120 and 130°, we readily find for 118°, assuming the vapor to be ideal, $L = 9344\ (1 + \alpha)$. Combining this result with that of Brown we infer that at 118° and 1 atm. the value of $(1 + \alpha)$ is 1.247. On the other hand, the value of pV at 118° and 1 atm. obtained by Ramsay and Young[9] is about 0.319 liter-atm. per gram which leads to a value of $(1 + \alpha)$ equal to 1.194. The difference in the calculated values of $(1 + \alpha)$ is probably due to an appreciable departure from ideal behavior when the vapor is saturated.

Summary

1. Values of pV have been determined for the vapor of very pure acetic acid at 25, 30, 35 and 40° and at pressures as low as 3 mm.

2. The equilibrium constant for the reaction: $(HOAc)_2 \rightleftharpoons 2HOAc$, has been determined for 25, 30, 35 and 40°. The heat of dissociation is calculated to be about 16,400 cal.

3. The vapor pressure of acetic acid has been measured at 25, 30, 35 and 40°. The heat of vaporization per 120 g. of acid at these temperatures is calculated to be 11,000, 11,110, 11,190 and 11,270 cal.

MINNEAPOLIS, MINN. RECEIVED SEPTEMBER 4, 1936

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(6) "International Critical Tables," Vol. III, p. 217.

(7) Brown, *J. Chem. Soc.*, **83**, 987 (1903).

(8) Landolt-Börnstein, "Tabellen," 1912, p. 388.

(9) "International Critical Tables," Vol. III, p. 437.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Use of Chromous Sulfate in the Removal of Oxygen from a Stream of Gas. A Comparison with Other Oxygen Absorbents

BY HOSMER W. STONE

The frequent need of a stream of inert gas of low oxygen content led the author to the observation that not only did the commercial nitrogen contain appreciable quantities of oxygen, but even the gas from the liquid carbon dioxide was contaminated. The usual methods of purifying the nitrogen proved unsatisfactory. This, together with the lack of data on the relative effectiveness of oxygen-absorbing reagents, led to the work reported in this paper.

A cylinder of commercial nitrogen, containing 0.3% oxygen, was chosen for reference. This gas was passed through the apparatus containing the absorbent to be tested, at a constant rate. The time which elapsed before sufficient oxygen escaped the absorbing reagent to color a very sensitive oxygen indicator has been taken as a measure of the effectiveness of that absorbent for removing oxygen from the stream of nitrogen. All of the reagents allowed detectable quantities of oxygen to pass, but in the case of the chromous solution the amount was so small that this reagent was selected as a standard for the comparison of the others. If the time required to color the indicator by the oxygen escaping the chromous sulfate absorbent is taken as 100%, then under the conditions used, none of the other reagents investigated exceeded 4% in their relative efficiency. The work deals with the relative rates of oxygen absorption and makes no attempt to compare the completeness of the reaction at equilibrium conditions.

Apparatus and Reagents

The illustration of the apparatus used requires some explanation. A single cylinder of commercial nitrogen, containing 0.3 volume percentage of oxygen, was used throughout the investigation. The flow of gas through the apparatus was maintained at a rate of 300 ml. per minute by the adjustment of a pressure reducing valve at the nitrogen cylinder. A pressure of about eight pounds per square inch (414 mm.) was required to produce the desired rate of gas flow. This rate refers to that which was measured on the flowmeter after the oxygen had been absorbed.

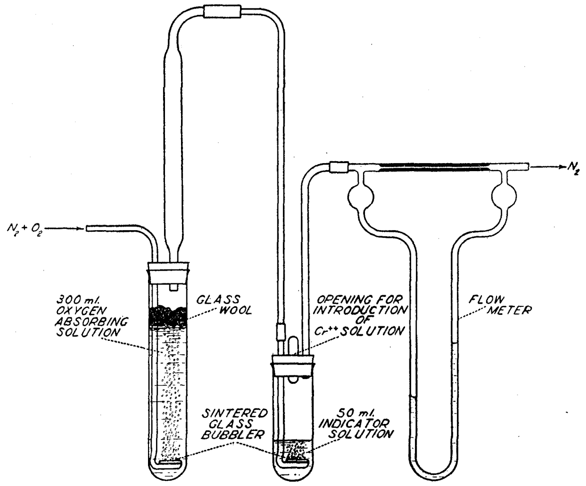

Fig. 1.—Apparatus for the determination of the efficiency of oxygen absorption.

The nitrogen entered the absorbing solution through a sintered glass bubbler. The bubbler, a product of the Jena Glass Works, catalog number 33cG4, was listed as having a pore size to from five to ten microns. The glass wool above the absorbing solution was introduced to overcome the troublesome foaming which occurred when the pyrogallate and the hyposulfite reagents were used as absorbents. The glass wool, together with the tower above it, prevented appreciable amounts of the absorbing solution from being carried into the indicator. The ammoniacal cuprous ammonium chloride reagent liberated so much ammonia gas that it was necessary to introduce a wash bottle containing 2 *N* sulfuric acid between the absorbing solution and the indicator when this reagent was used. When this was not done the basic effect of the ammonia changed the indicator from red to amber at a *p*H of from 6 to 7 and precipitated the hydroxides of the chromium ions.

The Jena glass bubbler in the indicator tube was listed as having pore sizes varying from 100 to 120 microns in diameter. A coarser pore size was used here than in the absorbing tube to reduce the amount of back pressure.

The indicator solution was 0.05 *M* in sulfuric acid and about 0.00025 *M* in the *o*-semidine indicator. The *o*-semidine used in the preparation of the indicator was *o*-amino-*m*-ethoxydiphenylamine and was prepared as described by Jacobsen.[1] A hydrochloric acid solution of this *o*-semidine[1] was oxidized by ferric chloride and the oxidation product recrystallized and thoroughly dried. A stock solution of this oxidation product dissolved in glacial acetic acid was used in making the indicator solution. The properties of this oxidation–reduction indicator were discussed by the author before the Division of Physical and Inorganic Chemistry at the 90th meeting of the American Chemical Society, San Francisco, California, August 19 to 23, 1935. This work has not yet been published.

The indicator was decolorized by the addition of 0.023 *N* chromous sulfate solution. (This chromous sulfate reducing reagent was used to decolorize the indicator in all of the experiments and should not be confused with the chromous reagent used as an oxygen absorbent.) At the end-point of the reaction in which the indicator was reduced by the chromous ion, one drop of the reducing reagent was sufficient to remove the last trace of indicator red and leave a slight excess of unoxidized chromous ion. This excess of chromous ion had to be oxidized by oxygen escaping the absorbing reagent before an indicator color change could appear.

The sensitivity of the indicator was determined by measuring the amount of distilled water, saturated with air, which was required to oxidize the slight excess of chromous ion at the end-point and to produce a distinct color change in the indicator. It required 0.2 ml. of this water which was 0.001 *N* in dissolved oxygen.

Procedure

The following method was used in testing each of the oxygen absorbing reagents. (1) 300 ml. of the reagent to be tested was placed in the absorbing tube. (2) The pressure of the nitrogen gas entering the apparatus was regulated to produce a flow of 300 ml. per minute as indicated on the flow meter. (3) After fifteen minutes of gas flow at this rate and with the gas still flowing the plug in the stopper of the indicator tube was removed and the indicator reduced by a dropwise addition of the 0.023 *N* chromous sulfate solution. Contamination by oxygen of the air during this operation was prevented by the gas which escaped from the opening.

(4) The opening in the stopper of the indicator tube was then closed and the gas allowed to flow through the system until the oxygen escaping the absorbing reagent was sufficient to produce a faint color change in the indicator. This first faint color change was the starting point in all of the runs at which the recorded number of

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[1] Paul Jacobsen, *Ann.*, **287**, 145 (1895); *ibid.*, **427**, 76 (1922).

drops of the reducing agent were added to the indicator solution. The desired number of drops of the 0.023 *N* chromous sulfate reagent were then added to the indicator and the time interval before the first faint color appeared in the indicator determined. From this observation, the time required to color the indicator, per drop of chromous reagent, was calculated.

(5) The indicator was again decolorized by the addition of a recorded number of drops of the chromous reducing agent and the time interval again determined. This operation was repeated until a nearly constant time interval was obtained. It usually required at least forty-five minutes of gas flow at 300 ml. per minute before this nearly constant value was reached. Up to this time, the intervals were shorter, due to the necessity of removing the air from the system. The data reported represent successive experiments on a single solution of the reagent, obtained after the nearly constant interval had been reached.

The potassium pyrogallate solution which was tested was prepared according to the specifications of Wolf and Krause,[2] who recommend a solution containing 18% potassium hydroxide, 15% pyrogallol and 67% water as absorbing oxygen most rapidly. The reagent containing 50% potassium hydroxide is the approved reagent for absorbing oxygen because it yields less carbon monoxide during its oxidation, even though it is slower in its absorption of oxygen.

The pyrogallate solutions gave trouble by foaming, by forming a precipitate in the glass filter plates, and by yielding a gaseous decomposition product which modified the indicator change. The foaming was overcome by the use of the glass wool. The clogging of the filter plate and the resulting diminution in the flow of gas was taken care of by increasing the nitrogen pressure. The undesirable effect of the decomposition gases on the indicator was minimized by using freshly prepared pyrogallate solution.

The interval of time required to bring back the color to the indicator was 0.30, 0.325, 0.325, 0.28, 0.33, 0.30, 0.28, 0.28 minute per drop of 0.023 *N* chromous sulfate solution. These values represent successive determinations on the same solution after the time interval had become nearly constant.

The oxygen-absorbing sodium hyposulfite reagent recommended by L. F. Fieser[3] consisted of 48 g. of sodium hyposulfite, 12 g. of β-anthraquinone–sodium sulfonate, 40 g. of sodium hydroxide and 300 ml. of water. He states that a train of three Friedrichs bottles containing this solution removed all traces of oxygen gas, even when the velocity was at its maximum. He also reported that, in a bubbling pipet, the absorption of oxygen by this reagent was more rapid than by the pyrogallate reagent.

This reagent, as the oxygen absorbent in a series of successive experiments on the same solution and using from six to fifteen drops of 0.023 *N* chromous reagent, showed the following time intervals in minutes per drop: 0.50, 0.50, 0.50 and 0.47.

The ammoniacal cuprous ammonium chloride reagent used to absorb the oxygen was prepared as directed by Badger.[4]

Five hundred ml. of 15 *N* ammonium hydroxide was mixed with an equal volume of ammonium chloride solution saturated at 23°. Sixty grams of copper ribbon (0.1 by 1 mm.) was immersed in the solution and air blown through the reagent until it became a dark blue in color. Nitrogen was then bubbled through the mixture for several hours so that much of the cupric ammonium complex was reduced to the cuprous form. This solution was siphoned into the absorption tube of the apparatus and the capacity of the absorbing reagent determined by titration against an acidified solution of potassium permanganate.

In experiments with this absorbent, the drops of 0.023 *N* chromous reagent added to the indicator solution varied from eleven to thirty. The minutes required to return the color to the indicator solution per drop of chromous reducing agent were 0.49, 0.36, 0.55, 0.57, 0.40, 0.55, 0.59. As in the other cases these data represent a series of successive experiments where the rate of nitrogen flow was 300 ml. per minute.

The chromous sulfate–sulfuric acid absorption solution was prepared in accordance with the recommendations of Stone and Beeson.[5] In this method the chromous sulfate is obtained by reducing a sulfuric acid solution of violet chrome alum with zinc amalgam in a Jones reductor.

Two series of determinations were made with this reagent in the absorbing tube. One series was carried out before any of the other reagents were tested and another series, with a fresh solution, after the other oxygen absorbents had been evaluated. The two series served as a check on the constancy of the technique used in conducting the experiments. The time interval required to color the indicator per drop of chromous reagent added was so long that only this one drop was used in these experiments. The series of experiments carried out before the other reagents were tested gave values of 13, 12, 12.5 minutes per drop of chromous to coloration of the indicator. The runs on the second solution, made after the other absorbents had been tested, gave 11.5, 13, 13.5, 14.25 minutes per drop.

The data obtained with the various reagents tested are summed up in the table.

A COMPARISON OF THE EFFICIENCIES OF VARIOUS OXYGEN ABSORBENTS, USING 300 ML. OF THE ABSORBING REAGENT, AND A RATE OF FLOW OF GAS OF 300 ML. PER MINUTE

Absorbent used	Normal capacity	Average drops of Cr^{++}	Average min. to coloration	Minutes per drop
Potassium pyrogallate	6.3	13.2	3.97	0.30
Quinone hyposulfite	4.8	10.2	5.0	.49
Cuprous chloride	1.2	19.3	9.39	.49
Chromous sulfate	0.4	1.0	12.82	12.82

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[2] Otto Wolf and Arthur Krause, *Arch. Warmenwirt*, **10**, 19–21 (1929).

[3] L. F. Fieser, THIS JOURNAL, **46**, 2639–2647 (1924).

[4] W. L. Badger, *Ind. Eng. Chem.*, **12**, 161–164 (1920).

[5] H. W. Stone and C. Beeson, *Ind. Eng. Chem., Anal. Ed.*, **8**, 188–190 (1936).

The values under the heading "Normal Capacity" in the table present the maximum concentration in equivalents per liter with respect to the reaction with oxygen. For the pyrogallate solution, the normality is based on von Kovács-Zorkoczy's[6] statement as to the capacity of pyrogallol and the quantity of this reagent used. The concentration of the hyposulfite reagent is based on a determination of the purity of the reagent and the amount used. The ammoniacal cuprous ammonium chloride was titrated with permanganate before and after the data were taken and found to change from 1.16 to 0.98 *N*. The chromous sulfate value is based on the amount of chrome alum used in preparing the reagent, though titration before and after one series of runs showed a variation from 0.31 to 0.12 *N* during the experiment.

Discussion

A comparison of the values set forth in the last column of the table shows that, under these conditions, chromous sulfate is at least twenty-five times more rapid in absorbing oxygen than any of the other reagents used.

No difference was found between Fieser's reagent and the ammoniacal copper chloride. The difference between these reagents and the pyrogallate is sufficient to prove that pyrogallate solutions are slower in their absorption of oxygen. Moreover, this superiority of the hyposulfite reagent over the pyrogallate is in agreement with the work of Fieser which has been quoted previously.

No data are given concerning the precise changes in the concentrations of the absorbing agents during the time that their relative efficiencies were determined. This is because variations in the concentration were found to have no effect on the results within the limits of the experimental observations. 0.3 *N* chromous sulfate was no more effective in absorbing oxygen in the apparatus than a 0.1 *N* solution. In either case the reaction appeared to be as rapid as one between ions.

Experiments in this Laboratory[7] showed that the rate of absorption of oxygen by chromous sulfate solutions, in an apparatus such as Fieser used, is too rapid to be measured. The concentration of the chromous sulfate was varied from 0.4 to 0.01 *N* and the concentration of the sulfuric acid from 3.0 to 0.12 without obtaining any measurable change in rate of absorption.

Since each of the reagents used in a particular series of determinations yielded a nearly constant interval of time for coloring the indicator, rather than a decreasing interval, it is clear that the change in concentration of the reagent, due to oxygen absorbed, did not affect the data presented.

It is the writer's opinion that the rate of reaction of the dissolved oxygen with the absorbent is so much greater than the rate at which the oxygen is dissolved by the bubbling process that the former factor can be neglected entirely. This opinion leads one to conclude that the high relative efficiency of the chromous reagent, as compared to the other absorbents, may be at least partially explained by the fact that the physical properties of the chromous solution favor a more rapid solution of the oxygen in the chromous reagent than in the other solutions.

In addition to the advantage of absorbing the oxygen at a much faster rate than the other reagents, the chromous sulfate may be used to reduce the oxygen content of carbon dioxide and other acid gases which could not be treated by the reagents which are basic. The liberation of ammonia gas by the ammoniacal cuprous chloride, the clogging of the filter plate pores by the pyrogallate and hyposulfite reagents, the formation of a troublesome foam, and the evolution of gaseous decomposition products are disadvantages found in working with the other oxygen absorbents which were not met with when using the chromous sulfate.

The desirability of comparing the rates of oxygen absorption, by these reagents, over a wide range of conditions was recognized early in the work. Many experiments were conducted at widely varying rates of gas flow, with longer absorption columns, and with air in place of the commercial nitrogen. Though the results of these experiments indicated that relative rates similar to those reported in this paper held over a wide range of conditions, satisfactory comparisons were obtained only under the method and system described. Serious difficulties arising from fundamental differences in the properties of the absorption reagents and from the character of the indicator led to the abandonment of further attempts at quantitative comparisons.

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(6) Etelka von Kovács-Zorkoczy, *Biochem. Z.*, **162**, 161 (1925).

(7) Ramsey, King and Klain, unpublished work.

Summary

1. A new oxidation–reduction indicator has been shown to be a satisfactory reagent for the detection of small amounts of oxygen.

2. A method of comparing the rates at which various reagents absorb oxygen from a stream of nitrogen has been described.

3. Chromous sulfate–sulfuric acid solutions have been shown to absorb oxygen from a stream of nitrogen at an unusually high rate under certain conditions. Adopting the results obtained with chromous sulfate reagents, as a standard, the relative oxygen-absorption rates as found in this same apparatus under similar conditions may be expressed as follows: potassium pyrogallate 2.3%, ammoniacal cuprous ammonium chloride 4%, alkaline sodium hyposulfite β-anthraquinone-sodium sulfonate 4%, and chromous sulfate–sulfuric acid reagent 100%.

LOS ANGELES, CALIF.

RECEIVED JULY 15, 1936

[CONTRIBUTION FROM THE DOHME LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF MARYLAND]

A Study of Promoter Action. The Oxidation of Aniline Sulfate by Hot, Concentrated Sulfuric Acid in the Presence of Copper and Mercury Sulfates[1]

BY M. M. HARING AND H. H. KAVELER

Oxidation by hot, concentrated sulfuric acid has many applications, of which one of the more important is the analytical method of Kjeldahl.[2] Numerous modifications of the method have been published, the use of copper and mercuric sulfate catalysts being emphasized. However, only Bredig and Brown[3,4] have made a study of the kinetics of the reaction and of the relation between catalytic effect and amount of the catalyst. They observed, among other things, that mixed copper and mercuric sulfates exhibited a catalytic effect greater than the additive value. However, they published only one set of data on mixed catalysts. It was the primary purpose of this investigation to study a wide range of catalyst ratios and total amounts.

Reagents.—Mercuric oxide was prepared by adding the calculated amount of sodium hydroxide to a solution of c. p. mercuric chloride heated to 70°. The precipitated red oxide was washed free of alkali and chlorides and dried at 100°.

Reagent copper sulfate pentahydrate was used without further purification.

The sulfuric acid used was reagent quality (sp. gr. 1.83–1.84) and was demonstrated to be free of the heavy metals.

The aniline sulfate was the purest obtainable. Analysis by the Kjeldahl method gave 9.77% nitrogen as against 9.86% theoretical.

Apparatus.—The apparatus used was similar to that described by Bredig and Brown.[3,4] The thermostat was modified to accord with modern practice. It maintained the experimental temperature of 275° to ± 0.1°. The reaction vessel and gas measuring apparatus are shown in Fig. 1, the volume of the reaction bulb being about 75 cc.

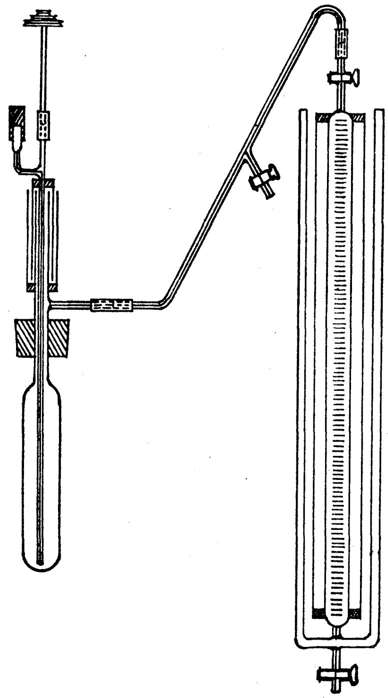

Fig. 1.

All weights and other measuring devices were checked for precision.

Procedure.—The desired quantity of the catalyst was introduced into the reaction flask through a long-stemmed funnel, followed by 50 cc. of sulfuric acid. After insertion in the bath, the mixture was stirred for one hour.

The stirring was stopped and the desired amount of a standard solution of aniline sulfate in sulfuric acid (about

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[1] Abstracted from a thesis submitted by H. H. Kaveler to the Graduate School of the University of Maryland in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Kjeldahl, *Z. anal. Chem.*, **22**, 366 (1883).

[3] Brown, Dissertation, Heidelberg, 1903.

[4] Bredig and Brown, *Z. physik. Chem.*, **46**, 502 (1903).

TABLE I

NO CATALYST

	1	2	3	V	K
45	0.4	...	...	..	...
60	.5	...	...	..	...
90	.8	...	...	..	...
120	1.0	...	1.1	1.05	0.554
150	1.3	...	1.4	1.35	.553
180	1.6	1.6	1.5	1.57	.563
240	2.1	2.1	2.0	2.07	.557
300	2.6	2.6	2.6	2.60	.553
360	3.1	3.3	3.1	3.17	.569
				Av.	.558

TABLE II

MERCURIC OXIDE CATALYST

	1 unit		2 units		4 units		8 units	
t	V	K	V	K	V	K	V	K
5	0.5	6.45	0.5	6.45	0.9	11.52	0.8	10.14
10	1.0	6.45	1.1	6.91	1.8	11.52	1.7	10.82
15	1.5	6.45	1.8	7.68	2.8	11.98	2.7	11.52
25	2.4	6.17	3.1	7.92	4.8	12.46	5.7	14.84
45	4.5	6.50	6.2	8.96	9.2	13.46	12.9	19.14
60	6.1	6.60	8.8	9.63	12.8	14.20	18.8	21.30
90	9.4	6.86	14.5	10.82	21.8	16.68	29.2	22.98
120	13.1	7.28	20.2	11.53	29.5	17.41	39.5	23.55
150	..	..	25.9	12.09	36.1	17.50	47.9	24.39
180	20.6	7.84	31.6	12.55	42.3	17.53	..	...
		Av. 6.65		9.80		14.78		21.14

TABLE III

COPPER SULFATE PENTAHYDRATE CATALYST

	1 unit		2 units		4 units		8 units	
t	V	K	V	K	V	K	V	K
5	0.2	2.30	0.5	6.45	0.7	8.75	1.1	13.81
10	0.6	3.68	1.2	7.60	1.4	8.98	1.8	11.52
15	1.0	4.30	1.8	7.68	2.5	10.75	2.6	11.05
25	2.0	5.16	3.4	8.85	4.2	10.87	4.7	12.16
45	4.7	6.76	7.2	10.44	8.5	12.39	10.5	15.40
60	7.1	7.71	10.5	11.55	12.3	13.62	15.5	17.43
90	11.5	8.47	16.9	12.70	19.7	14.97	25.4	19.73
120	15.9	8.94	22.7	13.07	26.4	15.41	34.4	20.72
150	20.1	9.18	27.7	12.99	32.7	15.64	42.0	20.86
180	23.9	9.21	31.7	12.59	38.5	15.70	48.0	20.78
		Av. 7.65		11.56		13.66		17.52

8% by weight) was run from a weight buret into the well on the side-arm of the stirrer. This was followed immediately by 1.0–1.5 cc. of sulfuric acid and the run started. The pressure was maintained at the atmospheric value throughout a run. 0.05–0.09 g. of aniline sulfate was used in all experiments. The weights of catalyst used were always 0.0305 g. of mercuric oxide and 0.0351 g. of copper sulfate pentahydrate or integral multiples thereof. These unit weights are in the same ratio as the molecular weights. The maximum amount of catalyst used in any experiment was a very small fraction of the solubility in sulfuric acid.[5]

Data and Calculations

For comparison purpose, all gas volumes were reduced to a weight of 0.0500 g. of aniline sulfate by proportion. Bredig and Brown[3,4] showed this procedure to be valid. All volumes likewise were corrected to standard conditions. From two to nine runs (in most cases four) were made for each quantity of catalyst. The volumes for each case were averaged at corresponding times, plotted on a large scale and the best smooth curve drawn. All data given below, save Table I, were obtained in this manner. Table I shows all the data. The variation in volumes from the mean for corresponding times for the different members of a series was seldom in excess of 5% and usually much less. In the following tables t is for times in minutes, V is the average volume in cc. and K is the monomolecular reaction constant for times in minutes, as obtained from $K = (2.303/t) \log (C_0/C)$. Purity of the aniline sulfate was considered in calculating C_0. The amount of catalyst is expressed in terms of unit weights as defined previously. The average K is based on the values at 45, 60 and 90 minutes. Early values for K for catalyzed reactions are too unsteady to give a good comparison. All values of K are included in the average for the uncatalyzed reaction. K values in all tables are $\times 10^4$.

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(5) See "International Critical Tables," Vol. IV, p. 42.

Table IV gives the ratios between the average velocity constants catalyzed and uncatalyzed.

TABLE IV

MERCURIC OXIDE CATALYST

1 unit	2 units	4 units	8 units
11.7	17.5	26.4	37.8

COPPER SULFATE PENTAHYDRATE CATALYST

1 unit	2 units	4 units	8 units
13.7	20.7	24.2	31.4

The data of Tables I, II and III are portrayed graphically in Figs. 2 and 3.

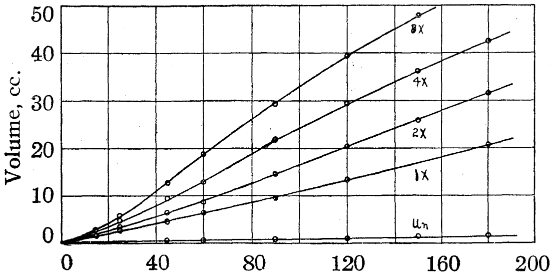

Fig. 2.—Mercuric oxide catalyst: x, units of catalyst; Un, uncatalyzed.

The data for mixed catalysts are given in the following tabulation. The various mixtures are identified thus: 1Hg–8Cu means one unit weight (0.0305 g.) of mercuric oxide and eight unit weights (0.2808 g.) of copper sulfate pentahydrate; and so on. Other symbols have the same significance as before.

TABLE V

	3Hg–3Cu		5Hg–1Cu		2Hg–4Cu		4Hg–2Cu	
	V	*K*	*V*	*K*	*V*	*K*	*V*	*K*
5	1.7	21.7	2.6	33.2	2.0	25.8	2.5	32.2
10	4.7	30.4	5.1	32.9	4.6	29.7	5.0	32.5
15	7.0	30.4	7.9	34.4	7.2	31.3	8.3	36.2
25	13.8	36.9	14.1	37.8	12.4	34.9	15.0	40.4
45	27.2	42.5	26.6	41.4	24.8	38.4	29.4	46.3
60	36.2	43.9	35.9	43.5	33.4	40.1	39.8	48.9
90	52.2	45.2	51.8	44.7	49.5	42.3	55.0	48.2
	Av.	43.9		43.2		40.3		47.8

	1Hg–1Cu		8Hg–8Cu		4Hg–1Cu		1Hg–4Cu	
t	*V*	*K*	*V*	*K*	*V*	*K*	*V*	*K*
5	1.1	13.8	3.2	41.0	2.2	28.1	1.5	19.3
10	2.5	16.1	8.3	53.5	4.0	26.0	3.0	19.4
15	3.7	16.0	14.6	65.4	6.1	26.4	4.8	20.7
25	6.8	17.3	29.9	84.9	10.9	28.8	8.6	22.6
45	13.8	20.5	53.6	93.4	22.5	34.5	17.6	26.5
60	19.2	21.8	65.8	91.1	30.2	35.8	25.0	28.4
90	29.4	23.1	82.0	82.6	44.6	37.4	39.8	32.6
	Av.	21.8		89.0		35.9		29.2

	1Hg–8Cu		8Hg–1Cu		4.5Hg–4.5Cu	
t	*V*	*K*	*V*	*K*	*V*	*K*
5	1.9	24.4	2.8	35.9	3.1	39.6
10	4.4	28.6	6.8	44.2	6.8	44.2
15	7.2	31.3	12.1	53.6	11.2	49.4
25	13.1	35.0	25.8	72.2	21.9	60.3
45	27.6	43.1	43.8	73.1	39.3	64.3
60	37.8	46.1	54.6	71.6	51.1	66.0
90	54.3	47.4	70.3	66.4	67.2	62.4
	Av.	45.6		70.4		64.3

The fact that the effect of mixed catalysts is more than additive is demonstrated by calculating the promotion factor. This is obtained by dividing the average *K* for a mixed catalyst (less *K* uncatalyzed) by the sum of the *K* values for the appropriate units of the pure catalysts (less 2 *K* uncatalyzed). Wherever these values had not been directly determined they were obtained by graphic interpolation. The promotion factors are given in Table VI.

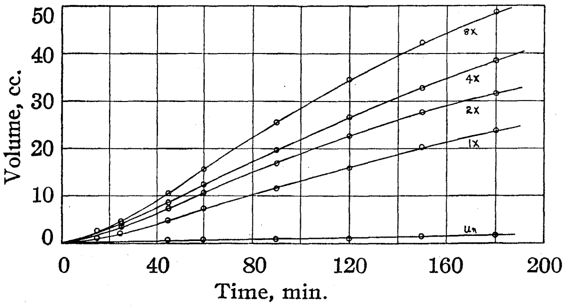

Fig. 3.—Copper sulfate pentahydrate catalyst, x, units of catalyst; Un, uncatalyzed.

TABLE VI

3Hg–3Cu	5Hg–1Cu	2Hg–4Cu	4Hg–2Cu
1.80	1.84	1.78	1.87
1Hg–1Cu	8Hg–8Cu	4Hg–1Cu	1Hg–4Cu
1.62	2.36	1.66	1.49
1Hg–8Cu	8Hg–1Cu	4.5Hg–4.5Cu	
1.95	2.52	2.22	

The effect is more apparent when graphically portrayed. This is given for the series containing six units of mixed catalyst. In Fig. 4 the volumes of gas liberated at 24, 45, 60 and 90 minutes are plotted against the Hg/Cu mole ratio. Values for six units of pure catalyst were obtained by graphic interpolation.

Discussion

The data of Tables II and III reveal that copper is a better catalyst than mercury at the lower concentrations but a poorer catalyst at the higher concentration, on a mole for mole basis. The catalytic effect increases with concentration of the catalyst, but is not directly proportional as claimed by Bredig and Brown.[3,4] However, examination of their data does not support their contention. Mixtures of the two catalysts show the same general proportionality. The mixtures with a high mercury content are better catalysts than those with a high copper content. Figure 4 shows that the most active mixture is approximately two moles of mercury to one of copper.

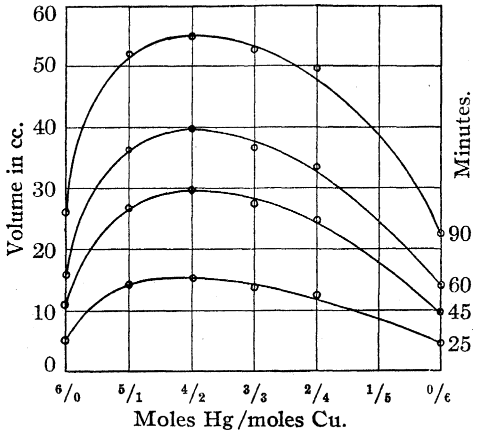

Fig. 4.—Variation of promoter effect with catalyst composition ratio and time.

Since both metals are good catalysts and all mixtures, as shown in Table VI, have activities far greater than the additive value, it is clear that this is a case of coactivation. A very interesting observation is that the promoter effect drops off with time.

Bredig and Brown[3,4] claimed this reaction to be monomolecular. The results of this study, particularly the data on the uncatalyzed reaction, support their contention. The values of K for the catalyzed reactions are far from constant, although they become more so, in most cases, after about an hour. Examination of Figs. 2 and 3 reveals that all curves have an inflection at about forty minutes. The curves of Bredig and Brown show the same inflection. This might be explained in four ways. (1) The cooling effect of introducing the sample might slow up the reaction for a brief interval. (2) The sample, due to inadequate stirring, might not be uniformly distributed immediately. (3) An undisturbed rate of gas evolution might not be obtained while the gas concentration in the mixture increased to saturation. (4) The inflection is real and due to a series of consecutive reactions of differing velocity. (1), (2) and (3) would be errors inherent in the method. As such they would be subject to variation. That two groups of investigators working entirely independently should duplicate these factors is highly improbable. Explanation (4) is almost certainly correct. Heated to 275°, a solution of aniline sulfate in sulfuric acid slowly darkens, going to green, then to black and finally to yellow, thus indicating numerous successive reactions. The equation for the reaction given by Bredig and Brown is

$$(C_6H_5NH_2)_2 \cdot H_2SO_4 + 28H_2SO_4 = 12CO_2 + 28SO_2 + (NH_4)_2SO_4 + 32H_2O$$

which is evidently only the sum of a series. Of course, with excess sulfuric acid this reaction would be pseudomonomolecular, but the evidence is against a single step. The data do not permit more than a guess at the probable path. Aniline blacks, sulfonated products and quinone are almost certainly produced. In fact the yellow needles of quinone were observed to crystallize out in several of the mixtures after cooling. However, the very good constancy of K uncatalyzed shows that, in the first stages, the reaction is monomolecular or at least pseudomonomolecular.

As to the mechanism of the catalysis and coactivation, the data afford little evidence. Aniline has been shown to form numerous complexes with mercuric and other metallic salts.[6,7,8]

Mercuriated aryls are also formed with aniline.[9]

The copper compounds are less easily prepared and are not as stable[9] (p. 774).

Such complexes might react to produce a compound more readily oxidized than aniline itself. A parallel case has been studied.[10]

The work of Bohnson and Robertson[11,12] on the decomposition of hydrogen peroxide by mixtures of copper and iron ions affords a possible explanation of the coactivation.

In this case it was shown that one metal continually regenerates the other in active form. Some support for this suggestion is found in the work of Germuth,[13] who showed that the rate of oxidation of mercurous to mercuric ion by atmospheric oxygen is appreciably increased by traces of cupric ion.

Summary

1. Copper and mercury sulfates are excellent

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[6] "International Critical Tables," Vol. IV, p. 199.

[7] Spacie and Ripan, *Bull. Soc. stiinte Cluj*, **1**, 542 (1922); see also *C. A.*, **18**, 1442 (1924) and **19**, 1995 (1925).

[8] Mathews and Benger, *J. Phys. Chem.*, **18**, 263, 667 (1914); Mathews and Spero, *ibid.*, **21**, 402 (1917); Hahn and Wolf, *Z. anorg. Chem.*, **144**, 128 (1925).

[9] Houben–Weyl, "Die Methoden der Org. Chem.," Georg Thieme, Leipzig, 1924, Vol. IV, pp. 921–945.

[10] Davis, Worrall, Drake, Helmkamp and Young, THIS JOURNAL, **43**, 594 (1921).

[11] Bohnson and Robertson, *ibid.*, **45**, 2512 (1923).

[12] Robertson, *ibid.*, **47**, 1299 (1925).

[13] Germuth, *Am. J. Pharm.*, **102**, 263 (1903).

catalysts for the oxidation of aniline sulfate by sulfuric acid, mercury being the better. The effect is not strictly proportional to the amount of the catalyst.

2. Together the two catalysts give effects much greater than the additive value. This is, accordingly, a case of coactivation. Mercury and copper in the ratio of two moles to one give the most pronounced effect.

3. The reaction is monomolecular or pseudo-monomolecular in the first stages.

COLLEGE PARK, MD. RECEIVED SEPTEMBER 17, 1936

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Condensations by Sodium. VIII. Solvent Exchange Reactions, Preparation of Phenylmalonic Acid, and Comments on Some Mechanisms of Reactions which Employ Sodium

BY AVERY A. MORTON AND INGENUIN HECHENBLEIKNER

When benzene or a mixture of benzene and ligroin was used as the solvent for the preparation of amylsodium from amyl chloride and sodium by the recently described[1] synthesis of organo-metallic compounds, the product after carbonation was benzoic instead of caproic acid. Exchange of phenyl for the amyl radical was complete and the yield of benzoic acid, calculated on the basis of a molecule of acid for every one of amyl chloride used, was as high as 78%. Toluene, dimethylaniline, anisole, diphenylmethane and fluorene, when used similarly either as solvents or as diluents in a ligroin solution, shared this interesting property so that the monocarboxylic acids formed as products of carbonation were phenylacetic, N-dimethylanthranilic, *o*-methoxybenzoic, diphenylacetic and diphenyleneacetic acids in yields of 40, 18, 20, 14 and 18.5%, respectively (see Table II). No attempt was made to obtain the maximum yields.

In order to illustrate the possibilities of extending this solvent exchange type of synthesis beyond the preparation of acids we have prepared phenylsodium by interaction of amyl chloride, sodium and benzene and then brought about its reaction with propyl chloride. Propylbenzene was found in substantial quantity. In a like manner phenylsodium was induced to react with ethylene oxide yielding β-phenylethyl alcohol as one of the products.

Syntheses of this type continued to show promise of use in the preparation of malonic acids. A notable example was the formation of phenylmalonic in addition to phenylacetic acid from the reaction in toluene solution. With amyl chloride in a mixture of toluene and ligroin a yield of 33% of phenylmalonic acid was obtained from the same run which yielded 40% of phenylacetic acid. With isobutyl chloride the yields were 20% of phenylmalonic and 11% of phenylacetic acid. When the addition of toluene was delayed until after all reactions between amyl chloride and sodium had ceased, the yields of phenylmalonic and phenylacetic acids were 28 and 5%, respectively. The method is therefore a far more convenient source of this compound than has hitherto been available. It is especially interesting to note that the yield of the malonic acid is often considerably in excess of that for the monocarboxylic acid.

Mechanism of Exchange Reactions.—Our work has now progressed to a point where we have assurance as to the manner in which some of the products are formed. The monosubstitution product, benzoic acid, arises from metathesis of the sodium compound with the hydrocarbon according to equation 1.

$$C_5H_{11}Na + C_6H_6 \longrightarrow C_5H_{12} + C_6H_5Na \quad (1)$$

Important evidence of the correctness of this view was furnished by (a) reserving the addition of benzene in experiments 3 and 4 until after the free radicals had disappeared and the formation of amylsodium had been completed, a condition which resulted in the entire replacement of caproic by benzoic acid among the products of carbonation and (b) by carrying out, as in experiment 6, an exchange reaction in the presence of carbon dioxide to remove amylsodium as fast as it was formed and thereupon failing to find any benzoic acid. Neither was this acid found in six experiments made under pressure of carbon dioxide. We therefore conclude that the free radi-

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[1] Morton and Hechenbleikner, THIS JOURNAL, 58, 1697 (1936).

cal amyl did not react with benzene under the conditions of our experiments and that the occurrence of benzoic acid was due to the reaction of the monosodium compound with benzene according to equation 1. A mild form of acidity on the part of the hydrogen atom in benzene which permits the formation of a stable salt, sodium phenide, is thus suggested. The much higher yield of benzoic acid (78%) than was usually obtained for caproic acid in like experiments reported in the previous paper may be interpreted as indicating the greater stability of phenylsodium in a Wurtz synthesis.

Although the free radical amyl was without a role in the solvent exchange reactions, some evidence suggesting that the radical amylidene was in part responsible for the formation of iso- and terephthalic acids was uncovered. In the aforementioned experiments on the interaction of benzene, amyl chloride and sodium, under pressure of carbon dioxide, a mixture of the two phthalic acids was obtained in each instance. On the reasonable assumption that carbon dioxide would remove the organo-dimetallic compound before it could react with benzene as effectively as it had in the case of amylsodium, we conclude that free amylidene must have reacted with benzene according to equation 2, and that the phenylene so

$$C_5H_{10}< + C_6H_6 \longrightarrow C_5H_{12} + C_6H_4< \qquad (2)$$

formed then added two atoms of sodium yielding phenylene disodium which was promptly carbonated, producing the mixture of phthalic acids.

Iso- and terephthalic acids may also be formed because of a reaction of amylidene disodium with benzene according to equation 3. Although the likelihood of benzene reacting with two molecules

$$C_5H_{10}Na_2 + C_6H_6 \longrightarrow C_5H_{12} + C_6H_4Na_2 \qquad (3)$$

of amylsodium (equation 4) appeared to be very

$$C_6H_6 + 2C_5H_{11}Na \longrightarrow C_6H_4Na_2 + 2C_5H_{12} \qquad (4)$$

good, we have so far been unable to produce evidence which would point conclusively to such a chemical change. The facts bearing on this point can be stated briefly. (1) When benzene was present at a temperature below 5° during or after the reaction of amyl chloride with sodium the subsequent carbonation yielded benzoic and butylmalonic but no phthalic acids. Apparently amylidene disodium reacted more sluggishly with benzene than did amylsodium so that at this temperature a solvent exchange reaction occurred with amylsodium only. (2) When benzene was allowed to react at 65° with the products of the reaction between amyl chloride and sodium, phthalic acids appeared among the products and the amount of butylmalonic acid was decreased. These two facts suggested that under these conditions bimetallation of benzene may have occurred by reaction 3. With toluene, it is true, we did obtain evidence that disubstitution by means of amylsodium had taken place, for the yield of phenylmalonic acid in one experiment was 28% under conditions which had produced butylmalonic acid in yields no higher than 24% and usually near 17% (see previous paper).

Mechanism of Malonic Acid Formation.—As an explanation for the occurrence of butylmalonic acid we favor that which pictures an initial formation of the free radical amyl, its disproportionation to amylidene and pentane, the addition of sodium to the former and the carbonation of the disodium product shown in sequence below.

$$C_5H_{11}Cl \xrightarrow{Na} C_5H_{11}- \xrightarrow{C_5H_{11}-} C_5H_{12} + C_5H_{10}< \xrightarrow{Na} C_5H_{10}Na_2 \xrightarrow{CO_2} C_5H_{10}(COONa)_2 \qquad (5)$$

Our opinion is founded on (a) the agreement of the experimental facts with all the results which would be predicted on the free radical basis, and (b) the inability to find any evidence to bolster up alternative mechanisms, *viz.*, one involving amylsodium and another the splitting out of hydrogen chloride.

A full discussion of our efforts to connect amylsodium with the formation of butylmalonic acid was included in the previous paper. That evidence, coupled with additional information in this paper, is overwhelmingly against any such idea. To conserve space we are limiting our present discussion of this point to only one of the ways in which amylsodium could conceivably be responsible for the occurrence of the dicarboxylic acids. The following sequence assumes a certain lability of the hydrogen atom on the alpha carbon atom of sodium caproate so that it reacts with amylsodium.

$$C_5H_{11}Na \xrightarrow{CO_2} C_5H_{11}COONa \xrightarrow{C_5H_{11}Na} C_5H_{12} + C_5H_{10}Na(COONa) \xrightarrow{CO_2} C_5H_{10}(COONa)_2 \qquad (6)$$

Four points can be cited against this mechanism: (1) the failure as reported in the previous paper to get an increased yield of butylmalonic acid when sodium caproate, prepared *in situ* by partial carbonation, was present during the addition of amyl chloride to sodium; (2) the destruction of most of the amylsodium, prior to carbonation by fourteen hours of heating at 80° while leaving the yield of butylmalonic acid unchanged, a fact which we interpreted in the previous paper as illustrating the surprising stability of amylidene disodium, obviously formed prior to carbonation; (3) the reaction in benzene solution recorded in this paper in which amylsodium was removed by complete reaction with benzene below 5° but from which butylmalonic acid was isolated among the carbonation products, thereby showing again that sodium amyl could not be a source of butylmalonic acid and that amylidene disodium must have been present before carbonation; (4) the unlikelihood that amylsodium would react with sodium caproate in the manner above indicated since Schorigin[2] has already shown in the case of phenylsodium and Gilman and Van Ess[3] have found with alkyllithium that the secondary products in reactions with carboxyl containing compounds were ketones and tertiary carbinols. In short, organo-metallic compounds of this type, when they do react with alkali salts of carboxylic acid, show a tendency to react with the carboxyl group after the usual manner of an ester with the Grignard reagent rather than with a weakly acid hydrogen atom on the alpha carbon atom. The above facts confirm the view expressed in the previous paper that amylsodium is in nowise connected with the formation of butylmalonic acid.

Splitting out of hydrogen halide from an alkyl halide was initially proposed by Michael[4] as a first step in the Wurtz synthesis. Acree[5] in a study of the action of phenylsodium on ethyl bromide suggested a similar role for phenylsodium as a means of accounting for the presence of ethylene among the products of the reaction. Ethylidene was assumed to be the intermediate. These assumptions are adaptations of the well-known activity of sodium ethylate in double bond formation with the exception that hydrogen halide is taken from the same rather than from adjacent carbon atoms. The equation for the reaction is

$$C_5H_{11}Cl \xrightarrow{\text{Na (or NaR)}} HCl + C_5H_{10}< \quad (7)$$

The corresponding equation for the formation of amylidene in the reaction of sodium on diamyl mercury would require the splitting out of $HHgC_5H_{11}$ instead of HCl. Reference to the work in the fifth paper[6] on the formation of butylmalonic acid in the reactions under pressure of carbon dioxide is sufficient to dispose of the possibility that amylsodium had caused the eviction of hydrogen chloride in this manner, since carbon dioxide should remove the organometallic compound as fast as it was formed. Other agents commonly employed in forming ethylenic bonds are not available under all conditions in these reactions. Thus sodium ethylate or sodium hydroxide could not be present in the autoclave reactions[6] in the presence of an excess of carbon dioxide and sodium carbonate on the other hand was not present when the formation of organo-alkali compounds[1] was carried out in absence of carbon dioxide. Metallic sodium, therefore, remains as the sole agent which might function in this manner and be present in all cases. Such an opinion of the special activity of sodium would appear to require considerable tinkering in an endeavor to link the general mechanism of double bond formation with the Wurtz synthesis. We have thought it worth while, however, to make one more attempt under conditions which are ordinarily quite favorable for the splitting out of hydrogen halide. Since the formation of phenylmalonic acid occurred with considerable ease we elected to try the reaction of benzyl chloride with sodium in the presence of sodium alcoholate, formed *in situ* by the addition of a little alcohol. A vigorous reaction ensued and the product had the customary dark color but no phenylmalonic acid could be found upon carbonation. If a substituted methylene radical were formed under these conditions, as might be thought possible from the opinion of Bergmann and Hervey,[7] metallic sodium did not serve as an interceptor. Further investigations of this idea did not appear promising.

As stated before the favored explanation for the occurrence of malonic acids is that the free radical amyl undergoes disproportionation forming an idene radical which then adds two atoms of sodium. This view is in full accord with every fact which has been brought out by these studies. Thus the yields of carboxylic acids in all cases, whether in the autoclave reactions (fifth paper),[6]

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(2) Schorigin, *Ber.*, **41**, 2723 (1908).

(3) Gilman and Van Ess, THIS JOURNAL, **55**, 1258 (1933).

(4) Michael, *Am. Chem. J.*, **25**, 419 (1901).

(5) Acree, *ibid.*, **29**, 588 (1903).

(6) Morton, LeFevre and Hechenbleikner, THIS JOURNAL, **58**, 754 (1936).

(7) Bergmann and Hervey, *Ber.*, **62**, 893 (1929).

the reactions with mercury diamyl (sixth paper),[8] the experiments in the isolation of the intermediate amylsodium (seventh paper),[1] or in the exchange reactions reported in this paper, have never been in excess of that which could be accounted for on this basis. Moreover, the amount of pentane recovered in the reaction of sodium with diamyl mercury[9] was close to that demanded by the theory. If we accept the view that the free radical mechanism pictures a correct outline of events, the isolation of butylmalonic acid means that in the disproportionation of free amyl an intermediate step is the formation of amylidene which then rearranges to amylene. Metallic sodium acted as an imperfect interceptor for the amylidene stage. The quantity of butylmalonic acid on this basis is actually a measure of the free radical known to have disproportionated.

Mechanism of the Wurtz Reaction.—In applying our data to the mechanism of the Wurtz–Fittig reaction we shall show that (a) free radicals are formed either before or simultaneously with the formation of alkylsodium, and (b) the free radical amyl undergoes disproportionation instead of dimerization to at least 92% (the true value may be even higher) from which it follows that decane is probably formed by the reaction of amylsodium with amyl chloride. Schlubach and Goes[10] represented the first step of the Wurtz–Fittig reaction as the formation of a free radical by the action of sodium on an alkyl halide according to equation 8. Subsequently the radical added sodium, dimerized or underwent disproportionation.

$$\mathrm{RX + Na \longrightarrow R— + NaX} \qquad (8)$$

See equations 9. In the final step the alkylsodium reacted with alkyl halide.

$$\mathrm{R—} + \begin{cases} \mathrm{Na \longrightarrow RNa} & (a) \\ \mathrm{R— \longrightarrow RR} & (b) \\ \mathrm{R— \longrightarrow R_{-H} + R_{+H}} & (c) \end{cases} \qquad (9)$$

Goldschmidt and Schön,[11] however, gave the first phase as shown in equation 10

$$\mathrm{RX + 2Na \longrightarrow + NaX} \qquad (10)$$

and have outlined the possibility of the occurrence of free radicals from the reaction

$$\mathrm{RNa + RX \longrightarrow R— + R— + NaX} \qquad (11)$$

Our experiments under pressure of carbon dioxide are equivalent to carrying out a Wurtz–Fittig reaction in the presence of an agent, carbon dioxide, which would trap the alkyl sodium but not the free radical. Since butylmalonic acid continued to be formed under these conditions, even when the pressure was as high as 900 pounds (60 atm), we conclude that free radicals must have been formed either prior to or simultaneously with the formation of alkylsodium as given in equation 8.

That the tendency of the amyl radical under these conditions was overwhelmingly toward disproportionation (equation 9c) rather than toward dimerization (equation 9b) can be seen by reference to one[12] of the experiments in which we were particularly successful in finding conditions under which metallic sodium acted as a nearly perfect trap for the amylidene. In this instance only 2%, calculated on the basis of the sodium, went to products[13] which were other than acids. When recalculated in terms of the amyl chloride consumed we find that 45.5% appeared as amyl sodium (caproic acid), 50% as a free radical which underwent disproportionation (butylmalonic acid) and only 4.5% as unknown (decane, pentane and pentene). The combined amount of free radical which was present and could either disproportionate or dimerize was therefore 54.5% and of this amount 92% is known to have taken the former path. Because of this great tendency for disporportionation it seems likely that decane, when synthesized from the action of sodium on amyl chloride, is formed largely by way of the amylsodium plus amyl chloride path. Particularly is this view made likely by reference to the 45.5% yield of amylsodium in the same reaction. As regards the formation of amylsodium by equation (9a) or (10) our data do not permit a differentiation.

Our conclusions on the mechanism of the Wurtz reaction can be summarized briefly. This synthesis occurs because of the reaction between amylsodium and amyl chloride, a view confirmed by (a) our isolation of the organo-metallic compound in quantity and (b) the evidence showing that the free radical amyl had scarcely any tendency to combine with itself forming decane. Having shown that free radicals are present either prior to or simultaneously with the formation of amylsodium, it is an entirely reasonable supposi-

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[8] Morton and Hechenbleikner, THIS JOURNAL, **58**, 1024 (1936).

[9] See reaction 20, Table I, ref. 8, p. 1026. By error the calculated amount of pentane was given as 1.08 instead of 0.79.

[10] Schlubach and Goes, *Ber.*, **55**, 2889 (1922).

[11] Goldschmidt and Schön, *ibid.*, **59**, 948 (1926).

[12] See reaction number 6, Table II, THIS JOURNAL, **58**, 756 (1936).

[13] By the term Wurtz in the former paper we included all reactions possible in a Wurtz synthesis. The figure was arrived at by difference. Hence the column marked Wurtz referred to decane, pentane and pentene.

tion that amylsodium is a consequence of the addition of an atom of sodium to the free radical.

Experiments

General Direction.—The usual method of carrying out the reactions, unless otherwise specified, was the same as described in the previous paper,[1] *viz.*, addition of amyl chloride to fine sodium sand with gentle stirring in the desired solvent. Such changes as were made necessary by the use of a different solvent are indicated clearly. The separation of the products was in general made possible by the fact that the aliphatic monocarboxylic acids could be extracted with petroleum ether, the malonic acids were usually soluble in cold or hot water, but could be extracted with ether, the phthalic acids were insoluble in water or ligroin. The melting points of the products were compared with those in Beilstein. The sodium sand was made up in large batches so that the grade did not change through a series of experiments. This precaution was necessary because the yields of acids were affected by the fineness of the sand. The data for the experiments are given as far as possible in tables followed by supplementary notes on each reaction. In the paragraph immediately following that section attention is called to the significance of each experiment. The numbering is for convenience only. Yields are calculated on the basis of the sodium employed except in reaction 3 in which the value is referred to diamyl mercury.

TABLE I

EXCHANGE REACTIONS WITH BENZENE

Constant factors. Eastman Kodak Co. *n*-amyl chloride used in all experiments except in number 3, where diamyl mercury and in number 5 where isobutyl chloride were used. Mallinckrodt thiophene-free benzene used.

No.	Sodium, g.	Amyl chloride, ml.	Benzoic acid		Phthalic acids		Butylmalonic acid	
			G.	%	G.	%	G.	%
1	15	30	6.4	21.4			3.5	17.5
2	15	20	15.7	78			0.43	3.2
3	4	10[a]	2.2	32	0.2	4		
4	10	20	2.3	11.5	.9	6.5	1.1	8.2
5	10	15	5.3	32			Traces	
6	5	30	0.0					

[a] Quantity of diamyl mercury in grams instead of ml.

1. Sodium sand in 150 ml. of benzene with 50 ml. of pentane to keep the mixture from solidifying. Temperature below 5° during addition of the chloride which required two hours. Stirred for fifteen minutes after addition was completed.

2. Sodium in 80 ml. of benzene and 50 ml. of pentane. Amyl chloride in 50 ml. of benzene. Temperature below −2° during addition of amyl chloride solution which required one hour. Stirred for one hour longer at room temperature.

3. Diamyl mercury used in place of amyl chloride. Sodium sand in 100 ml. of pentane. Mixture stirred for two hours following mixing of reagents, after which 100 ml. of benzene was added.

4. Sodium sand in 50 ml. of ligroin; amyl chloride in 50 ml. of same solvent. Addition time one and one-half hours, temperature 18–22°. Stood one hour at room temperature. Benzene, 100 ml., then added and mixture heated to 65° for one hour. The phthalic acid mixture contained 0.054 g. of the iso- form which was separated by the solubility of the barium salt.

5. Isobutyl chloride dissolved in 50 ml. of benzene. Sodium sand in 50 ml. of benzene. Time of addition one and one-quarter hours; temperature 25–30°. Mixture allowed to stand for two hours before carbonation.

6. Sodium sand in 30 ml. of benzene; amyl chloride added undiluted; temperature 10–20°. Carbon dioxide passed in during the addition of the alkyl chloride; reaction time one hour. No benzoic acid was obtained. Caproic acid, 23%. No analysis was made for butylmalonic acid.

Special attention is directed to (a) the absence of phthalic acids in 1 and 2 where the temperature of the reaction was below 5° and the presence of these acids where the temperature was 65° (experiment 4); (b) the very high yield of benzoic acid in number 2 where the concentration of benzene was less and the rate of addition of amyl chloride was greater than in number 1; (c) the exchange reaction, experiment 5, with isobutyl chloride and the small quantity of dicarboxylic acids among the products; (d) the failure to find benzoic acid when carbon dioxide was bubbled through the reaction mixture (experiment 6) indicating the ease with which amylsodium could be removed from the reaction before the latter could react with benzene; (e) the combined yields of phthalic and butylmalonic acids in experiment 4 which amounted to 14.7%, a value within the range of 13–17% noted in the previous paper for the yield of butylmalonic acid under the same conditions and hence suggestive of the formation of phthalic acids at the expense of butylmalonic acid in the exchange reaction; (f) the delayed addition of benzene to the reaction mixture in experiments 3 and 4 which showed that an exchange reaction had occurred between benzene and the organometallic compound.

7. Sodium sand in 25 ml. of ligroin and 25 ml. of toluene. Amyl chloride dissolved in 25 ml. of ligroin and 25 ml. of toluene. Addition at 0–5° for two and one-half hours. Stirred three hours at 40–45° during which time 100 ml. more ligroin was added because the mixture became so thick it could not be stirred. At the end of this time the almost solid greenish-yellow mass was carbonated.

8. Solvent conditions the same as in experiment 7. Isobutyl chloride used instead of amyl chloride. Addition time three hours at 0–5°. Stirred two hours at 40–45°. Carbonated at 60°.

9. Sodium sand in 50 ml. of ligroin. Time of addition two hours at 0–10°. Stood at room temperature for three hours. 100 ml. of toluene added and the mixture heated to 50° for ten minutes.

TABLE II

EXCHANGE REACTION WITH COMPOUNDS OTHER THAN BENZENE

No.	Sodium, g.	Amyl chloride, ml.	Solvent or diluent	Ml.	Mono-acid		Di-acid		Butylmalonic acid	
					G.	%	G.	%	G.	%
7	15	20	Toluene	50	9	40	5.0	33		
8	15	15	Toluene	50	2	11	2.4	20		
9	10	20	Toluene	100	1.2	5.2	4.15	28		
10	10	20	Anisole	50	5	20			Trace	
11	10	20	Diphenylmethane	20	4.8	14	None		Trace	
12	10	20	Dimethylaniline	50	5	18				
13	15	20	Fluorene	10 (g.)	6.5	18.5			1	7

10. Sodium sand in ligroin–anisole mixture, 25 ml. of each. Amyl chloride dissolved in the same mixture was added at 20–25° during one hour. *o*-Methoxybenzoic acid obtained. Melting point 99°. Recorded value in literature 98.5°.

11. Sodium sand and diphenylmethane in 50 ml. of ligroin. Amyl chloride in 50 ml. of ligroin added at 25–30° during one hour. Mixture stood twelve hours at room temperature before carbonation. Diphenylacetic acid m. p. 145–146° obtained. Recorded values in the literature vary from 144 to 149°. The corresponding malonic acid is unstable.

12. Sodium sand in a mixture of 50 ml. each of ligroin and dimethylaniline. Amyl chloride dissolved in 50 ml. of ligroin added at 0–10° during 1.25 hours. The mixture was allowed to stand for four hours before carbonation. N-Dimethylanthranilic acid of m. p. 68–70° was found. Recorded value in the literature is 70°.

13. Sodium sand and amyl chloride separately contained in 50 ml. of ligroin. Addition time one hour at 0–15°. Stirred twenty minutes at room temperature. Fluorene, 10 g., in 100 ml. of ligroin then added. Diphenyleneacetic acid obtained. Melting point of ethyl ester 44–45°. Recorded value in literature 43–45°. The corresponding malonic acid is unstable.

Special attention is directed to (a) the formation of substituted malonic acids with an aromatic compound containing a methyl group illustrated in experiments 7, 8, 9 with toluene; (b) the addition of fluorene to the reaction mixture after the formation of the organo-alkali compounds from amyl chloride and sodium had been completed, a method found satisfactory after other attempts in which fluorene was present during the first stage of the reaction had failed to give products which could be isolated readily; (c) the occurrence of ortho substitution products with anisole and dimethylaniline.

Reaction of Benzyl Chloride and Sodium Ethylate.—To a mixture of 15 g. of sodium sand and 20 ml. of benzyl chloride in 100 ml. of ligroin was added slowly 5 ml. of anhydrous ethyl alcohol at room temperature. The reaction mixture evolved a gas and turned a dark red color characteristic of the color present in any of the reactions in the absence of alcohol. After carbonation, however, scarcely a trace of acid was found to be present.

Propylbenzene from Amyl Chloride, Benzene, Sodium and Propyl Chloride.—To 75 g. of sodium sand suspended with stirring in 350 ml. of benzene and contained in a three-necked flask protected by an atmosphere of nitrogen was added 180 ml. of technical *n*-amyl chloride at 18° over a period of three hours. The mixture was then allowed to stand fourteen hours after which 100 g. of *n*-propyl chloride was added. The mixture was heated to 80° for two hours, after which it was decomposed and the hydrocarbon layer distilled. Propylbenzene, b. p. 159°, was obtained in a yield of 23% (30 g.). Higher boiling fractions were present which were not investigated.

Phenylethyl Alcohol from Amyl Chloride, Benzene, Sodium and Ethylene Oxide.—In a similar apparatus 20 g. of sodium sand was suspended in a mixture of 150 ml. of benzene and 50 ml. of ligroin. Amyl chloride, 40 ml., was added at 0° during two hours. The mixture was stirred for four hours after which 8 g. of ethylene oxide was passed in at 0°. The yield of phenylethyl alcohol obtained from the process was 12.5% (5 g.). About 3 g. of heptyl alcohol was also obtained. Higher alcohols insoluble in benzene were also present.

Exchange Reactions with Benzene under Pressure of Carbon Dioxide.—Six experiments were carried out in the autoclave described in a previous publication in this series. The amount of sodium sand was varied from 10 to 15 g. and the quantity of benzene varied from 100 to 120 ml. Amyl chloride, 120 ml. and carbon dioxide, 200 lb. (13 atm.) were present in each case. The temperatures varied from 80 to 132°. In no case was benzoic acid found to be present among the acids isolated from the reaction mixture, although caproic, 1 to 2.5 g. of phthalic (iso and tere mixture), and butylmalonic acids were readily obtainable.

Summary

A yield as high as 78% of benzoic acid can be obtained in an exchange reaction between amyl chloride, sodium and benzene. In varying yields phenylacetic, N-dimethylanthranilic, *o*-methoxybenzoic, diphenylacetic and diphenyleneacetic acids have been obtained in a similar manner from amyl chloride and sodium with toluene, dimethylaniline, anisole, diphenylmethane and fluorene.

Phenylsodium, prepared from amyl chloride and sodium has been treated with propyl chloride and ethylene oxide to yield propylbenzene and phenylethyl alcohol, respectively.

Phenylmalonic acid has been prepared by reaction of toluene with amyl chloride and sodium or with the products of the reaction of this chloride and the metal.

Evidence is presented to show that the formation of phenylsodium occurs from the action of amylsodium, but not the free radical amyl, with benzene.

The formation of iso- and terephthalic acids in the interaction of benzene, amyl chloride and sodium has been shown to be due probably to reactions of either amylidene or amylidene disodium with benzene.

Further discussion of the mechanism of the formation of butylmalonic acid from the reaction of amyl chloride and sodium has been made and the probable path has been judged to be by disproportionation of the free radical amyl.

In the disproportionation of this free radical to pentane and pentene, the presence of the intermediate state, amylidene, which rearranges to pentene has been indicated.

Application of these studies to the mechanism of the Wurtz–Fittig reaction has shown that it proceeds by means of the reaction of an alkylsodium with the alkyl chloride and that free radicals are present during the early stages.

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Reactions of Alkyl Sulfates, Tetraethyl Orthosilicate and Diethyl Carbonate in Friedel–Crafts Syntheses[1,2]

BY HOWARD L. KANE AND ALEXANDER LOWY

Alkylations by the method of Friedel and Crafts are generally carried out using the halides or olefins. Nevertheless, certain disadvantages, especially among the lower members, are inherent in both these methods (particularly the necessity for pressure apparatus or very high stirring speeds).

The use of esters other than the halides as alkylating agents also has been proposed. Among these esters are the alkyl chlorocarbonates,[3] ethyl toluene-*p*-sulfonate,[4] trialkyl or triaralkyl borates[5] and the esters of aliphatic acids such as ethyl acetate or ethyl valerate.[6] An apparent exception to this mode of behavior exists in the case of ethyl nitrate, which acts as a nitrating agent rather than an alkylating agent.[7]

The purpose of this investigation was to observe whether the alkyl esters of sulfuric, orthosilicic and carbonic acids were active in this type of synthesis. As was anticipated, these substances proved to be efficient alkylating agents. The conditions which influenced the yield of mono-alkylated benzenes were also observed, such as concentrations of reagents, duration of heating and reaction time.

It is probable that many other esters (such as the sulfites, phosphates, acid sulfates, etc.) can undergo this type of condensation. The exceptional case of the nitrate may likewise become normal under different experimental conditions. This generalization is in harmony with the observation of Slanina, Sowa and Nieuwland[8] that acidic substances promote the olefin–benzene condensation in the presence of boron fluoride, this probably occurring through the formation of alkyl esters.

In the present investigation it has been shown that dimethyl, diethyl, diisopropyl and dibutyl sulfates, tetraethyl orthosilicate and diethyl carbonate will condense with benzene in the presence of aluminum chloride. These reactions may be summarized by equations

$$3(RO)_2SO_2 + 6C_6H_6 + 2AlCl_3 \longrightarrow 6C_6H_5R + 6HCl + Al_2(SO_4)_3$$

$$3(RO)_2CO + 6C_6H_6 + 2AlCl_3 \longrightarrow 6C_6H_5R + 6HCl + Al_2(CO_3)_3$$

$$3(RO)_4Si + 12C_6H_6 + 4AlCl_3 \longrightarrow 12C_6H_5R + 12HCl + Al_4(SiO_4)_3$$

Experimental

The apparatus employed for the alkylations was the usual one-liter three-necked flask, into one neck of which extended a dropping funnel and thermometer. The cen-

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(1) Abstracted from a thesis presented by Howard L. Kane to the Graduate School in partial fulfilment of the requirements for the Ph.D. degree.

(2) Presented before the Division of Organic Chemistry of the American Chemical Society, September, 1936, in Pittsburgh, Pa.

(3) (a) Rennie, *J. Chem. Soc.*, **41**, 33 (1882); (b) Kunckell and Ulex, *J. prakt. Chem.*, (ii) **86**, 518 (1912).

(4) Clemo and Walton, *J. Chem. Soc.*, 723 (1928).

(5) Kaufmann, German Patent 555,403; French Patent 720,034.

(6) Kashtanov, *J. Gen. Chem.* (*U. S. S. R.*), **2**, 515 (1932).

(7) (a) Boedtker, *Bull. soc. chim.*, (iv) **3**, 726 (1908); (b) Tronov and Sibgatullin, *J. Russ. Phys.-Chem. Soc.*, **62**, 2267 (1930).

(8) (a) Slanina, Sowa and Nieuwland, THIS JOURNAL, **57**, 1547 (1935); (b) Wunderly, Sowa and Nieuwland, *ibid.*, **58**, 1007 (1936); (c) Ipatieff, Corson and Pines, *ibid.*, **58**, 919 (1936).

tral neck was fitted with a glass stopper and mercury seal, through which extended a motor-driven glass stirrer. The third neck was connected to a modified Hopkins-type reflux condenser. This condenser could be cooled by water in the usual way, or it could be packed with solid carbon dioxide. This latter procedure was employed when methyl or ethyl esters were the reactants.

The aluminum chloride used throughout was of 99.5% purity. The benzene was dried over sodium and distilled at 80–81°. The various esters were purified by vacuum distillation before use.

Diethyl Sulfate.—The experiment which gave the highest yield of ethylbenzene from diethyl sulfate is described below (IIA).

Benzene (574 g.) was stirred (1000 r. p. m.) with aluminum chloride (96 g., 0.72 mole), and cooled in an ice-bath. Diethyl sulfate (77 g., 0.5 mole) mixed with 50 g. of benzene (making a total of eight moles) was then added during four hours. The ice-bath was removed an hour later, and the mixture warmed slowly. After five and one-half hours the temperature had reached 70°, where it was maintained for two more hours. After cooling for one-half hour the product was poured over cracked ice. The total reaction time was thus thirteen hours, during the whole of which the reflux condenser was cooled by packing with solid carbon dioxide.

The benzene layer, when hydrolysis of the aluminum chloride was complete, was washed with dilute sulfuric acid, aqueous sodium bicarbonate and water. It was then dried over calcium chloride for one day.

The dried benzene layer was then fractionally distilled, and yielded 75.7 g. of ethylbenzene, boiling at 133–137°. Three and one-half grams of a product boiling in the diethylbenzene range (175–185°), and four grams of residue were also obtained. Calculation of the theoretical yields was made on the assumption that all alkyl groups in the various esters were active. On this basis 0.5 mole of diethyl sulfate should form 1.0 mole of ethylbenzene (106 g.). The above yield of 75.7 g. is thus 71.4% of the theoretical.

The effects of variation in aluminum chloride concentration are summarized in Table I. Comparison of IA with IB shows that low concentrations of aluminum chloride result in incomplete reaction. Comparison of IIA with IIB, on the other hand, shows that excessive amounts of aluminum chloride also cause a reduction in yield of ethylbenzene; the yield of higher-boiling products is correspondingly increased. The amount of aluminum chloride employed in IB and IIA is 2.2 times the stoichiometrical quantity required by the above equation.

TABLE I

DIETHYL SULFATE—EFFECT OF $AlCl_3$ CONCENTRATION

No.	Diethyl sulfate, g.	$AlCl_3$, g.	Benzene, g.	Molar ratio of $AlCl_3$ to diethyl sulfate	Ethylbenzene (133–137°) % yield	Diethylbenzenes (175–185°) % yield	Residue, g.
IA	38.5	24	312	0.72	36.5	21	3.5
IB	38.5	48	312	1.44	62.5	21	1.5
IIA	77	96	624	1.44	71.4	5	4.0
IIB	77	146	624	2.20	31.6	12	12.0

The effects of variation in temperature were studied in a series of experiments summarized in Table II. Best yields were obtained by conducting the reaction for the first few hours at low temperatures, and then heating for a short time (IIIA). Heating at 50 or 70° for the entire experiment gave much reduced yields of ethylbenzene (IIIB, IIIC).

TABLE II

DIETHYL SULFATE—EFFECT OF HEATING

Diethyl sulfate, 38.5 g.; $AlCl_3$, 48 g.; benzene, 312 g.

No.	Time at 10°, hours	Time at higher temp., hours	Higher temp., °C.	Ethylbenzene (133–137°) % yield	Diethylbenzenes (175–185°) % yield	Residue, g.
IIIA	5	1	70	66.5	18	2.5
IIIB	0	5.5	50	40.5	6	3.0
IIIC	0	5.5	70	36.7	6	4.5

The addition of calcium carbonate to react with hydrochloric acid had very little effect on the reaction. When 100 g. of calcium carbonate, 96 g. of aluminum chloride, 77 g. of diethyl sulfate and 624 g. of benzene reacted under the usual conditions (similar to IIIA, Table II), the yield of ethylbenzene was still 63.7%. Even when 1 g. of water and 1 g. of concentrated ammonium hydroxide were also added, the yield was 64.2%. This is surprising in view of the usual sensitivity of Friedel–Crafts reactions to moisture.

Dimethyl Sulfate.—Benzene (624 g., 8 moles) was stirred (1000 r. p. m.) with $AlCl_3$ (48 g., 0.36 mole) for one hour. Dimethyl sulfate (31.5 g., 0.25 mole) was then added during a two-hour period. The flask was kept at 25° during this addition, and for three hours longer. The temperature was raised to 70° during the course of one hour and maintained at that temperature for another hour. During the entire experiment the reflux condenser was cooled with solid carbon dioxide. The mixture was hydrolyzed with cracked ice. The benzene layer was separated, washed with aqueous sodium bicarbonate and water and then dried over calcium chloride for twelve hours. Fractional distillation of the product through a 66-cm. Young column gave 27.5 g. of toluene (108–113°), 3 g. in the xylene range (135–145°) and 1.5 g. of residue. The yield of toluene was thus 59.8%, based on both methyl groups of dimethyl sulfate.

Other reactions in which dimethyl sulfate was employed confirmed the result of the diethyl sulfate reactions where aluminum chloride concentration was concerned. The best yields were obtained with a ratio of aluminum chloride to ester of 1.44 to 1. Small variations in the neighborhood of this value were not attempted.

Dimethyl sulfate was very slowly reactive below 20°.

Diisopropyl Sulfate.—This ester was prepared by the reaction of isopropyl alcohol with sulfuryl chloride.[9] Levaillant reports 34% yield by this method, but by allowing the crude carbon tetrachloride solution to stand for two to three days (until the cloudiness disappeared) a yield of 48.6% was obtained. The product distilling at 74–80° under 3–4 mm. was employed.

The usual procedure as described above was effective except that it was necessary to reflux the crude product with aqueous sodium bicarbonate before washing. The ester reacted freely at 0°. The reaction between 91 g. (0.5 mole) of diisopropyl sulfate, 96 g. (0.72 mole) of alu-

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(9) Levaillant, *Compt. rend.*, **188**, 261 (1929).

minum chloride and 624 g. (8.0 moles) of benzene, gave 53.0 g. of isopropylbenzene (44.2%) boiling at 148–152°. Twenty-five grams of higher-boiling products was obtained.

Dibutyl Sulfate.—This ester was prepared by the method of Barkenbus and Owen[10] in 64% yield (b. p. 110–118° at 4–6 mm.).

Thirty-five grams (0.17 mole) of the dibutyl sulfate so prepared was treated in the usual way with 208 g. (2.67 moles) of benzene and 32 g. (0.24 mole) of aluminum chloride, except that heating was omitted. The reaction was conducted for six hours in an ice-bath, and then for fifteen hours at 30°. Stirring was continued at 1000 r. p. m. The product contained a bright cherry-red lower layer. After hydrolysis, refluxing with sodium bicarbonate, washing and drying, the entire mixture was fractionally distilled, yielding the following products: 165–175°, 19.5 g. (43.6% calculated as isomeric butylbenzenes); 175–185°, 5.5 g.; higher boiling products, 2.0 g.

Tetraethyl Orthosilicate.—Best yields of ethylbenzene were obtained when the ratio of aluminum chloride to tetraethyl orthosilicate was 2.88 moles to one. When 52 g. (0.25 mole) of the ester was treated with 624 g. of benzene and 96 g. of aluminum chloride, 56.5 g. of ethylbenzene (133–137°) was obtained (53.3% based on all ethyl groups of tetraethyl orthosilicate). The reaction was conducted for sixteen hours at 25° (reaction being slow at lower temperatures); the temperature was raised during five and one-half hours to 70°, and maintained there for four hours. Hydrolysis and fractionation were accomplished in the usual way, as with diethyl sulfate.

Diethyl Carbonate.—Fifty-nine grams of diethyl carbonate (0.5 mole), 96 g. of aluminum chloride (0.72 mole) and 624 g. of benzene (8.0 moles) were treated as described above for twenty-six hours at 25° and three hours at 70° (four hours were consumed in gradually raising the temperature from 25 to 70°). The reaction was slow at temperatures below 25°. After hydrolysis, washing, drying and fractionation as with diethyl sulfate, 59.8 g. of ethylbenzene (133–137°) or 56.4%, and 19.5 g. of higher boiling products were obtained.

Naphthalene.—Several experiments in which naphthalene reacted with diethyl sulfate in the presence of aluminum chloride and a solvent gave a product boiling in the ethylnaphthalene range, from which no pure compound could be isolated. The solvents used were carbon disulfide and *o*-dichlorobenzene.

In one experiment 128 g. of naphthalene (1.0 mole), 441 g. of *o*-dichlorobenzene (3.0 moles) and 77 g. of diethyl sulfate (0.5 mole) were stirred at 1000 r. p. m. for one hour. Then 147 g. of aluminum chloride (1.1 moles) was added in small portions during twenty-five and one-half hours. The temperature of an ice and salt bath was maintained at 0 ± 2° for the first fourteen and the last three hours, being permitted to warm up to 25° for the intervening time. Stirring was continued throughout the experiment. The black product was hydrolyzed and washed in the way described in the benzene experiments, and was then steam-distilled. The oil layer was separated, dried and fractionally distilled. Thirty-five grams of a hydrocarbon oil boiling at 240–270° was obtained along with 10 g. of higher boiling products. Redistillation of the 240–270° fraction gave 25 g. of a product boiling at 245–255°. β-Ethylnaphthalene boils at 251°, α-ethylnaphthalene at 258–259° corrected.

Flow Method.—An apparatus was devised in which the liquid reactants (benzene and diethyl sulfate, for example) could be made to flow over the aluminum chloride, contained in a long, narrow, inclined tube. The best yield obtained by this method was 25.7% of ethylbenzene.

Action of Aluminum Chloride on Alkyl Esters.—Aluminum chloride has been shown to react with tetraethyl orthosilicate in the absence of a solvent, the products being ethyl chloride and ether.[11] Dimethyl sulfate reacts with stannic chloride, forming methyl chloride and other products, also in the absence of a solvent.[12] To determine whether the course of these reactions would be altered at the dilutions employed in the alkylations described above, the following experiments were conducted.

38.5 g. of diethyl sulfate was treated with 48 g. of aluminum chloride in 300 g. of 90–100° olefin-free ligroin. The temperature was kept at 10–50°. The volatile products were condensed with solid carbon dioxide. Five grams of a product not ethyl chloride was obtained. Repetition of this experiment using 29.5 g. of diethyl carbonate in place of the sulfate, at temperatures below 50°, also gave 3 g. of a product, but no ethyl chloride.

That reaction of some kind did occur was evident from the fact that the aluminum chloride became gelatinous as the addition of ester proceeded. It is possible that the ligroin was not inactive, as had been supposed. Recent evidence shows that paraffin hydrocarbons are not inert in the presence of aluminum chloride, zirconium chloride and boron fluoride.[13]

Summary

1. The use of esters as alkylating agents in the Friedel–Crafts syntheses has been extended to include a number of new examples.

2. The best yields of mono-alkylated benzene obtained with the following esters were: dimethyl sulfate, 59.8%; diethyl sulfate, 71.4%; diisopropyl sulfate, 44.2%; dibutyl sulfate, 43.6%; tetraethyl orthosilicate, 53.3%; and diethyl carbonate, 56.4%.

3. The general conditions affecting the yield, such as reaction time, temperature and proportions of reagents have been studied. The best ratio of aluminum chloride to ester was 1.44 moles to one, except in the case of the silicate, where it was 2.88 to one.

4. Attempts to alkylate naphthalene with diethyl sulfate led to hydrocarbon oils which could not be fractionated into separate ethylated naphthalenes.

5. Attempts to use a flow method with diethyl sulfate gave much reduced yields.

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(10) Barkenbus and Owen, THIS JOURNAL, **56**, 1204 (1934).

(11) Stokes, *Am. Chem. J.*, **14**, 444 (1892).

(12) Boulin and Simon, *Compt. rend.*, **169**, 618 (1919).

(13) (a) Grosse and Ipatieff, THIS JOURNAL, **57**, 2415 (1935); (b) Ipatieff and Grosse, *ibid.*, **57**, 1616 (1935).

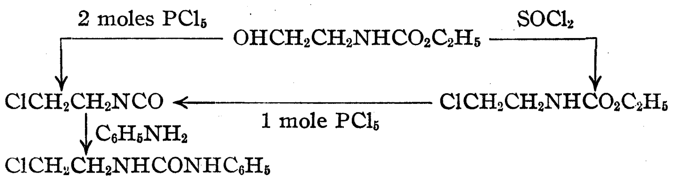
6. No ethyl chloride could be obtained by the action of diethyl sulfate or carbonate on aluminum chloride in ligroin.

PITTSBURGH, PENNA. RECEIVED OCTOBER 28, 1936

Syntheses from Ethanolamine. III. Synthesis of N-β-Chloroethyl Urethan and of β-Chloroethyl Isocyanate

BY HENRY WENKER

In extending a study of syntheses from enthanolamine, it has been found that N-β-oxyethyl urethan reacts with thionyl chloride to form N-β-chloroethyl urethan. Under the influence of phosphorus pentachloride, the latter compound yields β-chloroethyl isocyanate, which can also be prepared directly from the oxyurethan by using 2 moles of phosphorus pentachloride. The constitution of the isocyanate was confirmed by the preparation of the respective α-aryl-β-(β-chloroethyl) ureas from aniline and from *p*-phenetidine. The reactions involved are expressed by the formulas



Both compounds have not been described hitherto; their use for further syntheses is now being investigated.

Experimental

N-β-Chloroethyl Urethan.—One hundred and forty-three grams of thionyl chloride is added gradually to 133 g. of N-β-oxyethyl urethan. The reaction is finished by short heating on the water-bath and the product distilled *in vacuo*. With the exception of a small residue, all distilled from 128–130° at 13 mm. The yield was 138 g. or 91%.

Anal. Calcd. for $C_5H_{10}O_2NCl$: N, 9.3; Cl, 23.4. Found: N, 9.1; Cl, 23.2.

N-β-Chloroethyl urethan is a colorless, fairly mobile liquid possessing a slightly pungent odor. It dissolves readily in ethanol and ether, but not in water.

β-Chloroethyl Isocyanate.—Preparation from N-β-oxyethyl urethan: 133 g. of the urethan is dropped, under external cooling, on 420 g. of phosphorus pentachloride contained in a 2-liter flask. About one-half of the pentachloride remains undissolved, but heating on the water-bath soon produces a clear homogeneous solution. The product is then distilled very slowly, using an efficient fractionating column. Even so, there is a considerable intermediate fraction, until finally the pure isocyanate distils at 135°. The yield was 52 g. or 49%.

Anal. Calcd. for C_3H_4ONCl: N, 13.3; Cl, 33.6. Found: N, 13.0; Cl, 33.4.

The preparation from N-β-chloroethyl urethan is identical, except that for one mole of the urethan, or 151 g., one mole of pentachloride or 210 g. is used. The yield is the same as above.

β-Chloroethyl isocyanate is a colorless, mobile liquid, heavier than water and rapidly decomposed by it under evolution of carbon dioxide. The resulting solution is clear with silver nitrate, but on standing becomes cloudy. The isocyanate has an unpleasant odor and its vapor is very irritating on the eyes.

Ten and one-half grams of isocyanate was added to 9.3 g. of aniline dissolved in 50 ml. of ether. The solution boiled up spontaneously and a sludge of white crystals was formed. Crystallized from dilute ethanol, the product melted at 124°; the literature[1] gives 124° for α-phenyl-β-(β-chloroethyl) urea.

The isocyanate reacts similarly with *p*-phenetidine; the urea melts at 149°. It forms fine white crystals of silky luster.

Anal. Calcd. for $C_{11}H_{15}O_2N_2Cl$: N, 11.5; Cl, 17.9. Found: N, 11.2; Cl, 17.9.

Phosphorus pentoxide, which has been used successfully[2] for the preparation of phenyl isocyanate from phenyl urethan instead of the pentachloride,[3] was found to be unsuitable for the purpose of converting N-β-chloroethyl urethan into the isocyanate; upon heating decomposition with evolution of hydrogen chloride occurred.

Summary

N-β-Oxyethyl urethan reacts with thionyl chloride to form N-β-chloroethyl urethan; both urethans, the former with 2 moles, the latter with 1 mole of phosphorus pentachloride, yield β-chloroethyl isocyanate.

ELIZABETH, N. J. RECEIVED OCTOBER 26, 1936

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[1] Gabriel and Stelzner, *Ber.*, **28**, 2937 (1895).

[2] Hofmann, *ibid.*, **3**, 655 (1870).

[3] Lengfeld and Stieglitz, *Am. Chem. J.*, **16**, 71 (1894).

[CONTRIBUTION FROM THE BIOLOGICAL LABORATORY, COLD SPRING HARBOR]

The Calcium Binding Power of Egg Albumin

BY JULIUS C. ABELS

Since Rona and Takahashi[1] demonstrated that the calcium in protein systems is for the most part non-ionic, the manner by which this calcium is bound has aroused much study. The modes of linkage which at first present themselves are through one or more of the common free groups of the protein molecule: probably the amino, carboxyl, aliphatic or phenyl hydroxyl. We therefore thought it of interest to make protein preparations which lack one or more of these functional groups and then to note their calcium binding power. We have not been able to block the carboxyl, but in view of the results obtained (see below) we did not feel that this was necessary.

Experimental

A. Preparations.—1. Crystalline egg albumin was prepared by the method of Kekwick and Cannan.[2] This was recrystallized three times, and was used as the parent material for the other preparations as well.

2. Deaminized egg albumin was made in the usual way with nitrous acid at 20° in very dilute solution in order to avoid premature precipitation. This was then dialyzed in cellophane bags against running tap water and distilled water, and left in the ice chest overnight, during which time a slight precipitate formed; this was dissolved by adjusting the *p*H of the solution to 8.4 and finally by the addition of hydrochloric acid the *p*H was lowered to 7.8. This protein solution was concentrated by ultrafiltration. Amino nitrogen (gasometric Van Slyke) on five such preparations showed that complete deamination had been accomplished.

3. Five separate preparations of acetylated albumin were made by the method of Freudenberg.[3] Ether-extracted albumin was dried and finely suspended in a mixture of equal volumes of glacial acetic acid and quinoline, and to this acetic anhydride and quinoline were added slowly at 5°, the *p*H of the system being kept at about 6.5. Aliquots were precipitated daily with 4 volumes of ether, filtered, washed with slightly acidified water, and suspended in water at *p*H 5.0. This was dialyzed overnight against running tap water and then distilled water with constant mechanical agitation; and finally dissolved in water at *p*H 8.2. Acetyl determinations were made on these solutions by the method of Herriott,[4] and when a constant value of 28 acetyl groups per molecule of albumin (molecular weight 34,500) had been obtained on the aliquots of three successive days, the main mass of the preparation was treated similarly and concentrated by ultrafiltration.

4. Gelatin, also employed in this study, was Eastman Kodak purified product. This, as well as the other proteins used, was calcium free.

B. Methods.—The method employed in determining the bound calcium was essentially that of R. Loeb[5] in his study of the effect of proteins on the diffusibility of the calcium ion. Ten to twenty cc. of protein solution was placed in a cellophane bag, and a rubber stopper was fitted into the filled bag to avoid subsequent dilution. The sac was then suspended in a large volume (300–400 cc.) of 0.80% sodium chloride brought to *p*H 7.6 with sodium bicarbonate and sodium carbonate, and to this latter solution was added calcium chloride in amounts from 1.0 to 12.0 mml./liter. The use of the sodium chloride in this instance serves to reduce the Donnan equilibrium. These systems were set aside for thirty hours at 20° (at 30° in the case of the gelatin experiments), after which time samples were withdrawn from both the protein solution and dialysate for calcium[6] and chloride[7] determinations.

Results

The results are perhaps best stated in a table of typical experiments.

The table is for the most part self-explanatory. From the amount of calcium in the dialysate (column 2) and from the ratio of chloride in dialysate to chloride in protein solution (3), the amount of calcium in the protein solution due to the Donnan effect may be calculated (4). When this value is subtracted from the observed amount of calcium in the protein solution (1), the remainder is that bound to some free group or groups of the protein molecule.

Discussion

The following points which Loeb[5] has noted for egg albumin have been confirmed: that on the alkaline side of its isoelectric point there is always a binding of calcium, and as the protein concentration is increased the total amount of bound calcium is increased. The same has also been noted for gelatin. The values found for groups of calcium to egg albumin molecule (about 1:1) agree fundamentally with those noted by other workers using serum proteins and serum.[8,9]

It is apparent immediately that the calcium is not bound through a carbamino linkage, for, if

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(1) Rona and Takahashi, *Biochem. Z.*, **31**, 336 (1911).

(2) Kekwick and Cannan, *Biochem. J.*, **30**, 227 (1936).

(3) Freudenberg, *Z. physiol. Chem.*, **213**, 226 (1932).

(4) Herriott, *J. Gen. Physiol.*, **19**, 283 (1935).

(5) Loeb, *ibid.*, **8**, 541 (1928).

(6) Kramer and Tisdall, *J. Biol. Chem.*, **47**, 475 (1921).

(7) G. Smith, "Quantitative Analysis," The Macmillan Company, New York, 1922, p. 55.

(8) Marrack and Thacker, *Biochem. J.*, **20**, 580 (1926).

(9) Greenberg and Gunther, *J. Biol. Chem.*, **85**, 491 (1929–1930).

Table I

	1 Observed Ca mml./l. in protein soln.	2 Ca in dialysate mml./l.	3 Cl_d/Cl_p	4 Calcd. Ca in protein soln. mml./l.	5 Bound Ca in protein soln. mml./l.	6 Protein mml./l.	7 Groups of Ca to protein
Egg albumin	5.05	3.20	1.06	3.60	1.45	1.18	1.23
	4.70	3.56	1.04	3.94	0.76	0.60	1.26
Deaminized albumin	4.95	2.75	1.05	3.10	1.85	0.60	3.10
	6.45	3.40	1.08	3.95	2.50	1.16	2.16
Acetylated albumin	4.25	3.80	1.06	4.22	0.03	0.67	0.04
	3.15	2.88	1.05	3.18	− .03	.26	Approx. 0
"Deacetylated" acetylated albumin	4.42	3.27	1.05	3.60	.82	.64	1.29
	4.30	3.05	1.06	3.42	.98	.72	1.36
Gelatin	4.82	3.51	1.05	3.88	.94	.70[a]	1.34
	3.54	2.53	1.04	2.70	.84	.60[a]	1.38

[a] 34,500 was chosen arbitrarily as the molecular weight of gelatin to provide comparison with the ratios obtained for the egg albumin.

this were so, deamination of the albumin should result in a decrease of bound calcium instead of in an increase. These higher ratios might be interpreted as being due to (a) an increased calcium binding power of the protein resulting from the splitting of the chain in the course of deamination; (b) the substitution of functional hydroxyl groups for the amino, which is the result of a deamination in aqueous solutions; or (c) to both.

The substitution of hydroxyl groups was tested by using the acetylated albumin. Such experiments show that these proteins no longer have the calcium linkage; and since the acetylation has blocked the amino and hydroxyl groups, and not the carboxyls, we may conclude that the functional group is very probably the hydroxyl. This is further shown by the restoration of the calcium binding power of the protein when the acetyl groups are removed by treating the protein solution with alkali to *p*H 11.0, for two minutes, bringing back to *p*H 8.2, and removing the acetate by dialysis. That the hydroxyl group is not necessarily a phenolic one is seen from the fact that gelatin, with no phenyl groups, binds calcium to the same extent as does albumin. It would be interesting, however, to determine whether or not the phenolic radical plays any role; this might be done by correlating tyrosine values of partially acetylated proteins with their ability to bind calcium.

Summary

A study of protein derivatives seems to indicate that calcium is bound to albumin through an hydroxyl linkage.

Cold Spring Harbor, N. Y.

Received September 19, 1936

[Contribution from the Department of Chemistry, Stanford University]

The Spontaneous Stable Formation of Colloids from Crystals or from True Solution through the Presence of a Protective Colloid[1]

By J. W. McBain and M. E. Laing McBain

The subject of colloids has suffered greatly from the commonly accepted stigma that colloidal systems are inherently unstable and that they therefore show the effects of every chance incident in the history of each individual specimen. This discouraging view has probably arisen from the older habit of regarding colloids merely as fine dispersions without mention of any factor that should hold them in so unlikely a condition, much less cause them, when disturbed or destroyed, to revert spontaneously to that former state.

In 1926[2] one of us presented the argument that certain colloidal solutions, such as those of soap, must be regarded as stable in the strictest thermodynamic sense, because they exist in equilibrium with crystalloidal constituents and crystals, and hence must be as stable as these. This has been accepted by many leading colloid authori-

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(1) Read at the Pittsburgh meeting, September, 1936.

(2) J. W. McBain, "Colloid Symposium Monograph," Cambridge, 1926, p. 1; *Kolloid-Z.*, **40**, 1 (1926).

ties, such as Freundlich and von Weimarn, who agree that a large group of important colloids are as stably formed as ordinary solutions.

However, even now in 1936, according to von Buzágh's "Kolloidik,"[3] "eine sehr allgemein verbreitete Anschauung" is that colloidal sols cannot be stable.

Our explanation of true stability of a colloidal particle demands a spontaneous orientation of the molecules, with the soluble groups exposed to the solvent, such that the particle is self organizing and if disturbed would revert again to this equilibrium form. Thus soap solutions come to true reversible equilibrium and exhibit properties which become fully independent of their previous history just like any solution of sugar or salt.

In 1917 Pickering[4] stated that oils could dissolve in concentrated soap systems, as well as forming emulsions therein. However, his proof of this clear claim was doubtful, because he did not dissolve the oils directly but formed his systems by very indirect methods involving concentrated pastes of semi-solid soap and also mechanical working. Hence, his results were not definitely differentiated from those of von Weimarn who had specialized in producing admittedly unstable colloids by indirect methods.

In 1918 and 1921 McBain, Beedle, and Bolam[5] made the obvious suggestion that a water-soluble substance could be sorbed by a soap particle in aqueous solution. In 1932 Lester Smith, in a series of important and significant papers,[6] showed that the solubility of various liquids was much increased by the presence of 10% of soap, and, like Weichherz in 1929, he suggested that the increase was sorbed upon the soap micelles, possibly displacing water of hydration. The results depended upon the procedure and did not strictly demonstrate the existence of any true reversible equilibrium.

In Smith's second paper of 1932 he used a water-insoluble indicator dye, methyl yellow (0.32 part in 10^7 water), but (p. 1673) he first dissolved it in ether along with free fatty acids, and afterward produced soap by adding aqueous alkali and more ether (and usually methyl alcohol). This procedure too closely resembles von Weimarn's technique of forming unstable colloids *in situ* to carry any conviction as to the spontaneous formation of an inherently stable protected colloid.

We now make the definite suggestion that colloidal particles may be spontaneously and reversibly formed in solvents in which they are insoluble, provided that a suitable protective colloid is present to act as solubilizing or stable protective agent. For example, a true crystal insoluble in water can spontaneously pass into water containing a suitable stable colloid, and form colloidal particles in association with the stabilizing colloid.

Thus crystals of oil-soluble dyes, such as Yellow AB, Yellow OB, and Scarlet 9995X, pass directly into a 1% aqueous soap solution. Not only so, but such dilute soap solution will extract these dyes even from unsaturated solutions in kerosene, medicinal paraffin oil, paraffin wax, or benzene, etc. Conversely, equilibrium may be attained from the opposite direction, since each of these non-aqueous solvents will extract from the dye-containing soap solution a proportion of dye. Thus the two liquid layers, one a true solution, and the other a protected colloidal solution (incapable of existing without such protection) come into complete reversible equilibrium, the position of equilibrium being the same when approached from either side.

Therefore, we must conclude that a molecule in a crystalline space lattice or a molecule in true solution, saturated or unsaturated, is no more stable than a molecule in a colloidal particle suitably stabilized. The stabilizing force is that of adsorption within the particles of stabilizing colloids; in some extreme cases it may be direct chemical combination.

It appears likely that the colloidal particle is surrounded by the stable colloid rather than that according to the other extreme form of the previous suggestion of McBain and of Lester Smith the insoluble material coats the stable soluble colloid. Gurwitsch[7] likewise in showing that the amounts of oil which could be incorporated in soap solutions without turbidity were parallel to the known ease and extent of association of the soap molecules, had assumed that the oil molecules formed thick coatings around the soap micelles and made the micelles hydrophobic (that is, unstable).

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[3] A. von Buzágh, "Kolloidik," Theodor Steinkopff, Dresden, Germany, 1936, p. 41.

[4] S. U. Pickering, *J. Chem. Soc.*, **111**, 86 (1917).

[5] J. W. McBain and T. R. Bolam, *ibid.*, **113**, 825 (1918); F. C. Beedle and T. R. Bolam, *J. Soc. Chem. Ind.*, **40**, 27T (1921).

[6] E. Lester Smith, *J. Phys. Chem.*, **36**, 1401, 1672, 2455 (1932).

[7] L. Gurwitsch, *Kolloid-Z.* Ergänzungband, **36**, 196 (1925); see also "The Scientific Principles of Petroleum Technology," translated by Moore, D. Van Nostrand Co., New York, 1927, pp. 95–96.

Brintzinger and Beier[8] systematically studied the increase in solubility of a series of acids and bases in the presence of gelatine and of gum arabic in concentrations ranging from 0.5 to 6.0%. In most cases there was a marked increase in solubility, less in the case of gum arabic. In a few cases there was no effect and the solubility of anthranilic acid was actually lowered by the gum arabic. The authors considered that chemical combination, solution in and adsorption by the colloidal particles might all be involved. They also mentioned that urea is more soluble in blood or protein-containing liquids than in pure water. Similarly, in the well-known studies by Findlay and collaborators (1911–1914) the solubility of gases in water was sometimes increased and sometimes diminished by various colloids and mechanical suspensions.

To explain the continued existence of colloids requires some affinity between the solvent and the groups exposed on the outside of the particle. These groups may be supplied by part of the molecule of a stable colloid itself or by a sufficient amount of such exposed soluble groups supplied by a stable protective colloid.

Experimental

Experiments have been carried out both with commercial soap and sodium oleate, mostly 1% dissolved in water, but occasionally 0.5%. The non-aqueous phase has been benzene, toluene, kerosene, Nujol, xylene, soft paraffin wax, etc. Most of the experiments have been semi-quantitative, in addition to the significant qualitative observations mentioned in the text. A study of the partition coefficient in its dependence on concentration of dye and of stabilizing colloid is reserved for a later communication with T. M. Woo. Concentration of dye was determined colorimetrically against a reference solution of dichromate. For example, in four experiments the total system consisted of 40 g. of water, 2 g. of toluene, 0.4 g. of sodium oleate, and 0.001 g. of scarlet X; in two cases the dye was first dissolved in the toluene, and in the other two it was admixed with the aqueous soap. Thereupon, the two layers were brought into contact and placed upon a machine which imparted to the system an extremely slow swirling motion that avoided all breaking of the surface or emulsification. After twenty-four hours the colorimeter readings were 1.34, 1.3, 1.8 and 1.6, respectively, showing that within the somewhat large experimental error the same equilibrium was obtained from both sides. A typical result may be quoted from Mr. Woo's data for the system 0.5% potassium oleate, 40 g. of water, 0.04 *N* potassium hydroxide, 2 g. of toluene, and 0.1 g. of dye—the latter placed in two cases in the toluene and in two in the aqueous soap; the dye remaining in the soap layer after forty-eight hours was 0.0232, 0.0232 and 0.0237, 0.0237 g., respectively.

To avoid misunderstanding, it should be emphasized clearly that the processes pointed out above are different in kind from the familiar phenomena of peptization or of protective action on suspensions such as carbon black suspended in soap solution, or silver chloride in gelatine, or the peptizing of a gel to form a sol. In all cases of peptization it has been assumed that the peptizing agent merely separated already existing particles. Similarly, formation of ordinary (protected) colloid particles by the so-called condensation methods, whether physical or chemical, generate the colloid *in situ* from a high state of supersaturation. It is clear that both these processes differ from the extraction of a molecule from its stable space lattice or its unsaturated solution to create stable colloidal particles.

Likewise the processes here described differ from hydrotropy[9] where in general protective colloids are not involved. Doubtless however many examples there described may belong here, and in many cases the same forces, whether van der Waals or chemical, may be operative.

It is evident that if our conclusions are accepted there must already exist numerous unrecognized examples of such action. Many protected colloids containing a sufficient amount of truly stable protective agent may contain much more stable material than has hitherto been suspected.

Summary

Not only are many important colloids truly stable in that they form spontaneously and enter into reversible equilibrium with crystalloidal constituents and crystals, but otherwise unstable colloids may also exhibit similar properties characteristic of true stability if sufficient stable protective colloid is present.

Stanford Univ., Calif. Received October 7, 1936

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(8) H. Brintzinger and H. G. Beier, *Kolloid-Z.*, **64**, 160, 300 (1933); *ibid.*, **68**, 271 (1934); *Naturwissenschaften*, **20**, 254 (1932), includes even suspensions like charcoal.

(9) Neuberg, *Biochem. Z.*, **76**, 107 (1916); for later references see Kortüm, *Z. Elektrochem.*, **42**, 289 (1936); also Wilensky and Pawlowa, *Kolloid-Z.*, **76**, 188 (1936).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Resistance and Capacity Behavior of Strong Electrolytes in Dilute Aqueous Solution.[1] I. Method for the Simultaneous Observation of Conductance and Dielectric Constant at High Radio Frequencies

BY ORLAN M. ARNOLD AND JOHN WARREN WILLIAMS

The interionic attraction theory has been utilized by Debye and Hückel[2] and by Onsager[3] to demonstrate that a square root law is the correct one to explain the change in the electrical conductance of very dilute solutions of strong electrolytes with concentration. In such systems variations in the mobilities rather than in the number of the ions are responsible for the observed conductance changes. At the time Debye and Hückel first proposed their conductivity theory Sand[4] realized that if changes in the mobilities of the ions were caused by electrostatic forces, then measurements at very high frequencies and at very high field strengths should lead to enhanced conductances since in either event the effect of such forces would be reduced. At the present writing the existence of such increased conductances under these conditions has been established experimentally and elaborate theories have been worked out to describe them. The experiments to be discussed in the following article were designed to test further the validity of the theory of Debye and Falkenhagen[5] which describes the frequency variation of conductance in dilute solutions of strong electrolytes.

The ordinary bridge methods such as are used for the determination of resistance and capacity at audio frequencies are not generally satisfactory at the lower radio frequencies and they fail entirely when observations at the higher radio frequencies are required. At such high frequencies the standard resistance coils react inductively and capacitatively, changes in the position of the contact on a slide wire produce changes in the ratio of such inductances and capacities in an unknown way, and the arrangement and length of the lead wires can give rise to uncertainties. From time to time there have been proposed methods, making possible the observation of conductance and/or capacity change at the radio frequencies.[6-10] The method finally adopted by us resembled that of Sack and his collaborators, but it differed in so many important respects that we feel it necessary to devote this first article to a brief description of the apparatus itself and the theory upon which its use is based. This comparator-resonance method made possible the simultaneous observation of resistance and capacity change with frequency, at the same time it was flexible as regards frequency change. It did not permit absolute measurements to be made, but it did accomplish a comparison of conductance and dielectric constant of two solutions, a standard and an unknown.

Description of Apparatus

A schematic diagram of the apparatus is given in Fig. 1. As indicated, there are three distinct circuits, a generator, (I); an intermediate circuit (II); and a comparator circuit, (III). In use all parts of this apparatus were clamped in fixed position on a firm table.

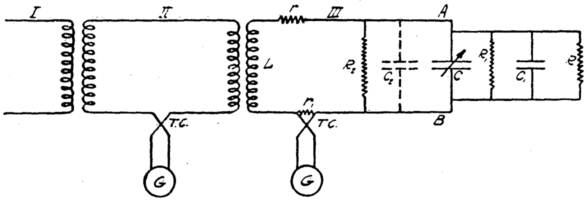

Fig. 1.—Schematic diagram of high frequency apparatus: L, inductance in the measuring circuit; C, capacitance of the variable precision condenser; R, resistance of the solution in the cell; R_1, resistance of the insulation of the precision condenser; R_2, resistance of the insulation of other parts of circuit; r, resistance of the leads in the measuring circuit; r_1 resistance of the heater in the thermocouple; C_1, capacitance of the measuring cell; C_2, capacitance between leads in the circuit; G, galvanometer; T. C., thermocouple.

A modified Hartley circuit, using an 01A tube, was found to be a satisfactory source of alternating current. In order to obtain uniform power output, good wave form and constant frequency at the high radio frequencies, it was

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(1) More complete details of this work may be found in the thesis of O. M. Arnold, presented to the Faculty of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy and filed in the library of the University of Wisconsin, June, 1934.

(2) Debye and Hückel, *Physik. Z.*, **24**, 305 (1923).

(3) Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).

(4) Sand, *Phil. Mag.*, **45**, 281 (1923).

(5) Debye and Falkenhagen, *Physik. Z.*, **29**, 401 (1928).

(6) Sack, *ibid.*, **29**, 627 (1928); [Brendel, Mittelstaedt and Sack, *ibid.*, **30**, 576 (1929); Brendel, *ibid.*, **32**, 327 (1931)].

(7) Deubner, *ibid.*, **30**, 946 (1929).

(8) Wien, *Ann. Physik*, [5] **11**, 429 (1931).

(9) Malsch, *ibid.*, [5] **12**, 865 (1932).

(10) Zahn, *Z. Physik*, **51**, 350 (1928); Rieckhoff, *Ann. Physik*, [5] **2**, 577 (1929).

necessary to adjust inductance and capacity to one another, to adjust a variable grid leak resistance, and to maintain constant filament and plate supply. The wave length range used in the experiments was approximately 10 to 180 meters.

The intermediate circuit connected the generator with the comparator circuit. It consisted of two plug-in variable coupling coils and sensitive thermocouple connected in series. The indicating instrument used with the thermocouple was a Rawson multimeter. This intermediate circuit was not tuned to the oscillator for several reasons. First, too strong coupling, which causes unsteadiness of the power output and of the frequency in the oscillator and which results in greater fluctuation of current in the measuring circuit, may be thus avoided. Second, the disturbing effects due to the presence of harmonics are reduced. Third, greater possibility is afforded for more complete electrostatic shielding. The comparator circuit consisted of an inductance L, a thermocouple of high sensitivity (connected to a Leeds and Northrup Type R galvanometer), a precision condenser of low capacity C, a conductance cell C_1, or resistance R, connected as shown with very short leads. A beam of light reflected from the galvanometer mirror and focused on a curved scale of two meter radius and 4,140 divisions served to measure the energy in the circuit.

The thermocouples used were of the vacuum type, No. 22C, manufactured by the Western Electric Company. In each case they were placed directly in series with the circuit rather than in auxiliary detector circuits as is usually done. In a long series of experiments the ever present possibility of error due to slight mechanical displacement of primary and auxiliary circuits is thus avoided; in addition, the sensitivity of the current measurements is increased to the extent that very feeble currents can be used with success. The use of feeble currents is advantageous because heating effects in the conductance cells should be reduced as much as possible.

The shielding and grounding of the several circuits presented many difficulties and much attention was given to their solution. For the highest efficiency it was found necessary to shield separately the various parts of the apparatus. The generator, the thermocouples, the inductance of the comparator circuit with its coupling coil of the tank circuit and the precision condenser were enclosed in copper-lined boxes. An additional electrostatic shield was placed about the coupling coil of the intermediate circuit adjacent to the inductance of the comparator circuit in order to enhance the magnetic induction and reduce the electrostatic induction. Those parts of the circuits which were grounded were connected to a metal rod sunk in moist earth exterior to the building proper. All alternating current lines connected to single phase motors in the immediate vicinity of the apparatus were grounded or choked.

Theory of the Circuit and Measurements

The method of interpretation of precision condenser readings in terms of the dielectric constants of the solutions may be described as follows: For pure capacities connected as shown in Fig. 1, $\bar{C} = C' + C_1 + C_2$, when the cell is connected in parallel, and $\bar{C} = C'' + C_2$, when the cell is disconnected. Here C' and C'' are the precision condenser settings for the two observations and $\bar{C}$ is the total capacity of the circuit. It is further evident that $C'' - C' = C_1$. When dilute electrolyte solutions are introduced into the cells, the situation becomes much more complicated. Nevertheless, one may compare with reasonable correctness the susceptibilities of two solutions of the same electrical conductance, provided the latter is not too great, by making observations of the changes in the apparent capacity C_{1A}, defined as $C''_A - C'_A$. Thus, differences in C_{1A}, from solution to solution, using the same cell in identical position at the same wave length may be interpreted directly in terms of dielectric constant change when reference is made to the behavior of a standard solution of known dielectric constant and like electrical conductance. The capacity C_2 is small enough so that $\bar{C}$ may be considered equal to C'' when the cell is disconnected from the circuit.

Both galvanometer deflections and precision condenser settings are made use of for the evaluation of the conductances of the solutions. The mathematical treatment of the comparator circuit for the conductance problem is complicated. There will be considered a definition of the total impedance of the circuit and a definition of the impedance from point A to point B in the circuit; then there will be described the two specific cases, one in which the conductance cell or other resistance is removed from the circuit, and the other in which the cell or resistance is connected in the circuit. In all these considerations the resistance R_2 has been neglected, since $R_2 >> R$. In the equations I is the current in the comparator circuit, I' is the current in the intermediate circuit, E is the voltage in the comparator circuit, Z designates an impedance, D is a galvanometer deflection and k is a proportionality constant.

Definition of Total Impedance of Circuit.—We may begin our consideration with the following relations

$$kD = I^2$$

$$\bar{r} = r + r_1$$

$$z_1 = \bar{R}_0 + j\bar{X}_0$$

In these equations z_1, $\bar{R}_0$ and $\bar{X}_0$ symbolize total impedance, resistance and reactances from A to B, respectively. Now, by definition

$$(j\omega L + \bar{r} + z_1)I + j\omega MI' = 0 \qquad (1)$$

After substituting for z_1, rearranging the real and the imaginary terms, squaring and substituting E for MI', one obtains for the current I the expression

$$|I| = \frac{E}{\sqrt{(\bar{r} + \bar{R}_0)^2 + (\omega L + \bar{X}_0)^2}} = \frac{E}{z_T} \qquad (2)$$

in which z_T is the total impedance.

The current I is the root mean square of the current amplitude. Since one is concerned with the current amplitude only, the phase angle may be neglected.

From equation (2) the total impedance may be expressed by the relationship

$$z_T^2 = (\bar{r} + \bar{R}_0)^2 + (\omega L + \bar{X}_0)^2$$

The total impedance is treated in the form of its square since it eliminates the square root term, and since the galvanometer deflection expresses the square of the current.

By further definition

$$\bar{X}_0 = \omega L_1 - (1/\omega\bar{C}_0)$$

where L_1 is the inductance and $\bar{C}_0$ is the total capacity, both across AB. Since L_1 is nearly if not exactly zero, the reactance for the part of the circuit from A to B may be expressed as $\bar{X}_0 = -1/\omega\bar{C}_0$. Thus, the expression for the total impedance of the circuit becomes

$$z_T^2 = (\bar{r} + \bar{R}_0)^2 + (\omega L - (1/\omega\bar{C}_0))^2 \qquad (3)$$

Definition of Impedance from A to B.—The quantities $\bar{R}_0$ and $\bar{C}_0$ must be determined for substitution in equation (3).

The admittance, Y, from A to B may be written

$$Y = \frac{1}{\bar{R}} + j\omega\bar{C} = \frac{1 + j\omega\overline{CR}}{\bar{R}}$$

or

$$\bar{z}_1 = \frac{\bar{R}}{1 + j\omega\overline{RC}} = \frac{\bar{R}(1 - j\omega\overline{CR})}{1 + \omega^2\bar{C}^2\bar{R}^2}$$

in which $\bar{R}$ represents R_1, R_2, and R in parallel, $\bar{C}$ is the effective capacity across AB, and $\bar{z}_1$ is the effective impedance, also across AB.

Rewriting the expression for $\bar{z}_1$, we have

$$\bar{z}_1 = \frac{\bar{R}}{1 + \omega^2\bar{C}^2\bar{R}^2} - \frac{j\omega\overline{CR}^2}{1 + \omega^2\bar{C}^2\bar{R}^2} = \bar{R}_0 + j\bar{X}_0 = \bar{R}_0 - \frac{j}{\omega\bar{C}_0}$$

The evaluation of $\bar{z}_1$ makes it possible to express z_T in terms of more readily accessible quantities. Since

$$R_0 = \frac{\bar{R}}{1 + \omega^2\bar{C}^2\bar{R}^2} \text{ and } \frac{1}{\omega\bar{C}_0} = \frac{\omega\overline{CR}^2}{1 + \omega^2\bar{C}^2\bar{R}^2}$$

substitution for $\bar{R}_0$ and $\dfrac{1}{\omega\bar{C}_0}$ in equation (3) gives

$$z_T^2 = \left(\bar{r} + \frac{\bar{R}}{1 + \omega^2\bar{C}^2\bar{R}^2}\right)^2 + \left(\omega L - \frac{\omega\overline{CR}^2}{1 + \omega^2\bar{C}^2\bar{R}^2}\right)^2 \qquad (4)$$

Case 1. Cell Not Connected.—In this case $\bar{R}_1$ is the only resistance to be considered for the evaluation of $\bar{R}$. Equation (4) becomes

$$z_{T_1}^2 = \left(\bar{r}_1 + \frac{R_1}{1 + \omega^2\bar{C}^2R_1^2}\right)^2 + \left(\omega L - \frac{\omega\bar{C}R_1^2}{1 + \omega^2\bar{C}^2R_1^2}\right)^2 \qquad (5)$$

The subscript 1 is used for the total impedance of the circuit when the conductance cell or other resistance is not connected across AB. Since R_1 is high in magnitude, equation (5) reduces to

$$z_{T_1}^2 = \bar{r}_1^2 + \omega^2L^2 - \frac{2L}{\bar{C}} + \frac{1}{\omega^2\bar{C}^2} = \bar{r}_1^2 + \left(\omega L - \frac{1}{\omega\bar{C}}\right)^2$$

At resonance $\omega L = \dfrac{1}{\omega\bar{C}}$, and the impedance becomes

$$z_{T_1}^2 = \bar{r}_1^2 \qquad (6)$$

Case 2. Cell Connected in Parallel with Precision Condenser.—The resistances contained in $\bar{R}$ appearing in equation (4) are now R and R_1. Since R_1 is large and may be neglected ($R_1 >> R$), the expression for the impedance assumes the form

$$z_{T_2}^2 = \left(\bar{r}_2 + \frac{R}{1 + \omega^2\bar{C}^2R^2}\right)^2 + \left(\omega L - \frac{\omega\bar{C}R^2}{1 + \omega^2\bar{C}^2R^2}\right)^2$$

The subscript 2 indicates that the cell or resistance is now connected in the comparator circuit If the quantity $\omega^2\bar{C}^2R^2$ is large compared to 1, the expression reduces, at resonance, to

$$z_{T_2}^2 = \left(\bar{r}_2 + \frac{R}{1 + \omega^2\bar{C}^2R^2}\right)^2 \qquad (7)$$

Relationship between Galvanometer Deflection and Electrical Conductance.—From Ohm's law

$$I_1^2z_{T_1}^2 = E_1^2 \text{ and } I_2^2z_{T_2}^2 = E_2^2$$

Therefore

$$I_1^2z_{T_1}^2 = I_2^2z_{T_2}^2, \text{ since } E_1 = E_2 \qquad (8)$$

The voltage is maintained constant for any set of observations having to do with a given solution.

From equations (6), (7) and (8) we have

$$\frac{I_1^2}{I_2^2} = \frac{z_{T_2}^2}{z_{T_1}^2} = \frac{kD_1}{kD_2} = \frac{\left(\bar{r}_2 + \dfrac{R}{1 + \omega^2\bar{C}^2R^2}\right)^2}{\bar{r}_1^2} \qquad (9)$$

At any one frequency the total impedance of the circuit without the cell is always the same. Thus the numerical value for the resistance of any solution, as compared to that of a potassium chloride solution, may be obtained from the ratio which forms equation (9), provided the resistances of the two solutions are nearly of the same magnitude.

The solution of this expression for R in a series of measurements at any wave length is facilitated by the construction of an interpolation table for R and kD_2/kD_1, to be used at that wave length. The values of $\bar{r}$ and $\omega^2\bar{C}^2$ are constant for any wave length and may be obtained either by the proper calibration of the members of the circuit or by solving for one or the other by the substitution in the equation of known values of R and kD_2/kD_1. The latter known quantities must have been obtained from a series of measurements with a standard resistance. The quantities $\bar{r}$ and $\omega\bar{C}$ do not have to be precise for if approximate constant values are used throughout, the relative values of kD_2/kD_1 and R will be correct.

We wish to express our indebtedness to Professor Edward Bennett of the Department of Electrical Engineering of this University and to Dr. Ronold King of the Department of Physics of Lafayette College for their helpful advice.

Summary

A method is described which serves for the simultaneous observation of electrical conductance and dielectric constant of very dilute electrolyte solutions at high radio frequencies. The apparatus which was used may be described as being of the comparator-resonance type. It consists of three distinct units, a variable high frequency oscillator circuit, an intermediate circuit and a comparator circuit with thermocouple–galvanometer measuring system.

The mathematical theory of the circuits is considered. Dielectric constant change is calculated from a comparison of the resonance settings of the standard variable precision condenser in the comparator circuit with the conductance cell connected and disconnected. For the evaluation of electrical conductance change there are required observations of the comparator circuit galvanometer deflections, again at resonance and with the cell connected and disconnected. It is further pointed out that the method developed may be applied to the measurement of high frequency currents through other types of resistances.

MADISON, WIS. RECEIVED AUGUST 17, 1936

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Resistance and Capacity Behavior of Strong Electrolytes in Dilute Aqueous Solution. II. The Dispersion of Electrical Conductance[1]

BY ORLAN M. ARNOLD AND JOHN WARREN WILLIAMS

Some years ago it was pointed out by Debye and Falkenhagen[2] that as a necessary consequence of the postulated existence about any central ion of an ionic atmosphere with a finite time of relaxation, there must result an electrical conductance which is dependent upon the frequency of the field which is used to measure it. If an alternating field is applied, each ion in the solution will acquire a periodic motion. If the frequency is low enough (1000 cycles, for example) there will be produced in each instant a dissymmetry in the ionic atmosphere which corresponds to the momentary velocity of the ion. But if this frequency is increased to a point where the period of oscillation of the ion becomes comparable with the time required for the formation of its atmosphere any dissymmetry of the latter, necessary for the existence of the electrical force of relaxation, will decrease. Thus, depending upon the time of relaxation of the atmosphere about any particular ion there will be a frequency at which the dissymmetry of the atmosphere no longer can be formed in the normal way, and as the frequency is increased above this value the electrical force of relaxation will diminish and the mobility of the central ion will increase until such time as the frequency has been made so high that the dissymmetry of the ionic atmosphere disappears entirely.

The results of the calculations of Debye and Hückel[3] and of Onsager[4] for the molar conductance of a solution at zero, or very low, frequency may be expressed in the form

$$\bar{\Lambda} = \bar{\Lambda}_0 - \bar{\Lambda}_{I_0} - \bar{\Lambda}_{II}$$

Here $\bar{\Lambda}$ is the molar conductance of the solution at a finite concentration, $\bar{\Lambda}_0$ is the molar conductance at infinite dilution, $\bar{\Lambda}_{I_0}$ is the electrical

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(1) A preliminary and incomplete report of this work has appeared in another place [Williams and Arnold, *Acta Physicochim., U. R. S. S.*, **3**, 619 (1935)]. This report gives as well provisional data for the dielectric constants of very dilute electrolyte solutions at two high frequencies.

(2) Debye and Falkenhagen, *Physik. Z.*, **29**, 121, 401 (1928).

(3) Debye and Hückel, *Physik. Z.*, **24**, 305 (1923).

(4) Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).

force of relaxation expressed in conductance units, and $\overline{\Lambda}_{\text{II}}$ is the electrophoretic force, again expressed in conductance units. The molar conductance of the solution as a function of the frequency ω, used to measure it may be written in similar fashion as

$$\overline{\Lambda} = \overline{\Lambda}_0 - \overline{\Lambda}_{\text{I}\omega} - \overline{\Lambda}_{\text{II}}$$

in which at zero frequency, $\overline{\Lambda}_{\text{I}\omega} = \overline{\Lambda}_{\text{I}_0}$. When at extremely high frequencies the dissymmetry of the ionic atmosphere has disappeared entirely, $\overline{\Lambda}_{\text{I}\omega} \longrightarrow 0$, and the molar conductance approaches the limiting value

$$\overline{\Lambda} = \overline{\Lambda}_0 - \overline{\Lambda}_{\text{II}}$$

The mathematical treatment of Debye and Falkenhagen has led to the following expression for the electrical force of relaxation expressed as conductance.

$$\overline{\Lambda}_{\text{I}\omega} = \frac{|e_1e_2|}{3DkT}\kappa\overline{\Lambda}_0\chi(\omega,\theta,q)$$

where

$$\chi(\omega,\theta,q) = \frac{\sqrt{q}}{\left(1-\frac{1}{q}\right)^2 + \omega^2\theta^2}\left[\left(1-\frac{1}{q}\right)\left(\overline{R}-\frac{1}{\sqrt{q}}\right) + \omega\theta\overline{Q}\right]$$

$$\overline{R} = \frac{1}{\sqrt{2}}\sqrt{\sqrt{1+\omega^2\theta^2}+1}$$

$$\overline{Q} = (1/\sqrt{2})\sqrt{\sqrt{1+\omega^2\theta^2}-1}$$

and the other symbols have the significance usually assigned to them in the discussion of the interionic attraction theories. Thus

$$Q = \frac{(\overline{L}_1z_1 + \overline{L}_2z_1)\,z_1z_2}{(z_1+z_2)(\overline{L}_1z_2^2 + \overline{L}_2z_1^2)}$$

$$\theta = \frac{z_1^2z_2^2}{z_2^2\overline{L}_1 + z_1^2\overline{L}_2} \times \frac{15.33 \times 10^{-8}}{kTq\kappa^2}$$

and

$$\kappa^2 = \frac{4\pi}{DkT}\frac{e^2N\gamma}{1000}\Sigma\nu_iz_i^2$$

In this article are recorded measurements of the electrical conductance of dilute aqueous solutions of potassium chloride, barium chloride, magnesium sulfate, lanthanum iodate, cerium sulfate, praseodymium sulfate and luteo chloride at the wave lengths 15, 30, 50, 75, 100, 130 and 170 meters.

High Frequency Conductance Measurements

The comparator-resonance method described in the first paper of this series[5] was employed for the measurement of the variation of conductance at the high frequencies. In order to ensure high precision the different members of the circuit were carefully calibrated as follows.

The precision condenser was calibrated by the substitution method in a heterodyne circuit for its absolute value in capacity at several different points. This condenser was calibrated twice for its linearity in capacity. The type R galvanometer was calibrated for its deflections on a circular scale by the ordinary differential direct current method. Known resistances were introduced in series with the galvanometer. From more than three hundred points over the whole range a smooth curve showing deviations from a linear relation between the current and the deflection was obtained. This curve gave the correction for the galvanometer deflections. The thermocouple in the measuring circuit and the Type R galvanometer connected to this thermocouple were calibrated for forty points on the galvanometer scale by reversing the several values of direct current through the heater of the thermocouple. This thermocouple was also calibrated in terms of microvolts in the Electrical Engineering Standards Laboratory of the University with the use of a White potentiometer. The thermocouple was twice again calibrated as located in the circuit, first with the White potentiometer and then with a microammeter. The procedure in each case was to reverse the direct current through the heater.

Careful physical measurements of size, length and position of wires in the circuit were made and independent determinations of ω, L and $\overline{C}$ showed that at resonance, $\omega L = 1/\omega\overline{C}$.

Audio Frequency Conductance Measurements

The conductance of the electrolytes at audio frequencies was determined by using the ordinary type of bridge arrangement. The measurements were accurate to 0.01% as shown by calibrations and results with standard solutions. The standard resistances were a set of Curtis-wound coils of resistance 100,000 to 1000 ohms and a dial box giving resistances from 1000 to 1 ohm. These resistances previously had been calibrated by the U. S. Bureau of Standards. Heavy connecting wire was used between members of the circuit. Careful shielding of leads was required. Two compensating condensers with capacity 3000 $\mu\mu F$ and 300 $\mu\mu F$ were used for balancing capacity in the different arms of the bridge. A Kohlrausch eleven-turn slide wire manufactured by the Leeds and Northrup Company was employed to obtain the balance point. The alternating current was furnished by a vacuum tube generator. A vacuum tube amplifier was used in the detection of the point of balance.

Design and Construction of Conductance Cells

In the selection of the conductance cells consideration had to be given to the magnitude of the resistance demanded at each of the several short wave lengths by the characteristics of the circuit. The range of values of resistance required for the highest sensitivity at each wave length was determined experimentally. Table I gives the approximate ranges at the wave lengths selected for measurements.

It has been demonstrated as well that these values are theoretically correct, using the other constants of the measuring circuit and the equation for the currents in the circuit. The ranges of the resistance for a particular wave length may be changed by variation of the characteristics of the circuit.

At the beginning of the work much attention was given to the construction and properties of the conductance cells.

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(5) Arnold and Williams, THIS JOURNAL, **58**, 2613 (1936).

TABLE I

MAGNITUDE OF RESISTANCES FOR CHOSEN WAVE LENGTHS

Wave length meters	Approximate range of resistances, ohms.
170	25,000 to 75,000
130	25,000 to 75,000
100	25,000 to 100,000
75	25,000 to 65,000
50	5,000 to 20,000
30	2,500 to 7,500
15	400 to 1,600

The conductance of standard potassium chloride solutions at audio frequencies was studied in cells constructed with different kinds of glass and electrode material in a variety of shapes. Many irregularities of conductance were observed. Several important observations, later found mentioned in a publication by Jones and Bollinger,[6] were made in this preliminary work.

Many of the cells which are used for the determination of low frequency conductance are not suited at all for work at high frequencies because of arrangement of electrodes and of the proximity of mercury contact arms and filling tubes. The closeness of these arms introduces serious errors at high frequencies.

The cells finally designed for the high frequency measurements were similar to the one shown in Fig. 1. The exterior dimensions, especially with respect to electrode position and filling arms, were kept constant. This uniformity of construction was essential, first, in order that the cells would fit a standard clamp in the thermostat bath to give reproducible position from experiment to experiment, and second, in order that any capacitative effects between the electrode leads and filling arms, if not entirely eliminated, be reduced to a minimum and be nearly the same from cell to cell.

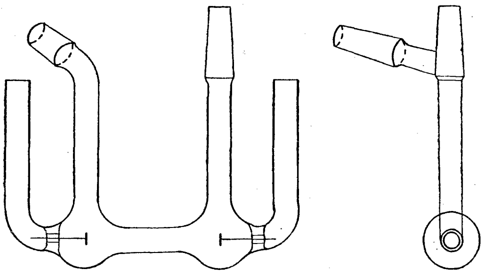

Fig. 1.—Conductance cell.

From conductance data found in standard tables, it was possible to compute the size and spacing of electrodes as well as the size of the body of a cell to be used with a given electrolyte at any of the wave lengths chosen. The cells were constructed with either Jena Geräte or Jena 16_{III} glass. Bright platinum electrodes were employed throughout. Eight cells were so constructed.

Special seasoning of the cells was accomplished by a carefully controlled steam-bath in which the cell was first brought gradually up to the temperature of steam, after which a current of steam was forced through the cell for several hours, then the cell was caused to cool slowly. At times when the cells did not contain a solution they were kept soaking with high grade conductivity water.

Calibration of Cells.—For the determination of the ordinary cell constants a 0.01 demal solution of potassium chloride served as electrolyte. Conductance values of Parker and Parker[7] were used in these calibrations.[8] The cell constants given in Table II, obtained by means of two different standard solutions, show a maximum deviation from the average of less than one part in ten thousand except in the case of cell number eight.

Temperature Control.—A thermally insulated thermostat bath of 23 liters capacity was filled with light oil in order to avoid electrostatic disturbances common to a water-bath and to ensure as complete electrical insulation as possible for the measuring cell. The container was grounded further to reduce electrical disturbances. It was possible to maintain the temperature of the bath to 0.001° for a considerable length of time. The maximum deviation allowed for a measurement was 0.002°.

Preparation and Purification of Materials.—One of the prime requisites of conductance measurements is that only pure materials be used since foreign substances are apt to give large errors from which indefinite or wrong conclusions will be drawn. This is especially true with the quantitative measurements of the small conductance effects at high frequencies. Since the frequency effect is a function of the valence of the ions involved, the presence, in small numbers, of foreign ions of the higher valence types would mask the effect of lower valence types.

Purification of Conductance Water.—The water was prepared by four or five distillations. Water, after having been distilled for general laboratory purposes, was distilled in a large block tin condenser. At the same time the steam and condensing liquid were washed by a stream of purified air. Only the middle portion of the distilled water was retained. The water was next distilled through a newly designed, all Pyrex, well-seasoned still which had a trap of direction reversing type and baffle domes for entrapping the spray. Glass dust shields protected the ground glass joints. Again only the middle portion of the water was retained. This water was then distilled in an all quartz distillation apparatus. The quartz condenser arm was air cooled. The receiver was always one of the transparent quartz flasks used in the work. The rate of distillation was maintained so that there was always an escape of steam which prevented foreign gases from diffusing back into the flask and which kept the distilled portion at nearly the boiling point. The first and last portions were always rejected. The process was sometimes repeated with the glass or quartz still. After cooling the water the quartz container was placed in a vacuum degassing tower and the evacuation was continued until the bubbling ceased. A stream of purified nitrogen was introduced into the chamber. The water, which was of exceptional quality, was found to depreciate readily in purity. Since considerable time was required to make the measurements it was decided to let the water "age" a part of a day before the solution was prepared. This procedure was followed in order that any unavoidable change of conduc-

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(6) Jones and Bollinger, THIS JOURNAL, **53**, 411 (1931).

(7) Parker and Parker, *ibid.*, **46**, 312 (1924).

(8) At the time the extensive and involved computations required by this work were made, the newer and more exact data of Jones and Bradshaw [*ibid.*, **55**, 1780 (1933)] were not available.

TABLE II

CELL CONSTANT DATA

Number of standard solution	Number of cell							
	1	2	3	4	5	6	7	8
2	0.043467	1.0582	0.57737	1.8265	11.498	1.1326	0.25371	8.3143
3	.043458	1.0583	.57726	1.8263	11.497	1.1323	.25371	8.3169
Av.	.043462	1.0583	.57731	1.8264	11.498	1.1324	.25371	8.3156

tance of solvent would take place before, rather than during, the measurements. The specific conductance of the aged water when used was in the vicinity of 0.360×10^{-6}.

Potassium Chloride.—The potassium chloride (Mallinckrodt, "Reagent Quality") was recrystallized four times from aqueous solutions made with the best grade of conductance water obtainable. The salt, after drying in an oven at 110° and after standing for considerable time in a closed container, was analyzed for moisture content. The salt contained 0.15% water as shown by three determinations with a maximum deviation of 0.01%. Correction was made on this basis when a standard potassium chloride solution was prepared.

Magnesium Sulfate.—The magnesium sulfate (Mallinckrodt "Reagent Quality") was further purified by recrystallizing four times from the best grade of boiled conductance water. The salt was slowly dried by placing it in a desiccator above sulfuric acid and phosphorus pentoxide and by passing a stream of purified nitrogen over it. Several sets of analyses were performed. The water content at the beginning was not constant. After the salt had stood over the pentoxide for a year an analysis was again made by the pyrophosphate method. With three determinations the average of a salt in a sample was 74.23% with a maximum deviation of 0.04%.

Lanthanum Iodate.—The lanthanum iodate was obtained through the generosity of Professor V. K. La Mer of Columbia University who furnished a sample of the purified $La(IO_3)_3$ used in a study with Goldman.[9] At the time of the measurements an analysis was made for the water content of the salt. Three determinations by the thiosulfate method gave an average of 97.40% lanthanum iodate with a maximum deviation of 0.1%. The analytical reagents were either of reagent quality or they were further purified.

Cerium Sulfate and Praseodymium Sulfate.—Samples of these salts were procured from our Division of Analytical Chemistry. Further purification of the salts was accomplished by repeated crystallizations of the salts from the best grade of conductance water. Saturated solutions of the cerium and praseodymium sulfates were prepared at 0° and then the temperature was elevated to 80° for the former and to 75° for the latter. About five-sixths of the praseodymium salt precipitated out each time, but the amount was somewhat less in the case of the cerium sulfate. The purified samples were dried carefully. Due to the small quantity of the purified salts chemical analyses were omitted and the determination of the concentrations used in the measurements was made by using conductance data given in the "International Critical Tables."

Barium Chloride.—The barium chloride (Mallinckrodt "Reagent Quality") was not purified further. However, an analysis of the usual kind for the determination of water of hydration was carried out. The average percentage of barium chloride in a sample was found to be 85.27% with a maximum variation between the three determinations of 0.05%.

Luteo Chloride.—The luteo chloride was a Kahlbaum preparation. Due to the small quantity available further purification or chemical analysis was not attempted.

Technique Used in Measurements

Preparation of Solutions.—The solutions were prepared by the volumetric method in a 500-ml. calibrated Pyrex flask which had been well-seasoned by continued soaking with conductance water. The conductance water was transferred from the quartz container in the nitrogen filled degassing chamber through a siphon into the volumetric flask, placed in another chamber which was filled with purified nitrogen gas. The sample of salt was weighed on an analytical balance which had been adjusted to a sensitivity of 0.01 mg. The same calibrated set of weights was used for all weighings throughout the experimental work. After the addition of the sample of salt to the water in the volumetric flask the latter was placed in the bath at 25.000 ± 0.002°. After temperature equilibrium had been reached the total volume was brought to the 500-ml. mark.

The Filling and Handling of Cells.—The cells were first rinsed repeatedly with the solution to be used and then filled by siphon in a chamber filled with purified nitrogen gas. Contamination of the dilute solutions with foreign gases was thus eliminated. The filled cells used in an experiment were placed in the thermostat and the audio frequency resistance of the solution in each cell was determined.

High Frequency Procedure.—To carry out the measurements at any one of the higher frequencies, the cell adapted to that particular wave length was placed in the special holder in the thermostat. The zero position of the galvanometer light beam was noted. After all parts of the high frequency circuits were adjusted to the predetermined settings for that wave length, the oscillator was started and the circuits tuned so that the maximum deflection at resonance was approximately 400.0 on the galvanometer scale. The generator was always started two or more hours before the experiment began so that stability of power output could be maintained in all of the high frequency circuits. Any lack of stability could be detected by the shift of the galvanometer light on the scale. All of the observations at the high frequencies were made after midnight in order to avoid as far as possible external electrical disturbances.

The galvanometer deflection and the precision condenser reading were recorded. The cell was then connected in parallel with the precision condenser and the galvanometer deflection and precision condenser setting at resonance were again noted and recorded. Four to ten consecutive sets of such readings were taken for a particular solution at each wave length. Besides the observations for the

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(9) La Mer and Goldman, THIS JOURNAL, 51, 2632 (1929).

solution, the same type of readings were made for two low inductive fixed resistances. The resistances were of the same order of magnitude as that for the cell with electrolyte. With any series of solutions these same fixed resistances were inserted repeatedly and observations were made at the time the solution was studied at that wave length. Thus these fixed resistances served as a check and reference for shift or disturbances from experiment to experiment. These fixed resistances were checked frequently by resistance determinations with the audio frequency bridge and were found to stay constant to well within 0.1%. It is imperative for such comparison measurements that the same cell be used for any particular wave length with a series of solutions.

Results

Conductance at Audio Frequency.—Although the determination of conductance at an audio frequency (1000 cycles), was not the chief object of the measurements being reported, it was part of the necessary procedure for each solution, since these data furnish a basis for reference. To illustrate the accuracy of these results data may be given for the reference potassium chloride solutions. For 0.005 normal potassium chloride the values of the observed molar conductance are 143.63 and 143.61 for two experiments as compared to Shedlovsky's[10] observed value 143.64 and his calculated value 143.65. For 0.002 normal potassium chloride in another experiment the observed value was 145.83 as compared to Shedlovsky's observed value 145.79 and calculated value 145.81.

Theoretical Values of High Frequency Change of Conductance.—In order to interpret the experimental observations it was necessary to calculate the changes in conductance of standard potassium chloride solutions at the different frequencies. It is assumed in the interpretation of the observations made with higher valence type salts that the small changes to which potassium chloride solutions are subject obey the Debye–Falkenhagen equation. This assumption has been made by other observers. The theoretical values were calculated for the other salts studied.

Because of the difficulty in adaptation and because of desire for greater accuracy the interpolation table given by Debye and Falkenhagen[2] for the ratio $\overline{\Lambda}_{I\omega}/\Lambda_{I_0}$ at definite values of q and $\omega\theta$ was not used.

The predicted conductance changes were calculated by using an equation given in the introduction. In addition to certain universal constants ($T = 298$, $e = 4.770 \times 10^{-10}$, $D = 78.54$, $k = 1.371 \times 10^{-16}$), it was necessary to have figures for the limiting molar conductances, $\overline{\Lambda}_0$ of the several salts. The following figures were obtained from standard sources of reference: KCl, 149.82; $BaCl_2$, 282.13; $MgSO_4$, 267.0; $La(IO_3)_3$, 336.8; $Ce_2(SO_4)_3$, 953.9; $Pr_2(SO_4)_3$, 945.5; $Co(NH_3)_6Cl_3$, 540.0. The mobility of the luteo ion, $Co(NH_3)_6^{+++}$, is somewhat uncertain.[11] The value 104.6 for $^1/_3$ $Co(NH_3)_6^{+++}$ was deduced from conductance data given by Harkins, Hall and Roberts.

The experimental work was arranged in three series of experiments, as shown in Table III. Here are presented theoretical and experimental values for the increase of molar conductance $\overline{\Lambda}_{I_0} - \overline{\Lambda}_{I\omega}$ of the different salts at the several high frequencies used in the measurements. Thus, these data indicate the amount by which the limiting molar conductance is changed due to changes in the electrical force of relaxation produced by the application of the fields of high frequency. It is also possible to obtain at once values for $\overline{\Lambda}_{I\omega}$, and $\overline{\Lambda}_{I\omega}/\overline{\Lambda}_{I_0}$ if it is desired to express the changes in this way.

Example of the Calculation of the Conductance from the Experimental Observations.—In order to illustrate the method by which the data of the foregoing tables have been obtained, the observations in the case of the 0.0006443 molar magnesium sulfate solution at 50 meter wave length are considered in detail. Galvanometer deflections with the cell in the circuit and with the cell out of the circuit are given in Table IV, Part A. Here the two columns at the right give the deflections corrected for the zero of the galvanometer as recorded in column two at the left. Part B of the same table gives average deflection values for the cell and fixed resistances.

In Part C are found the ratios of the galvanometer deflections with and without the cell or fixed resistance in the circuit for an experiment (14) with the standard potassium chloride solution and for an experiment (18) with the magnesium sulfate solution. The same cell and fixed resistances were used in both runs.

Any shift in the zero of the galvanometer after the beginning of the observations or any shift due to other disturbances from experiment to experiment should be detected through the ratios observed for the standard fixed resistances. Thus,

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(10) Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

(11) Harkins, Hall and Roberts, *ibid.*, **38**, 2643 (1916).

TABLE III

INCREASE OF MOLAR CONDUCTANCE WITH CHANGE OF FREQUENCY[a]

Wave length					170	130	100	75	50	30	15
Salt	Concn., molar	$\bar{\Lambda}_0$	$\bar{\Lambda}_{I_0}$		$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I_\omega}$	$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I_\omega}$	$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I_\omega}$	$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I_\omega}$	$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I_\omega}$	$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I_\omega}$	$\bar{\Lambda}_{I_0}-\bar{\Lambda}_{I_\omega}$
					First Series						
No. of cell used					8–5	8–5	8–5	8–5	5	4	6
KCl	0.00500	149.82	2.412	T	0.003	0.005	0.007	0.012	0.027	0.068	0.211
$BaCl_2$	.00280	282.13	10.522	T	.008	.012	.024	.044	.096	.253	.804
				E	.09	.07	...	...	...	...	.96
$MgSO_4$	.00387	267.0	30.248	T	.021	.031	.052	.083	.176	.475	1.611
				E	.051	.035	...	...	...	.72	...
					Second Series						
No. of cell used					5	5	5	5	4	6	7
KCl	0.00200	149.82	1.524	T	0.009	0.016	0.026	0.043	0.086	0.181	0.377
KCl	.00197	149.82	1.513	T	.010	.016	.026	.045	.087	.182	.379
$BaCl_2$	.00112	282.13	6.653	T	.033	.056	.094	.163	.325	.696	1.502
				E	.19	.03	...	.54	...	...	1.67
$MgSO_4$	.00155	267.0	19.132	T	.065	.105	.176	.301	.627	1.450	3.488
				E	.06	.45	.51	.52	...	...	3.65
					Third Series						
No. of cell used					5	5	5	5	4	7	7
KCl	0.000985	149.82	1.070	T	0.025	0.040	0.062	0.096	0.161	0.268	0.432
KCl	.00100	149.82	1.079	T	.025	.039	.061	.094	.159	.267	.431
$BaCl_2$	.000561	282.13	4.708	T	.090	.147	.230	.360	.620	1.061	1.762
				E	.20	.41	.18	.54	.73	1.01	1.70
$MgSO_4$	.000774	267.0	13.528	T	.166	.277	.448	.721	1.326	2.466	4.443
				E	...	.27	.62	1.08	1.54	2.41	...
$MgSO_4$	.000644	267.0	12.340	T	.219	.354	.556	.881	1.542	2.696	4.554
				E	...	.19	.40	.46	1.91	2.43	4.88
$La(IO_3)_3$	.000445	336.8	10.726	T	.231	.373	.580	.888	1.512	2.546	4.156
				E	.18	.56	...	.78	2.25	2.56	5.52
$Ce_2(SO_4)_3$	.000366	953.9	93.448	T	.428	.725	1.153	2.010	4.053	8.896	19.868
				E	.60	.38	1.01	1.47	3.47	8.96	18.85
$Pr_2(SO_4)_3$	.000366	945.5	92.522	T	.392	.719	1.143	1.992	4.050	8.883	19.857
				E	..	.65	1.54	1.85	3.88	9.75	20.33
$Co(NH_3)_6Cl_3$	.000253	540.0	12.211	T	.299	.476	0.731	1.123	1.864	3.065	4.890
				E	.44	.83	0.51	1.78	...	5.49	6.04

[a] T indicates theoretical value; E indicates experimental value.

this added information obtained by using the fixed resistances R18 and R17 made it possible to correct the magnesium sulfate values for any deviation or shift taking place during an experiment. Part D of Table IV shows the ratios of the fixed resistances referred to the values obtained in experiment 14 as standard. The average ratio 1.0027 is the factor by which the magnesium sulfate ratio is corrected to 0.5303. It is to be regarded as a coincidence that the thermocouple correction exactly cancels the adjustment in opposite sense for the galvanometer. The thermocouple correction is determined from calibration curves in which the square of the current through the thermocouple heater is plotted as a function of the galvanometer deflection.

The next step is to evaluate these current ratios for the two solutions in terms of the relative ohmic resistances. The relative values of resistance are obtained from the relation[5]

$$\frac{I_2^2}{I_1^2} = \frac{\bar{r}_1^2}{\left(r_2 + \frac{R}{1 + \omega^2C^2R^2}\right)^2} = \frac{kD_2}{kD_1}$$

From the portion of the interpolation table which forms Part E of Table IV, the ratios for potassium chloride and magnesium sulfate (Part D) are identified with the relative resistances 12,792 and 12,504, respectively. By using the theory of Debye and Falkenhagen the actual resistance in the cell at 50 meters for the potassium chloride solution is calculated to be 13,422 ohms. By direct proportion, using this ohmic resistance

TABLE IV

INTERPRETATION OF EXPERIMENTAL OBSERVATIONS

Part A

No. of cell or R placed in circuit	Zero of galv.	Deflection of galv. without R or cell corrected for zero	Deflection of galv. with cell or R corrected for zero
C4	0.6	402.0	212.4
		401.4	212.4
		401.4	212.4
R18	.6	401.4	242.9
		401.2	242.8
		400.2	242.4
R17	.6	400.2	243.6
		400.2	243.6

Part B

Av. defl. of galv. without cell	Av. defl. of galv. with cell	Av. defl. of galv. without R18	Av. defl. of galv. with R18	Av. defl. of galv. without R17	Av. defl. of galv. with R17
401.6	212.4	400.9	242.7	400.2	243.6

Part C

No. of expt.	Cell solution	Ratio of galv. defl. conductance cell	Ratio of galv. defl. resistance R18	Ratio of galv. defl. resistance R17
18	$MgSO_4$	0.5289	0.6053	0.6087
14	KCl	.5367	.6071	.6101

Part D

No. of expt.	Salt	Ratio with R18	Ratio with R17	Av.	Ratio with conductance cell
14	KCl	1.0000	1.0000	1.0000	0.5367
18	$MgSO_4$	1.0030	1.0023	1.0027	.5303

Part E

R	R^2	$\omega^2C^2R^2$	$\frac{R}{1+\omega^2C^2R^2}$	$\left(r_2+\frac{R}{1+\omega^2\bar{C}^2R^2}\right)$	$\left(r_2+\frac{R}{1+\omega^2\bar{C}^2R^2}\right)^2$	$\frac{kD_2}{kD_1}$
12,500	156.25 × 10⁶	6396.1	1.9540	7.3445	53.942	0.5302
12,525	156.88	6421.7	1.9501	7.3406	53.884	.5308
....	....	....	....	....	....	...
12,775	163.20	6680.6	1.9120	7.3025	53.327	.5363
12,800	163.84	6706.8	1.9082	7.2987	53.271	.5369

for the potassium chloride solution and the two relative values given in the table, the actual ohmic resistance for the magnesium sulfate solution is calculated to be 13,120 ohms. But the resistance of the magnesium sulfate solution in the same cell at the audio frequency was 13,235 ohms, therefore an increase in conductance has been observed. Interpreted in terms of molar conductance the quantities $\bar{\Lambda}_0$ and $\bar{\Lambda}_\omega$ are found to be 225.62 and 227.53, respectively. Then

$$\bar{\Lambda}_\omega - \bar{\Lambda}_0 = \bar{\Lambda}_{I_0} - \bar{\Lambda}_{I\omega} = 1.91$$

The theoretical value of $\bar{\Lambda}_{I_0}$ is 12.34. Thus $\bar{\Lambda}_{I\omega} = 12.34 - 1.91 = 10.43$. If the data for a given solution are referred to figures for several standard potassium chloride solutions the above procedure must be repeated.

Discussion

Since the appearance, in 1928, of the quantitative theory describing the dispersion of electrical conductance for dilute solutions of strong electrolytes there have been published the results of a number of experimental researches intended to test the validity of the theory. Reference may be made to important contributions in this field by Sack,[12] Zahn,[13] Rieckhoff,[14] Brendel,[15] Deubner,[16] M. Wien,[17] Malsch,[18] Gärtner,[19] and others. In some cases it was possible to measure only the order of magnitude of the conductance increase at a single high frequency, in others

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(12) Sack, *Physik. Z.*, **29**, 627 (1928).

(13) Zahn, *Z. Physik*, **51**, 350 (1928).

(14) Rieckhoff and Zahn, *ibid.*, **53**, 619 (1929); Rieckhoff, *Ann. Physik*, [5] **2**, 577 (1929).

(15) Brendel, Mittelstädt and Sack, *Physik. Z.*, **30**, 576 (1929); Brendel and Sack, *ibid.*, **31**, 345 (1930); Brendel, *ibid.* **32**, 327 (1930).

(16) Deubner, *ibid.*, **30**, 946 (1929); **33**, 223 (1932); *Ann. Physik*, [5] **5**, 305 (1930).

(17) Wien, *Physik. Z.*, **31**, 793 (1930); *Ann. Physik*, [5] **11**, 429 (1931).

(18) Malsch, *Physik. Z.*, **33**, 19 (1932); *Ann. Physik*, [5] **12**, 865 (1932).

(19) Gärtner, *Physik. Z.*, **32**, 919 (1931).

complications served to render difficult any interpretation in terms of the theory, but in the main the results of these studies have been consistent with the requirements of the theory.

It has been our plan to make, in extremely dilute aqueous solutions of strong electrolytes, a more systematic study of the theory than has hitherto been attempted. Thus, instead of confining our attention to observations of the behavior of the solutions at one, or at most, several wave lengths, we have sought to make the measurements over a considerable frequency range. Again, we have been interested in a comparison of the magnitude of the conductance increase for electrolytes of as many different valence types and ion sizes as conveniently possible. To a lesser extent we have been able to study the effect of concentration changes in the solution of some of the salts. The results of the experimental work are compared with the requirements of the theory in Table III.

It is at once evident that the agreement between theory and the results of our experiments at each of the seven wave lengths is as good as can be expected when the difficult nature of the measurements is considered. The influence of variation in the valence type of the dissolved salt in changing the values of $\bar{\Lambda}_{I_0} - \bar{\Lambda}_{I_\omega}$ in the dilute solutions is consistent with the requirements of the theory. Thus, at any one wave length, barium chloride solutions show much less actual increase in conductance than do solutions of salts of higher valence types. The lanthanum iodate and luteo chloride solutions (3–1 valence type) show more significant increases and, when the relative concentration is taken into consideration, the magnesium sulfate solutions (2–2 valence type) show an even greater dispersion. The increased conductance is so pronounced in the case of the cerium sulfate and praseodymium sulfate in solution (3–2 valence type) that it can be measured with a very considerable degree of accuracy.

The measurements are much less complete as regards the effect of concentration change, but again, insofar as our experiments extend, this influence is entirely consistent with the predictions and requirements of the dispersion theory. The data for barium chloride and magnesium sulfate solutions are the only ones which are now involved. The change of conductance with frequency is very small at the higher concentrations in the wave length region in which these studies were made. The theory predicts that in order to observe large changes of conductance at the higher concentrations it will be necessary to measure the effects at much higher frequencies than were available to us. However, this shift of the critical frequency range toward the shorter wave lengths is indicated clearly by the experimental data for both barium chloride and magnesium sulfate solutions, with the more pronounced increases in conductance being observed in the solutions of lower concentration. For the study of the effect of changes in concentration measurements of Wien[17] with magnesium sulfate and barium ferricyanide solutions at 10, 20 and 40 meters are especially deserving of mention.

The significance of experiments of the type made by us now can be suggested. In the interionic attraction theories the fundamental idea is that the ions cannot be distributed at random in a solution, since, owing to the coulomb forces, there must be an excess of positive ions in the neighborhood of a negative ion and *vice versa*. Thus each ion is considered to be surrounded by a symmetrical ionic atmosphere with distribution of charge depending upon the square root of the concentration. It order to explain the ordinary conductance behavior of an electrolyte solution the number of the ions and their mobilities must be considered. The interionic attraction theory describes the effect of the electrical forces on the ionic mobilities by assuming the ionic atmosphere to have a definite time of formation and relaxation. On the basis of this assumption, if a constant current passes through such a solution the average distribution of ions is changed and the ionic atmosphere loses its central symmetry, but if a high frequency voltage, with time necessary for one vibration comparable to the time of relaxation, is applied, the dissymmetry of the atmosphere is greatly reduced and a conductance larger than that measured at ordinary low frequencies ought to result. If the experimentally observed conductances show satisfactory agreement with the requirements of the dispersion theory, as they do in the cases investigated by us, it can be claimed that the existence of such an atmosphere about each ion with finite time of relaxation, is definitely proved.

According to the theory the time of relaxation of the atmosphere (which is responsible for the dispersion effect) depends only on the mobilities of the ions and the forces between them. Thus, only the valence of the ions, the viscosity and dielectric constant of the solvent, and certain other physical factors are involved. If we wish to investigate whether or not in an ionic solution the chemical nature of the solvent and the affinities of ions play an important role, experiments of the type described above in which these factors are varied can give valuable information. In the experiments here reported a nearly ideal ionic behavior is observed, but it is probably accounted for because only extremely dilute aqueous solutions were considered. But even if the chemical nature of the solvent and the affinities of the ions are predominant factors, such experiments as these are still of significance because they explain and predict the behavior of ideal electrolytes and make possible a measure of the deviations from ideality in the actual solution.

Summary

1. A quantitative experimental study of the dispersions of the electrical conductance for strong electrolytes of several valence types in extremely dilute aqueous solutions has been made. The conductance of these solutions was observed at frequencies corresponding to the seven wave lengths, 15, 30, 50, 75, 100, 130 and 170 meters. In addition, observations were made at the frequency 1000 cycles.

2. The results of the experiments have been compared with the requirements of the dispersion theory. They are found to be in satisfactory quantitative agreement, indicating once more that in all probability the purely physical interionic attraction theory does adequately explain and describe the behavior of an ideal electrolyte.

MADISON, WIS. RECEIVED AUGUST 17, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermodynamics of Cadmium Chloride in Aqueous Solution from Electromotive Force Measurements[1]

BY HERBERT S. HARNED AND MARGARET E. FITZGERALD

Measurements of the electromotive forces of the cell

$$\text{Cd–Cd}_x\text{Hg (11\%)} \mid \text{CdCl}_2(m) \mid \text{AgCl–Ag} \qquad (1)$$

have been made at 5° intervals from 0 to 40°, inclusive, and throughout a cadmium chloride concentration range of 0.0005 to 1 *M*. From the results, the standard potential of the cell, E_0, the activity coefficients and other thermodynamic properties of cadmium chloride have been computed.

Experimental Procedure

The silver–silver chloride electrodes of the kind designated by Harned[2] as type (2) were used. The cadmium amalgam was prepared from pure redistilled Kahlbaum cadmium and distilled mercury. The amalgam electrodes containing 11% of total cadmium were made individually in each cell vessel.

Mercury and an excess of cadmium were introduced in a suitable glass vessel which was then evacuated. This mixture was placed in a water-bath at 60° for fifteen minutes, and was shaken frequently. The saturated amalgam formed in this manner was allowed to flow through a sealed tube into the amalgam electrode compartments of four cells where it covered the sealed in platinum wires which made contact with the external leads. Since this operation was carried out *in vacuo*, the amalgam was free of oxide. In the case of cells containing dilute solutions ($m < 0.05$ *M*) the silver chloride electrode was immersed in the same compartment as the amalgam. On the other hand, with higher concentrations of solution the life of the cell was found to be considerably increased by separating the electrode compartments by means of a tube and a stopcock which was closed at times when actual measurements were not in progress.

A standard concentrated stock solution was made from a high-grade carefully purified cadmium chloride and conductivity water. Its strength was found by gravimetric determination of its chloride content. More dilute solutions were prepared by adding weighed amounts of the standard solution to water. The cell solu-

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(1) This communication contains material from a Dissertation presented to the Graduate Faculty of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

(2) Harned, THIS JOURNAL, **51**, 416 (1929).

tions were then boiled *in vacuo* to remove dissolved air, and kept under hydrogen. Corrections were made for the water boiled off during this process and vacuum corrections were made for all weighings.

The cells came to equilibrium in one to two hours after preparation. Four cells were measured at each concentration. The temperature control was within ±0.02°.

Experimental Results

Electromotive forces were determined at thirty-odd concentrations ranging from 0.0005 to 1 *M* and at 5° intervals from 0 to 40°. These were smoothed to round concentrations from a graph of *E versus* log *m*. The actual values may be expressed conveniently by means of the quadratic equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (2)$$

Values of E_{25}, a and b are given in Table I. In the last column are given the average deviation between the observed results and those computed by the equation. In other words, Δ is the sum of the magnitudes of deviations at the nine temperatures divided by nine.

TABLE I

CONSTANTS OF EQUATION (2)

E = Electromotive Force of the Cell: $Cd\text{–}Cd_xHg \mid CdCl_2(m) \mid AgCl\text{–}Ag$

m	E_{25}	$a \times 10^6$	$b \times 10^6$	Δ,mv.
0.0005	0.8539	560	−3.48	0.14
.001	.82997	494	−3.40	.10
.002	.80701	430	−3.30	.06
.005	.77851	356	−3.13	.18
.007	.76862	338	−3.02	.07
.01	.75846	305	−2.93	.07
.02	.73976	242	−2.55	.11
.05	.71739	185	−2.05	.04
.07	.70974	161	−1.88	.05
.1	.70175	136	−1.68	.06
.2	.68656	104	−1.30	.09
.5	.66864	48	−0.80	.13
.7	.66258	29	− .62	.08
1.0	.65640	12	− .44	.15
	$E_{0(25)}$	$a_0 \times 10^6$	$b_0 \times 10^6$	
E_0:	.57390	−394	−3.63	.09

Similar cells have been measured at 25° by Horsch,[3] Lucasse[4] and from 0 to 45° by Quintin.[5] Since Horsch and Lucasse used amalgams of different compositions which were unsaturated, the absolute values of their electromotive forces are different from the present results. Graphs of the data of Horsch, Lucasse and the present results *versus* log *m* were found to be parallel, which indicated the same effect of change in concentration in all cases. Lucasse did not state the strength of the amalgam employed. The explanation of the difference between our results and those of Horsch is due not only to the difference in amalgam strength but also to the fact that Horsch employed silver–silver chloride electrodes prepared in the manner described by Lewis and Brighton.[6] These were found to be several millivolts different from the type of electrode employed by us. On the other hand, our results are in close agreement with those of Quintin who also employed the saturated amalgam.

The experimental accuracy was in general of the order of 0.1 mv. At the higher concentrations (>0.1 *M*), the experimental error was found to be somewhat greater than this.

Evaluation of the Standard Potential of the Cell

The electromotive force of the cell may be represented by the equation

$$E = E_0 - k \log 4m^3\gamma_{\pm}^3 \qquad (3)$$

where E_0 is the standard potential, m and $\gamma_{\pm}$ are the molality and stoichiometrical activity coefficient of cadmium chloride and k equals 2.303 $RT/2F$. By replacing $\log \gamma_{\pm}$ by $(-\mu\sqrt{m} + B'm)$ where μ is the limiting slope of the Debye and Hückel theory, we obtain

$$E + k \log 4m^3 = 3ku\sqrt{\mu} = E_0 - B'm = E_{\text{H}} \qquad (4)$$

The left-hand side, plotted against $\sqrt{m}$, was found to give a curve at all temperatures of which the slope increased with decreasing concentration. The data of Horsch in very dilute solutions at 25° was plotted in this way and although a fairly representative straight line could be drawn, the uncertainty of this method of extrapolation was great. Further, these graphs possessed slopes about twice that predicted by theory. This uncertainty is shown by earlier extrapolations. Getman[7] plotted this function against $\sqrt{\mu}$, using Horsch's data and found E_0 to be 0.6215. La Mer, Gronwall and Greiff[8] plotted the same data against $\sqrt{m}$ and obtained 0.5790 for E_0 but did not consider this a proper value. Instead they applied their extension of the Debye and Hückel

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(3) Horsch, THIS JOURNAL, **41**, 1787 (1919).

(4) Lucasse, *ibid.*, **51**, 2597 (1929).

(5) Quintin, *Compt. rend.*, **200**, 1579 (1935).

(6) Lewis and Brighton, THIS JOURNAL, **39**, 1908 (1917).

(7) Getman, *J. Phys. Chem.*, **35**, 588 (1931).

(8) La Mer, Gronwall and Greiff, *ibid.*, **35**, 2245 (1931).

theory using an apparent ionic diameter "a" of 1 Å., and obtained 0.6230 for E_0.

According to equation (4), if cadmium chloride were a completely dissociated electrolyte, a plot of $E + k \log 4m^3 - 3k\mu\sqrt{m}$ should be linear with m in dilute solutions. That this is not the case confirms the view derived from conductance data that cadmium chloride is incompletely dissociated.

The dissociation mechanism which from the character of the data appears to be most suitable is

$$\text{CdCl}_2 = \text{Cl}^- + \text{CdCl}^+ \rightleftharpoons \text{Cd}^{++} + \text{Cl}^- \qquad (5)$$

according to which cadmium chloride is completely dissociated while the ion CdCl^+ is partially dissociated. It is probable that both cadmium chloride and CdCl^+ are incompletely dissociated. The above assumption neglects the first dissociation as having a negligible effect compared to the second in dilute solution. If α is the degree of dissociation of CdCl^+ and K the dissociation constant of this equilibrium, then the former is given by the equation

$$\alpha = \frac{1}{2}\left\{ -\left(1 + \frac{K}{m\gamma'_{\text{Cd}}}\right) + \sqrt{\left(1 + \frac{K}{m\gamma'_{\text{Cd}}}\right)^2 + 4\,\frac{K}{m\gamma'_{\text{Cd}}}} \right\} \qquad (6)$$

if γ^1_{Cl} is assumed to equal γ'_{CdCl}.

Some idea of the magnitude of K may be gained by considering the conductance data of Wershoven[9] at 18°, from which Noyes and Falk[10] calculated degrees of dissociation. These estimates place K between 0.007 and 0.02. From the same data, Reghellato and Davies[11] found, by means of Onsager's theory and by assuming a reasonable value for the mobility of the ion CdCl^+, an equilibrium constant of 0.0101 at 25°.

Our first step was to compute α by equation (6) for values of K in the neighborhood of 0.01 (0.005 to 0.015). γ'_{Cd} was computed from the Debye and Hückel equation

$$\log \gamma'_{\text{Cd}} = -2u\sqrt{\mu'}/(1 + A\sqrt{\mu'}) \qquad (7)$$

employing a value of the mean apparent diameter "a" of 5 Å. The primed quantities are real, while the unprimed quantities are stoichiometrical. Thus, μ' is $\Sigma m_i' z_i^2/2$ where m_i' represents the actual ionic concentrations. This required the following procedure. An initial value of α was assumed for values of K and m under consideration. From this, μ' was calculated from the relation

$$\mu' = (2\alpha + 1)m \qquad (8)$$

and γ'_{Cd} was obtained by equation (7). Then α was recalculated by equation (6) using this value of γ'_{Cd}. From this value of α another γ'_{Cd} and μ' were found, and equation (7) applied again. This process was repeated until the same value of α, to a few ten thousandths of a unit, was obtained twice. This procedure was carried out at 0, 25 and 40° to obtain values of α from 0.0005 to 0.5 M with various values of K.

Equation (3) is written in terms of the stoichiometric activity and coefficients and molality. It may also be written in terms of the real activity coefficient $\gamma'_\pm$ and actual ionic concentrations in the form

$$E = E_0 - k \log \alpha(1 + \alpha)^2 m^3 \gamma_\pm^3 \qquad (9)$$

From the definition of E_{H} in equation (4), we have

$$E_{\text{H}} - E_0 = E - E_0 + k \log 4m^3 - 3\,ku\sqrt{\mu} \qquad (10)$$

which combined with equation (9) gives

$$E_{\text{H}} - E_0 = k \log 4 - \log \alpha(\alpha + 1)^2 - 3k \log \gamma' - 3ku\sqrt{\mu} \qquad (11)$$

The right side of this latter equation was computed for various values of K and plotted against $\sqrt{m}$, using the activity coefficient of barium chloride obtained by Tippetts and Newton[12] for the real activity coefficient of cadmium chloride, $\gamma'_\pm$. This substitution is a reasonable one in dilute solutions and increases in validity with decreasing concentration. In Fig. 1 the general form of these curves are illustrated by the smooth lines.

The function, E_{H}, computed from E by equation (4) was then plotted for 0, 25 and 40° against $\sqrt{m}$ and compared to the curves calculated by equation (11) and for values of K varied by one thousandth unit. In Fig. 1 plots of this function are shown together with the curves which fitted them best. The values of the dissociation constants employed finally were 0.013, 0.011 and 0.010 at 0, 25 and 40°, respectively. The values of the right-hand member of equation (11) were read off the curves and subtracted from the original unsmoothed E_{H} functions. According to equations (10) and (11), this gave

$$E_0 = E + k \log \alpha(1 + \alpha)^2 m^3 \gamma'^3_\pm \qquad (12)$$

The values of E_0 obtained in this manner were averaged by drawing a straight line of zero slope through the points obtained by plotting against $\sqrt{m}$. The actual plots of these functions com-

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[9] Wershoven, *Z. physik. Chem.*, **5**, 481 (1890).

[10] Noyes and Falk, THIS JOURNAL, **34**, 475 (1912).

[11] Reghellato and Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

[12] Tippetts and Newton, THIS JOURNAL, **56**, 1675 (1934).

puted from the unsmoothed electromotive forces are also shown in Fig. 1.

In order to obtain E_0 at the other temperatures, the correction factors, $E_H - E_0$, used for each concentration at 0, 25 and 40° were plotted against temperature and smoothed curves drawn through three points. The correction factors read from these curves at the intermediate temperatures were then applied in the manner previously described to E_H, and the values of E_0 so obtained were averaged. These standard potentials are given in the second column of Table II.

TABLE II

STANDARD POTENTIALS OF:

Cd–Cd_xHg (11%)|$CdCl_2$ (m)|AgCl–Ag; E_0
Cd-Cd_xHg (11%)|Cd^{++}; E_0'.Cd(s)|Cd^{++}; E_0''

t	E_0	E_0'	E_0''	$E_0''_{(25)}$
0	0.58151	0.3452	0.4006	0.4007[3]
5	.58039	.3465	.4010	.3986[18]
10	.57900	.3477	.4013	.3967[7]
15	.57755	.3491	.4016	.3982[8]
20	.57581	.3403	.4018	.3964[20]
25	.57300	.3515	.4020	.4026[14]
30	.57175	.3326	.4021	.4009[19]
35	.56955	.3539	.4020	.3960[7]
40	.56730	.3553	.4026	.4020[a]

[a] This investigation.

These results may be represented by the equation

$$E_0 = E_{0(25)} + \alpha_0(t - 25) + b_0(t - 25)^2 \qquad (13)$$

similar in form to equation (2). Numerical values of the constants of this equation are given at the bottom of Table I.

The function computed by equation (11) is certainly of the same form in dilute solutions as when computed from the observed electromotive forces. This gives us confidence that the method of extrapolation here employed is reasonable and that the values obtained for E_0 are a close approach to the true values. We note that the dissociation constant seems to decrease with increasing temperature but do not regard this determination as an accurate evaluation of this quantity.

Standard Potential of the Electrode: Cd(s)|Cd^{++}

The standard potential of the two-phase amalgam electrode of 11% total cadmium content, E_0', can be computed readily from the values of E_0 by subtracting the standard potentials of the hydrogen silver–silver chloride cell given by Harned and Ehlers[13] at the corresponding temperatures. The potentials thus obtained for the electrode Cd–Cd_xHg (11%) / Cd^{++} are represented by E_0' and are given in the third column of Table II. Quintin[14] obtained 0.3491, 0.3521 and 0.3553 at 15, 25 and 35°, respectively, from an apparently identical cell by an application of the La Mer, Gronwall and Greiff[8] method. These values are in fair agreement with those obtained by us.

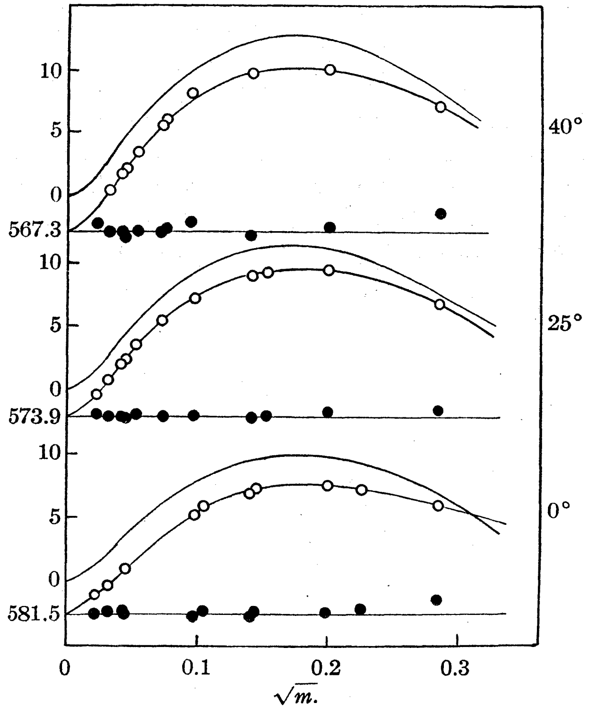

Fig. 1.—Extrapolation functions at 0, 25 and 40° (scale in millivolts, diameters of circles, 0.8 mv.): (1) Curves without points are theoretical according to Eq. (11). $E_H - E_0$ is plotted. (2) Circles represent plots of E_H according to Eq. (4). (3) Dots represent E_0 according to Eq. (12). (4) The dissociation constants were 0.010, 0.011 and 0.013 at 40, 25 and 0°, respectively.

Parks and La Mer[15] have measured the potential of cadmium amalgam of the same composition as that employed in the present investigation against cadmium. From their results and the values of E_0' in Table II, the values of the standard potential, E_0'', of the electrode Cd(s) / Cd^{++}, given in the fourth column of this table from 0 to 30° were computed. The values at 35 and 40° were computed from the results of Getman[16] for γ-cadmium. According to Cohen,[17] cadmium metal exists in three forms. Getman[16] measured cells of cadmium against cadmium amalgam over a time interval and found that only 10% main-

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(13) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

(14) Quintin, *Compt. rend.*, **200**, 1754 (1935).

(15) Parks and La Mer, THIS JOURNAL, **56**, 90 (1934).

(16) Getman, *ibid.*, **39**, 1806 (1917).

(17) Cohen, "Physico-chemical Metamorphosis," McGraw-Hill Book, Co., Inc., New York, 1926, p. 43.

tained the original high value for the electromotive force which was due to γ-Cd, while the potentials of the other 90% dropped in value due to a change to α- or β-Cd. Parks and La Mer's results agreed with those obtained for γ-Cd by Getman, so that the values given by us in Table II are taken to refer to γ-Cd.

There have been many attempts to provide a sound extrapolation of the existing data on cadmium chloride at 25°. The last column of Table II contains values of E_0'' obtained by the investigators mentioned at the bottom of the table. The first four values were derived from Horsch's data, the fifth from Horsch's and Lucasse's and the remainder each used their own experimental results.

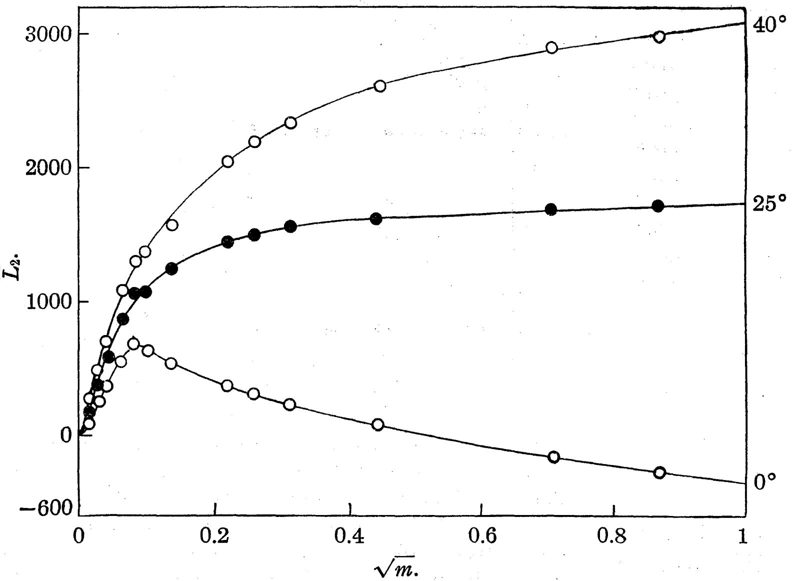

Fig. 2.—Relative partial molal heat content, $\bar{L}_2$, *versus* $\sqrt{m}$.

Brewster measured the potential of a cell with a liquid junction containing stick cadmium and calomel electrodes. German's second value was obtained from measurements of a cell containing cadmium in the form of a single crystal and a calomel electrode.

Some of the values have been changed. Horsch's[3] and Lewis and Randall's[18] values have been recalculated after correcting the silver chloride and calomel electrodes as indicated by the more recent values of the activity coefficient of hydrochloric acid. Quintin's silver chloride electrode was assumed to be the same as the type used by us. A correction of 0.0534 volt for the amalgam electrode used by Horsch was added to the value of E_0 obtained from his data, and one of 0.0505 volt to those obtained from amalgams of 11% total cadmium content. All results should refer to γ-Cd, although there remains some doubt regarding Getman's cell containing a single crystal. If this is α-Cd, a correction of 0.0031 volt should be added to Getman's second value.

The principal cause of the difference in values of these standard potentials is due to the methods of extrapolation. The first two determinations were made without the use of the limiting theoretical law of Debye and Hückel. This combined with giving too great weight to the determinations at extreme dilutions (<0.0004 *M*) tends to give results that are too low. Getman's extrapolation of Horsch's data and Brewster's[19] extrapolation of his own results were made by a plot suggested by equation (4). Again, the curve through the results in the concentration range available possesses a slope greater than the theoretical, and as a result intercepts the axis at zero molality at a value of E_0 which is too low. Getman's second value was computed by equation (3) from his results, and Horsch's activity coefficients. Activity coefficients computed from a low value of E_0 would be too large, which would make Getman's second value low also.

La Mer, Gronwall and Greiff could only fit the observed results with their equation upon the assumption of an apparent ionic diameter of 1 Å. Quintin's extrapolation seems reasonable, although the uncertainty is somewhat large because of the small number of points used. Scatchard and Tefft[20] used a function similar to equation (11) but made a rough application only and in our opinion placed too much weight on Horsch's results in very dilute solutions.

This critique of methods of extrapolation along with our experience indicates that the higher values of E_0'' (~ 0.402 volt) are more likely to be correct.

Activity Coefficient, Relative Partial Molal Heat Content and Specific Heat

The stoichiometric activity coefficient $\gamma_{\pm}$ may be computed from the values of E in Table I and

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(18) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 360.

(19) Brewster, *Rec. trav. chim.*, **46**, 378 (1927).

(20) Scatchard and Tefft, THIS JOURNAL, **52**, 2272 (1930).

the values of E_0 in Table II by means of equation (3). Unfortunately, accurate freezing point and vapor pressure data have not been obtained for cadmium chloride solutions so that values of the activity coefficients derived from the different colligative properties are not available for comparison. Because of this, we have not tabulated activity coefficients.

The relative partial molal heat content, $\bar{L}_2$, has been computed from equations (2) and (13) by the method given by Harned and Thomas.[21] For a bi-univalent electrolyte, equation (17) of Harned and Thomas is

$$\bar{L}_2 = 2\alpha + 2\beta T^2 \tag{14}$$

where the constants α and β may be computed from the constants of equations (2) and (13). Equation (14) is a necessary consequence of the quadratic temperature variation of E and E_0, and should only be applied to the temperature range (0 to 40°) in which the experimental results were found to conform closely to the quadratic relationship. In Table III, values of α and β are given at the concentrations designated. Values of $\bar{L}_2$ at 25° are recorded in the table and plots of this quantity at 0, 25 and 40° are shown in Fig. 2. In the last column of the table, values of the relative partial molal specific heat, $\bar{C}_p - \bar{C}_{p_0}$, at 25° computed from the equation

$$\bar{C}_p - \bar{C}_{p_0} = 4\beta T \tag{15}$$

are also given. We have been unable to find accurate calorimetrically determined values of these quantities so that further confirmation or disproof of the accuracy of these results and calculations cannot be obtained at the present time.

TABLE III

$\bar{L}_2$, AND $(\bar{C}_p - \bar{C}_{p_0})$ IN CALORIES. CONSTANTS OF EQ. (14)

m	$-\alpha$	β	$\bar{L}_{2(298)}$	$(\bar{C}_p - \bar{C}_{p_0})_{298}$
0.0005	207	0.0035	186	4
.001	277	.0053	387	6
.002	392	.0076	566	9
.005	590	.0115	868	14
.007	710	.0141	1077	17
.01	885	.0160	1075	19
.02	1577	.0248	1254	30
.05	2566	.0364	1446	43
.07	2861	.0401	1505	48
.1	3232	.0449	1556	54
.2	3943	.0538	1634	64
.5	4946	.0652	1689	78
.7	5303	.0693	1708	83
1.0	5674	.0736	1720	88

Summary

1. Measurements of the cells Cd–Hg_xCd (11%) | CdCl_2 (m) | AgCl–Ag from 0 to 40° and at concentrations from 0.0005 to 1 M have been made.

2. The standard potential of the cell from 0 to 40° has been computed by a method which assumes incomplete dissociation of an intermediate ion, the dissociation constant of which was estimated to be 0.013, 0.011 and 0.010 at 0, 25 and 40° respectively.

3. The standard potential of the electrode: Cd_γ(s) | Cd^{++}, has been computed from 0 to 40°.

4. The relative partial molal heat content and specific heat of cadmium chloride in aqueous solution have been calculated.

NEW HAVEN, CONN. RECEIVED AUGUST 20, 1936

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[21] Harned and Thomas, THIS JOURNAL **58**, 761 (1936).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

The Nature of Electrode Reactions. I. Factors Affecting the Electrochemical Reduction of N-Nitrosomethylaniline[1]

BY JOHN E. WELLS, DONALD E. BABCOCK AND WESLEY G. FRANCE

Alpha methylphenylhydrazine was first prepared electrochemically by Backer[2] through the reduction of phenylmethylnitramine and later[3] from the corresponding methylphenylnitrosamine. Tinned copper cathodes were used in both instances but no detailed study of the reaction was made.

The present work consists of the investigation of the influence of the following factors on the electrochemical reduction of N-nitrosomethylaniline at copper, lead, cadmium, mercury and cadmium amalgam electrodes: (1) temperature, (2) current density, (3) acid concentration of the catholyte, (4) the extent to which the cathodes dissolve during the course of the reduction and the amount of chemical reduction produced thereby, (5) the magnitude of the potential drop at various current strengths resulting from the presence of the depolarizer.

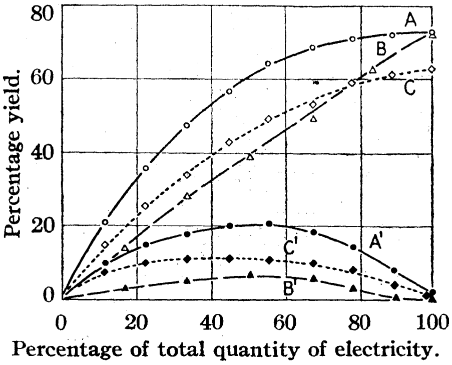

Fig. 1.—A and A′, 2 amp. per 2/3 dm.² at cadmium cathode; B and B′, 3 amp. per 2/3 dm.² at cadmium cathode; C and C′, 2 amp. per 2/3 dm.² at cadmium amalgam cathode.

The cell used was similar to that previously described.[4] The nitrosomethylaniline was specially prepared to ensure a high degree of purity by the method of Reverdin and de la Harpe.[5] A weighed sample of the nitrosamine was placed in the cathode compartment of the cell with 200 ml. of electrolyte of known acid concentration, a further portion of the same acid solution was added to the anode compartment and the cell placed in a thermostat. The electrolyte was rapidly stirred and a constant current was maintained until the theoretical quantity of electricity required for the reduction had passed. Throughout the course of the reduction small samples of the catholyte were removed at ten minute intervals and analyzed for cathode metal ions and hydrazine content. The hydrazine was determined by a modified method of Strache,[6] and the metal ion content by electrotitration. The collected data are contained in the accompanying table and curves.

In Fig. 1 curves A, B and C, indicate the yield of hydrazine at various time intervals corresponding to the passage of definite percentages of the total quantity of electricity theoretically required for the reduction. A′, B′ and C′ are plots of the concentrations of the metal ions present in the catholyte at these same intervals in terms of the chemical equivalents of methylphenylhydrazine based on the equation

$$C_6H_5(CH_3)NNO + 4H^+ + 2Cd = 2Cd^{++} + HOH + C_6H_5(CH_3)NNH_2$$

These data show that during the course of the reduction the cadmium at first dissolves but later redeposits on the cathode and at the higher current densities the dissolution of the electrode is diminished and the final yield of the hydrazine is increased. The curves in Fig. 2 in which the percentage yield is plotted against the current density show that the maximum yield for each electrode occurs at some definite current density. At current densities above or below this value the yields are smaller. The decreasing order for the optimum current densities of the electrodes is lead, cadmium, cadmium amalgam, mercury and copper. The same order was observed for the decreasing values of the maximum yields at the various electrodes.

From the curves in Fig. 3 in which the yields are plotted against the temperature it is clearly evident that a decrease in the temperature of the

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[1] Presented in part before the Organic Division of the American Chemical Society at the Chicago meeting, September, 1933.

[2] Backer, *Rec. trav. chim.*, **31**, 142 (1912).

[3] Backer, *ibid.*, **32**, 39 (1913).

[4] Cook and France, *J. Phys. Chem.*, **36**, 2383 (1932).

[5] Reverdin and de la Harpe, *Ber.*, **22**, 1906 (1889).

[6] Strache, *Monatsh.*, **12**, 526 (1891); **13**, 229 (1892).

reduction results in an increase in the yields at all electrodes. The temperature is of further importance in that it affects the velocity of the undesirable side reactions. The first and most important of these is the rearrangement of the N-nitrosomethylaniline into *p*-nitrosomethylaniline, from which the desired hydrazine cannot be obtained. At the higher temperatures at which this reaction is most rapid the yields for all electrodes were very low. The nitrosomethylaniline solidifies at a temperature of from 7–8° in 1.0 *N* hydrochloric acid, and therefore below this temperature all reductions drop to a negligible value. The maximum yields were obtained at temperatures just above the freezing point of the depolarizer.

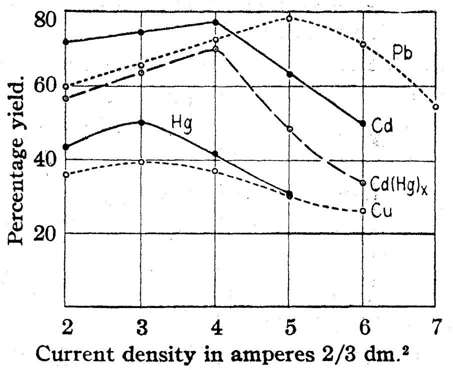

Fig. 2.

The data presented in Fig. 1 indicate conclusively that the electrochemical reduction is accompanied by a certain amount of purely chemical reduction when cadmium and cadmium amalgam electrodes are used. In order to study further the extent of the chemical reduction the following experiments were carried out over a selected range of temperatures and acid concentrations. The cells were set up exactly as before using the same quantity of depolarizer but without any current flowing. After a period of ninety minutes, the time required for the electrochemical reduction, the catholyte solution was analyzed for hydrazine content. These results are recorded in Table I.

These data together with those of Fig. 1 show that the dissolution of the electrode is a direct function of the temperature and acid concentration and an inverse function of the current density. It is interesting to note that whereas cadmium and the cadmium from the amalgam dissolved appreciably the other electrodes of copper, lead and mercury did not. However traces of these latter metals were usually found in the catholyte solutions. In the case of the cadmium amalgam the magnitude of the chemical reduction of the nitrosamine was diminished to a very small value. This decrease corresponded to the lowered concentration of cadmium in the amalgam relative to that of the pure metal.

TABLE I

REDUCTION BY PURELY CHEMICAL MEANS WITH THE SAME ELECTRODES USED IN THE ELECTROCHEMICAL REDUCTIONS

Current passed in this case is zero, for 90 minutes in each case with 200 ml. of electrolyte

Acid HCl normality	Electrode metal	Temp., °C.	Yield, %
1.0	Cd	20	66.0
0.75	Cd	20	53.3
.50	Cd	20	35.6
.10	Cd	20	8.4
1.00	Cu	20	0.0
1.00	Pb	20	.0
1.00	Hg	20	.0
0.90	Cd	23	66.7
0.90	Cd(Hg)$_x$	22	16.2
1.00	Cd	15	57.5
1.00	Cd	10	31.2
1.00	Cd	5	0.0

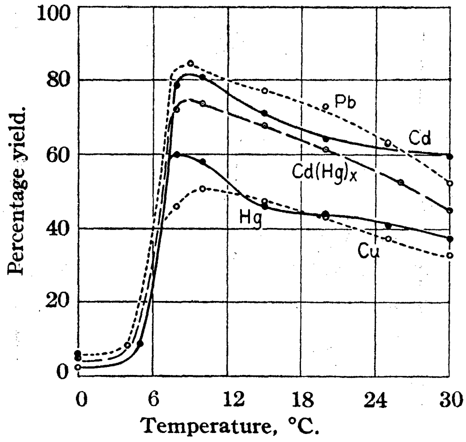

Fig. 3.

The copper cathodes appeared to be oxidized, presumably by the NO group of the nitrosamine. This fact together with the presence of the metal ions in the catholyte is strongly suggestive of the existence of a tendency on the part of the metal of the electrode to combine with the nitrosamine adsorbed on the surface of the electrode.

Liebreich considered the tendency of the metals[7] to dissolve or corrode as being a function of their overvoltage values. He regarded the hydrogen as acting in two ways, one to reduce the metal oxide or form hydrides and two to be evolved as

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(7) Liebreich, *Korrosion Metalschutz*, **3**, 78–82 (1927).

gaseous hydrogen. The same conclusion was reached by Theil and Echell.[8]

The magnitude of the potential drop of the cathodes at various current strengths due to the presence of the depolarizer was determined and found to be appreciable in all cases, the decreasing order of magnitude being cadmium amalgam, lead, cadmium and copper. These results are expressed graphically in Fig. 4 in which the potential drop ($-\Delta E$ volts) due to the presence of the depolarizer is plotted against the corresponding current strengths (amperes) at which the electrode potentials were measured. When considered in relation to the dissolution of the cadmium amalgam electrodes, these results suggest the possibility that the loss in the overvoltage value of the electrode due to the depolarizer may be the direct cause of the dissolution. This view is given added support by the fact that at the higher current densities and hence higher overvoltage values, the concentrations of the metal ions in the catholyte solutions were lower.

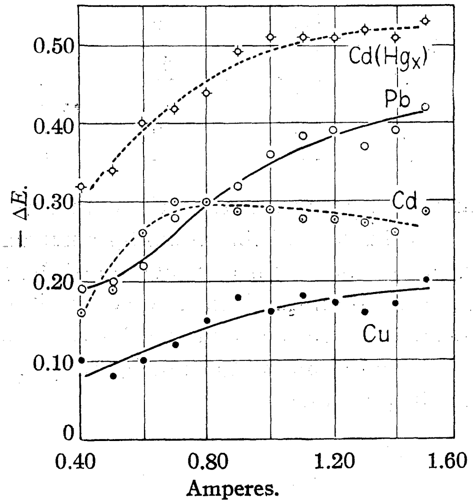

Fig. 4.

Summary

The results of this investigation may be summarized as follows.

1. The electrochemical reduction of N-nitrosomethylaniline proceeds most readily at a temperature slightly above the freezing point of the depolarizer.
2. For Cd, Cd(Hg)$_x$, Pb, Cu and Hg the optimum current density is a specific characteristic of the electrode material.
3. In the main electrochemical reactions the acid concentration is not a major factor; however, the kind and concentration of acid and also the temperature may determine the course and extent of undesirable side reactions.
4. Purely chemical reductions and associated side reactions may occur along with the electrochemical reductions at the active electrodes employed in this investigation.
5. The dissolution of the electrodes may be the result of the drop in the cathodic overvoltage due to the presence of the depolarizer.
6. The electrochemical reduction of N-nitrosomethylaniline provides a highly satisfactory way of preparing α-methylphenylhydrazine, giving yields as high as 85%.

COLUMBUS, OHIO RECEIVED JULY 3, 1936

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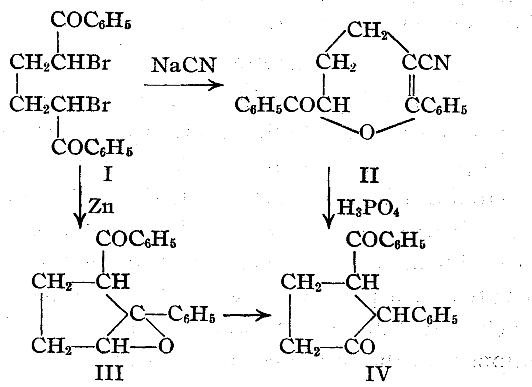
(8) Theil and Echell, *Korrosion Metalschutz*, **4**, 121-133 (1928).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

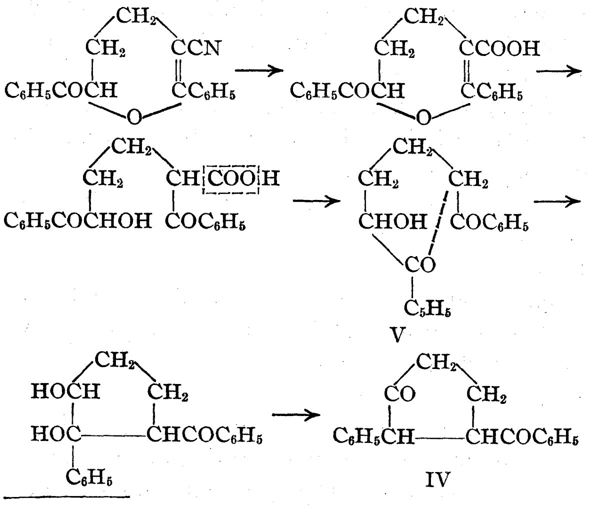
A Cyclopentane Derivative from 1,4-Dibromo-1,4-dibenzoylbutane

BY REYNOLD C. FUSON, ARNOLD LIPPERT, R. V. YOUNG AND H. H. HULLY

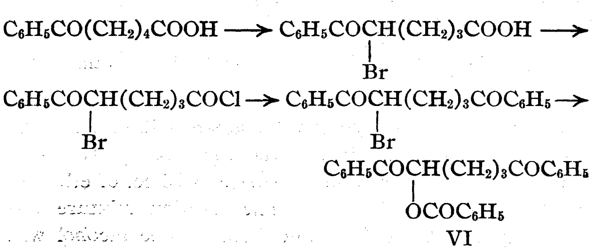
A cyclopentane derivative (IV) was obtained by rearrangement of the oxide (III), which is formed when 1,4-dibromo-1,4-dibenzoylbutane (I) is treated with zinc.[1] It has now been found that this transformation of the diketone (I) into the cyclopentanone can be effected in another way. The first step involves the action of sodium cyanide on the dibromo diketone, and gives a cyano dihydro-1,4-pyran (II).[2] When this nitrile is heated with sirupy phosphoric acid, it is converted to the cyclopentanone (IV).



This curious change of II into IV involves hydrolysis of the cyano group, opening of the dihydro-1,4-pyran ring, decarboxylation of the resulting acid and finally closure to the cyclopentanone. It seems probable that these reactions take place in the following sequence



In an effort to gain some insight into this complex change, we have prepared the benzoate of the hydroxy diketone (V) and subjected it to the action of phosphoric acid. The synthesis of the benzoate (VI) was accomplished by the following series of transformations



$$C_6H_5CO(CH_2)_4COOH \longrightarrow C_6H_5CO\underset{Br}{CH}(CH_2)_3COOH \longrightarrow$$
$$C_6H_5CO\underset{Br}{CH}(CH_2)_3COCl \longrightarrow C_6H_5CO\underset{Br}{CH}(CH_2)_3COC_6H_5 \longrightarrow$$
$$C_6H_5CO\underset{OCOC_6H_5}{CH}(CH_2)_3COC_6H_5$$

VI

This benzoate should be hydrolyzed by the hot 85% phosphoric acid to the hydroxy diketone (V), and the latter, if really an intermediate in the process, should yield the cyclopentanone. The result of the test was an 80% yield of the expected compound (IV). This lends support to the proposed mechanism.

Experimental

The transformation of the cyano compound (II) into the cyclopentanone (IV) can be effected by use of sulfuric acid or phosphoric acid. The best yields were obtained by use of the following procedure. Ten grams of the cyano compound was dissolved in 300 cc. of 85% phosphoric acid and 25 cc. of 95% ethyl alcohol. The mixture was stirred for eighteen hours and then heated under reflux on a hot-plate for eight hours. When the reaction mixture had cooled, it was placed in a 2-liter beaker and diluted to a volume of 1800 cc. by addition of water. The yellow solid which separated over a period of several hours was removed by filtration and recrystallized from ethyl alcohol. The melting point was 159–159.5° (corr.) and was not depressed by admixture with 2-phenyl-3-benzoylcyclopentanone. The yield was 40% of the theoretical amount.

The benzoate of 1-hydroxy-1,4-dibenzoylbutane was synthesized by the following series of reactions.

δ-Bromo-δ-benzoylvaleric Acid.—Thirty grams of δ-benzoylvaleric acid, prepared according to Hill,[3] was dissolved in 300 cc. of hot carbon tetrachloride. To this solution was added 25 g. of bromine through a capillary tube extending beneath the surface of the liquid. The reaction was complete in about ten minutes. Air was then drawn through the warm solution until the volume was about 150 cc. When cooled, the solution deposited crystals which were purified by precipitation from a cold ethyl acetate solution by the addition of petroleum ether (25–45°). The yield is 30 g. of product which melts at 109–110°,

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(1) Fuson and Farlow, THIS JOURNAL, **56**, 1593 (1934); Babcock and Fuson, *ibid.*, **58**, 2325 (1936).

(2) Fuson, Kuykendall and Wilhelm, *ibid.*, **53**, 4187 (1931).

(3) Hill, *ibid.*, **54**, 4105 (1932).

Anal. Calcd. for $C_{12}H_{13}O_3Br$: C, 50.52; H, 4.60; Br, 28.04. Found: C, 50.63; H, 4.87; Br, 27.83.

1-Bromo-1,4-dibenzoylbutane.—Twenty grams of δ-bromo-δ-benzoylvaleric acid and 14 cc. of thionyl chloride were warmed gently on the steam-bath for one hour; then the excess thionyl chloride was removed by heating the reaction mixture to 60° under diminished pressure. The δ-benzoyl-δ-bromovaleryl chloride thus obtained was added dropwise to an ice-cold suspension of 18 g. of aluminum chloride in 100 cc. of benzene. After the addition of the acid chloride the reaction mixture was allowed to stand overnight at room temperature. Decomposition of the complex gave 13 g. of 1-bromo-1,4-dibenzoylbutane which melted at 62–63°.

Anal. Calcd. for $C_{18}H_{17}O_2Br$: Br, 23.16. Found: Br, 23.31.

The Benzoate of 1-Hydroxy-1,4-dibenzoylbutane.—Five grams of 1-bromo-1,4-dibenzoylbutane was dissolved in a solution of 1.2 g. of sodium benzoate in 75 cc. of ethyl alcohol and 10 cc. of water. The reaction mixture was heated under reflux for three hours. The alcohol was then removed from the solution and the residue was taken up in ethyl acetate. Addition of petroleum ether (b. p. 25–45°) to the solution precipitated crystals which melted at 110–111°. Three grams of the keto ester was obtained.

Anal. Calcd. for $C_{25}H_{22}O_4$: C, 77.75; H, 5.78. Found: C, 77.67; H, 5.89.

2-Phenyl-3-benzoylcyclopentanone.—A solution of 5 g. of the benzoate of 1-hydroxy-1,4-dibenzoylbutane in 60 cc. of alcohol was added to 200 cc. of 85% phosphoric acid and the mixture heated under reflux for twelve hours. At the end of this time, the reaction mixture was poured into 200 cc. of ice water and allowed to stand about thirty minutes. The precipitate was decolorized with norite and recrystallized from ethyl alcohol. There was obtained 3 g. of fine, colorless needles, melting at 156–158°. A mixed melting point with an authentic sample of 2-phenyl-3-benzoylcyclopentanone showed no depression.

Summary

Hot phosphoric acid converts 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran (II) to a cyclopentanone derivative. A mechanism is postulated which involves the formation of 1-hydroxy-1,4-dibenzoylbutane as an intermediate. The benzoate of this compound has been prepared and treated with phosphoric acid; the product is the cyclopentanone in question. This result lends support to the proposed mechanism.

Urbana, Illinois Received October 26, 1936

[Contribution from the Chemical Laboratory of the University of Illinois]

Dihydro-1,4-pyrans. V. The Structure of the 3-Cyano Derivatives

By H. H. Hully, F. H. Brock and Reynold C. Fuson

In a previous paper[1] the cyano compounds resulting from the action of sodium cyanide on certain 1,4-dibromo-1,4-diaroylbutanes were assigned tentatively a dihydro-1,4-pyran structure. Strong support for this structure was obtained by degradation of the cyano compound obtained from 1,4-dibromo-1,4-dibenzoylbutane. Use of the Beckmann rearrangement led to a series of derivatives whose properties were in accord with predictions based on the structure originally assigned (I).[2] The end-product of this degradation has subsequently been definitely identified as α-hydroxy-δ-benzoylvaleric acid (II).[3] In view of these results, it seems certain that the original cyano compound has the dihydro-1,4-pyran structure.

In the search for confirmatory evidence, we have studied the effects of certain oxidizing and reducing agents on this dihydro-1,4-pyran.

Concentrated nitric acid attacks the ethylenic bond and produces the nitric ester of a nitro alcohol. By analogy with similar cases[4] we have assigned structure III to this compound. Its formation was the first definite proof of the presence of the ethylenic bond in the parent substance.

Catalytic hydrogenation, however, did not affect the ethylenic bond. On the contrary, the carbonyl group was attacked preferentially. The resulting alcohol (IV) was found to yield a urethan when treated with phenyl isocyanate. Treatment with chromic acid oxidized the alcohol to the original ketone. Concentrated nitric acid converted the carbinol (IV) into the same derivative (III) which was obtained from the original cyano pyran (I).

Ozone attacked the ethylenic linkage and produced an ozonide which led to ring opening in the expected manner. The cleavage product (V), when treated with alkali, gave benzoic acid (one

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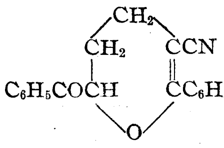
[1] Fuson, Kuykendall and Wilhelm, This Journal, **53**, 4187 (1931).

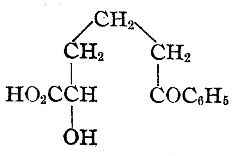
[2] Kao and Fuson, *ibid.*, **54**, 313 (1932).

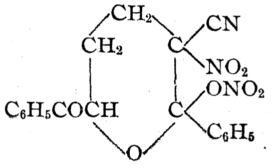
[3] Fuson, Wojicik and Turck, *ibid.*, **56**, 235 (1934).

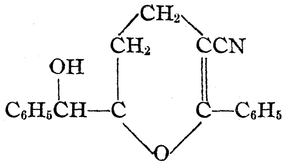
[4] See, for example, Van Der Lee, *Rec. trav. chim.*, **47**, 920 (1928).

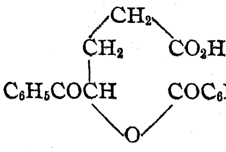
mole), and a mixture of compounds from which succinic acid was isolated.

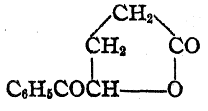

I


II


III


IV


V


VI

Attempts to synthesize this open-chain derivative were, however, unsuccessful.[3] To this end γ-bromo-γ-benzoylbutyric acid was prepared and treated with silver benzoate. The only product which could be obtained was the γ-benzoylbutyrolactone (VI).

Experimental

The Action of Nitric Acid on 2-Phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran.—One gram of 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran was dissolved in 5 cc. of glacial acetic acid and a solution of 1 cc. of concentrated nitric acid (sp. gr., 1.42) in 3 cc. of glacial acetic acid was added slowly. The reaction mixture was heated at 100° for one hour. Oxides of nitrogen were evolved during this time. The solution was then poured into 200 cc. of ice water, the precipitate collected on a filter and crystallized from ethyl alcohol. There was obtained 1 g. of a product melting at 139.5–140°, with evolution of oxides of nitrogen.

Anal. Calcd. for $C_{19}H_{15}O_7N_3$: C, 57.43; H, 3.81. Found: C, 57.31, 57.29; H, 4.04, 3.93.

This compound, to which was assigned formula III, was also made by the action at 0° of fuming nitric acid on the carbinol (IV).

Reduction of 2-Phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran.—Seven and eighteen-hundredths grams of 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran was dissolved in 300 cc. of ethyl acetate and treated with hydrogen under a pressure of three atmospheres for fourteen hours in the presence of a platinum oxide catalyst. The platinum was removed from the solution, and the ethyl acetate removed by distillation. The residue, after several recrystallizations from dilute alcohol, melted at 110–113°.

The carbinol could not be purified satisfactorily, since deposition of an oil always accompanied crystallization. Treatment of the carbinol with phenyl isocyanate, however, gave the corresponding urethan, which could be satisfactorily purified by crystallization from ethyl alcohol. The melting point is 137–138°.

Anal. Calcd. for $C_{26}H_{22}O_3N_2$: N, 6.83. Found: N, 6.92.

Oxidation of the Carbinol.—One gram of the carbinol was dissolved in 10 cc. of glacial acetic acid, and to this was added 0.2 g. of chromic anhydride in 40 cc. of acetic acid. The solution was warmed on the steam cone for ten minutes. The solution was then diluted with 200 cc. of water, neutralized with aqueous sodium hydroxide and extracted with ether. Evaporation of the ether left a residue which melted at 105–106° after recrystallization from ethyl acetate. A mixed melting point with 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran gave no depression. The yield was practically quantitative.

Ozonolysis of 2-Phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran.—Two grams of 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran was dissolved in 40 cc. of glacial acetic acid and a moderate stream of ozone was bubbled through the solution for seven hours. The ozonide was decomposed by the addition of water. After several hours crystals were deposited; these were dissolved in ethyl acetate and reprecipitated by the addition of petroleum ether (b. p. 25–45°). After several recrystallizations, the acid melted at 113°; yield 0.5 g.

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.2; H, 5.14; neut. equiv., 312. Found: C, 69.39; H, 5.27; neut. equiv., 316.

The semicarbazone melted (from an alcohol–water mixture) at 190–195°, with decomposition.

Anal. Calcd. for $C_{19}H_{19}O_5N_3$: C, 61.8; H, 5.15. Found: C, 62.2; H, 5.4.

Hydrolysis of the Benzoate of γ-Hydroxy-γ-benzoylbutyric Acid (V).—Sixteen-hundredths of a gram of the benzoate of γ-hydroxy-γ-benzoylbutyric acid, which was produced by the ozonolysis just described, was treated with an excess of sodium hydroxide solution and allowed to stand overnight. The solution was then acidified and concentrated to a volume of 5 cc.; it was then extracted with ether. Evaporation of the ether left crystals which melted at 182–184°. A mixed melting point with succinic acid showed no depression.

Summary

Further evidence has been obtained in confirmation of the dihydro-1,4-pyran structure previously assigned to the cyano compound derived from 1,4-dibromo-1,4-dibenzoylbutane by the action of sodium cyanide.

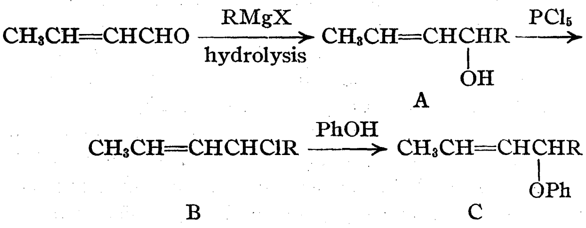
URBANA, ILLINOIS RECEIVED OCTOBER 30, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Rearrangements of α-Propylcrotyl Chloride and α-Propylcrotyl Phenyl Ether

BY CHARLES D. HURD AND JONATHAN W. WILLIAMS

The rearrangement of several α-alkylcrotyl phenyl ethers was studied by Hurd and Cohen.[1] The ethers were synthesized from crotonaldehyde by the following series of steps.



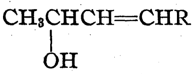
$$CH_3CH{=}CHCHO \xrightarrow[\text{hydrolysis}]{RMgX} CH_3CH{=}CH\underset{\displaystyle OH}{CHR} \xrightarrow{PCl_5}$$

A

$$CH_3CH{=}CHCHClR \xrightarrow{PhOH} CH_3CH{=}CH\underset{\displaystyle OPh}{CHR}$$

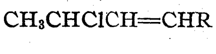
B C

Rearrangement of (C) by heating at 230° yielded the phenol (D), $C_6H_4{<}^{OH}_{CH(CH_3)CH=CHR}$. It was not established whether or not A, B and C were free from allylic isomers E, F and G, respectively.



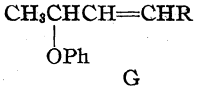
$$CH_3\underset{\displaystyle OH}{CH}CH{=}CHR$$

E



$CH_3CHClCH{=}CHR$

F



$$CH_3\underset{\displaystyle OPh}{CH}CH{=}CHR$$

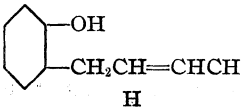
G

This question was significant since an allylic rearrangement of α-alkylallyl alcohols, $CH_2{=}CHCHOHR$, does occur during reaction with halogen acids. Until recently it was thought that the rearrangement into $CH_2XCH{=}CHR$ was complete. In the case of α-methylallyl alcohol, it has been established[2] that the related bromide is an equilibrium mixture of 1-bromo-2-butene and 3-bromo-1-butene, the former predominating. It would be reasonable to assume, therefore, that B (as prepared) would be a mixture of B and F, in which case C would be admixed with G.

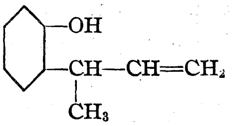
The R-groups in the α-alkylcrotyl compounds of Hurd and Cohen were methyl, ethyl and propyl. It was decided to study the last of these, although the second would have been equally appropriate. The first was inapplicable (since B = F). It was planned to test for the presence of isomeric pairs by ozonolysis. Compounds A to C would yield acetaldehyde or acetic acid, whereas E to G would produce butyraldehyde or butyric acid. Mixtures of isomeric pairs would produce corresponding mixtures of acetic and butyric acids.

It was found by this means that the propylcrotyl alcohol was practically pure A. Conversion to the chloride did cause some isomerization, but B predominated over F. About the same ratio (80:20) was observed in the case of the phenyl ether, showing that the latter was a mixture of C + G, with C in considerable excess.

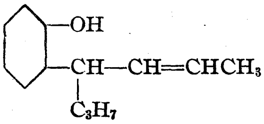
The rearrangement of C into D involves an inversion of the propylcrotyl group. Claisen[3] was the first to call attention to such an effect. He demonstrated that (H), which may be formed



H



I



J

from phenol by direct crotylation, differs from I, the chief product formed on pyrolysis of phenyl crotyl ether. Evidence in support of Claisen's viewpoint was obtained in the present work. Rearrangement of propylcrotyl phenyl ether (the mixture of C + G) yielded a mixture of phenols (D + J). Analysis showed that the ratio of phenols in the (D + J)-mixture corresponded within limits of experimental error to the ratio in (C + G).

Experimental Part

2-Heptene-4-ol, 4-chloro-2-heptene, α-propylcrotyl phenyl ether and α-methyl-δ-ethylcrotylphenol were prepared as described by Hurd and Cohen.[1] The boiling points taken, respectively, were 60–65° (23 mm.), 140–145°, 170–173° (35 mm.) and 190–195° (18 mm.). For ozonizations, 2 to 3 g. was dissolved in 150–250 cc. of carbon tetrachloride and a stream of ozonized oxygen was conducted through the solution. The solvent was then distilled off and 100 cc. of water added to the residue of oily ozonide. After ten hours, 0.5–1 g. of sodium hydroxide and silver oxide (from 10 g. of silver nitrate) were added and the mixture refluxed for three hours. It was then filtered, acidified with dilute sulfuric acid and the volatile acid distilled. The moist silver oxide served not only to oxidize the aldehydes to acids, but also to convert the α-chloroaldehydes (from B or F) to non-volatile α-hydroxy

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(1) Hurd and Cohen, THIS JOURNAL, **53**, 1917 (1931).

(2) Winstein and Young, *ibid.*, **58**, 104 (1936).

(3) Claisen and Tietze, *Ber.*, **58**, 275 (1925); **59**, 2344 (1926).

acids. Analysis of the volatile acids was by Duclaux determinations[4] on 100-cc. specimens.

Duclaux values of 6.4, 6.9, 7.3 were obtained for the first three 10-cc. portions of distillate collected from the volatile acids from 2-heptene-4-ol. This represents nearly pure acetic acid. The slight deviation may be due to the presence of α-hydroxyvaleric acid, whose influence in this determination is unknown. Confirmation that the volatile acid was acetic was the conversion of 0.5 g. of the sodium salts to 0.5 g. of *p*-bromophenacyl acetate, m. p. 84–85°, by reaction in 50% alcohol with *p*-bromophenacyl bromide.

The volatile acids from the 4-chloro-2-heptene gave a Duclaux value of 23.3 for the first 30 cc. of distillate. From this, these simultaneous equations are applicable: $\text{Ac} + \text{Bu} = 100\%$; $0.197\ \text{Ac} + 0.448\ \text{Bu} = 23.3\%$. Solving, Ac (for acetic) = 86%; Bu (for butyric) = 14%. Hydrolysis of the chloride (3 g.) to the alcohol (1.6 g.; 62% yield), b. p. 60–65° at 23 mm. and subsequent ozonolysis of the alcohol as before gave confirmatory evidence that a mixture was involved. The value for 30 cc. of Duclaux distillate was 22.2, indicative of 90% Ac and 10% Bu.

Duclaux analysis of the volatile acids from α-propylcrotyl phenyl ether (after ozonolysis, etc.) gave 24.7 as the value for 30 cc. of distillate. This represents 80% Ac, 20% Bu and indicates that the ether is a mixture of C and G possibly in the ratio of 80:20. The assumption that the volatile acids are exclusively acetic and butyric may not be entirely correct in this case since a small portion of the volatile acid may come from the aromatic part of the molecule. The figures, however, seem fairly reliable.

The product of rearrangement, namely, α-methyl-δ-ethylcrotylphenol, was treated analogously. The Duclaux value for 30 cc. of distillate was 40.3. Calculation gives 18% Ac, 82% Bu, which indicates that the phenol is chiefly D together with a smaller amount of J. The preponderance of butyric acid in the volatile acids was witnessed by converting the acids to dry sodium salts (0.5 g.) and treating the latter with *p*-bromophenacyl bromide. *p*-Bromophenacyl butyrate, m. p. 63°, was formed abundantly.

Summary

Partial allylic rearrangement of 4-chloro-2-heptene into 2-chloro-3-heptene is encountered during synthesis of the former from 2-heptene-4-ol (α-propylcrotyl alcohol). α-Propylcrotyl phenyl ether and its rearrangement product were prepared and their structures determined by ozonolysis. The evidence obtained supports the contention that the allyl group undergoes inversion during rearrangement of allyl phenyl ether into *o*-allylphenol.

EVANSTON, ILL. RECEIVED SEPTEMBER 15, 1936

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(4) Virtanen and Pulkki, THIS JOURNAL., **50**, 3143 (1928); McNair, *ibid.*, **55**, 1471 (1933).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Adsorption by Dehydrated Chabasite as a Function of the Water Content

BY ARTHUR B. LAMB AND JOHN C. WOODHOUSE

Vom Rath[1] in 1876 demonstrated that crystals of chabasite, a hydrated calcium, sodium, aluminum silicate, on dehydration retain their original form and clarity unchanged even when the loss of water amounts to nearly one-fifth of their original weight and a still larger fraction of their original volume. Friedel[2] in 1896 found that these dehydrated crystals adsorb gases with marked avidity. Especially interesting is the more recent discovery made independently by several investigators[3] that such an adsorption does not take place with gases whose molecules are larger than a certain definite limiting size and so cannot enter the pores of uniform and atomic dimensions characteristic of this adsorbent.

Impressed by the interesting potentialities of these "crystallogenetic"[4] adsorbents as we have called them, we have now made a careful study of the development of the adsorptive activity of chabasite as it is progressively dehydrated. As a criterion of this activity we have used the adsorptions of hydrogen, oxygen and carbon dioxide upon it, since they represent gases which are, respectively, very slightly, moderately and largely adsorbed.

No similar study, so far as we are aware, has been made.

Apparatus

The samples of chabasite were dehydrated and the adsorption of the resultant product measured in the apparatus shown in Fig. 1.

The manometer C was of the constant-level type. The mercury level on the adsorbent side was kept exactly at (1) by the use of the mercury reservoir B, placed under any de-

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(1) G. vom Rath, *Pogg. Ann.*, **158**, 396 (1876).

(2) Friedel, *Bull. Soc. franc. mineral*, **19**, 93–118, 363–384 (1896).

(3) Lamb, U. S. Patent 1,813,174 (Applied for September 25, 1925); McBain, *Colloid Sym. Mon.*, **4**, 1 (1926); *Kolloid Z.*, **40**, 1 (1926); Schmidt, *Z. physik. Chem.*, **133**, 280 (1928).

(4) That is, adsorbents which owe their adsorptive activity to the crystal structure of the parent substance from which they have been prepared.

sired pressure by air supplied from a hand pump. B was connected by a valve to C. The side of C away from the adsorbent was evacuated through the stopcock A by a diffusion pump sealed to the system.

Purified and triply distilled mercury was then admitted to C from B, and as high a vacuum as possible obtained with the diffusion pump. The empty manometer tube had been previously cleaned, and dried, by the passage through the heated tube of dry air for long intervals. The mercury level was gradually raised by pressure from B, with the tube being kept hot, and under the low pressure provided by the diffusion pump. In about two hours it had risen to point (3) where the 7-mm. internal diameter tube joined a capillary tube 800 mm. long, leading downward and terminating in the stopcock. This downward tube was now likewise roasted, still under the low pressure, and any residual adsorbed gases removed. Mercury was boiled over from (3) to fill the heated downward tube with its vapor, the stopcock was closed and the capillary tube filled with mercury. Thus a high vacuum was ensured on this arm of the manometer. The arrangement was such that if by any chance gas entered the evacuated arm, the procedure of evacuation could be conveniently and quickly repeated. Pressures between 1000 and 1950 mm. were read to 1 mm. and between 100 and 1000 to 0.5 mm. on a calibrated millimeter scale. Pressures between 5 and 100 mm. were read to 0.1 mm. and below 5 mm. to 0.02 mm. by means of a cathetometer.

The adsorption cell D shown above in Fig. 2, usually of quartz but sometimes of Pyrex, was attached to the apparatus by interchangeable ground joints. Its volume (5–7 cc.) from (A) to (B) was first determined accurately; this volume was then charged with 10–14 mesh chabasite through the 5 mm. tube and this was sealed off flat at (C). Since the residual volume of the small tube could be computed accurately from its linear dimensions, the total volume of the cell could be ascertained to within 0.005 cc. The density of the undehydrated chabasite was determined to the second decimal place and using this value and taking the density of the water in the chabasite as unity, the free space in the cell containing wholly or partially dehydrated adsorbent was computed. The free space in the adsorption apparatus between 1 and 2 was also measured accurately by displacement of mercury. It amounted to only between 1.2 and 1.6 cc. in the several arrangements of apparatus used. The total free space in the apparatus ranged between 1.2 and 1.7 cc. per gram of anhydrous chabasite with a maximum uncertainty of ±0.1 cc.

During measurements the cell was surrounded by suitable constant temperature jackets employing transition points, and preferably boiling points of stable substances.

The mercury-operated gas buret, G, had a capacity of 103.47 cc. It was provided with a stirred water jacket and could be read to about ±0.01 cc., but readings usually were taken only to ±0.05 cc. Gases were thus measured to within 0.02 cc. or less per gram of anhydrous chabasite. By means of the leveling bulb gas volumes were measured at atmospheric pressure and at the temperature of the jacket. Corrections were made to standard conditions, taking account of individual deviations from the gas laws.

In order to be sure whether water and the several gases employed were really adsorbed reversibly, it was necessary to measure accurately the several temperatures of dehydration and gas adsorption. Up to 356° (the boiling point of mercury) jackets employing vapors from the refluxing of

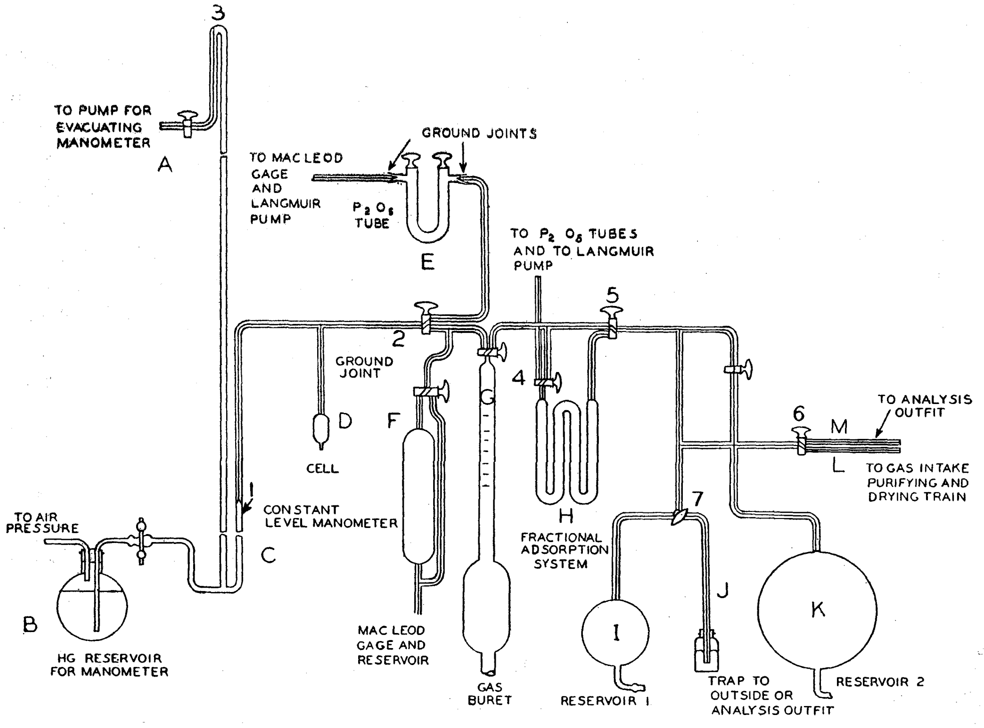

Fig. 1.—Apparatus.

stable compounds were employed. Above 356° there was used a closed tubular electric furnace.

Below 300°, temperatures were checked by a nitrogen-filled glass thermometer. From 300 to 750° they were measured by a nitrogen-filled quartz thermometer and above that by a thermoelectric pyrometer.

The vapor jackets gave all temperatures identical with the boiling points of the compounds used. When the electric furnace was employed, thermometers and cell were so placed that no part of the adsorbent was subjected to a temperature of more than ±5° from that recorded.

At higher temperatures, control was important also in order to prevent injury to the adsorbent through overheating. The observations of earlier experimenters[5] regarding the reversibility of hydration and dehydration below 600° were checked quantitatively.

Materials

Chabasite.—This consisted of six samples which so far as we know represent collections made in the vicinity of Aussig, Bohemia. The small crystals as received were removed from their rocky matrix, crushed sufficiently to pass a 10- and be retained on a 14-mesh-to-the-inch sieve and the fragments examined individually with a microscope and a polariscope to ensure the absence of any foreign material. Each sample thus secured, usually weighing from 75 to 100 grams, was then exposed in a desiccator over 24% aqueous sulfuric acid at about 20° (aqueous pressure 15 mm.) for at least two weeks, and during the last day as nearly as possible at exactly 20°. After this equilibration samples kept for an additional three months under the same conditions showed no further gain or loss in weight. The water contents of these samples were determined by heating 2–4 g. portions at 900–950° to constant weight. The following results, each representing the mean of two concordant duplicate analyses, were obtained for the six chabasite samples: 22.25, 22.23, 22.34, 22.27, 22.27 and 22.30; average 22.28% H_2O.

Hydrogen, Oxygen and Carbon Dioxide.—Selected samples of the compressed or liquefied commercial gases were analyzed carefully and found to be, respectively, 99.0–99.25, 99.5 and 99.88% pure as drawn from the cylinders. The gases were then dried over phosphorus pentoxide and introduced into the adsorption apparatus where they were further purified by means of fractional adsorption.

For this purpose they were allowed to enter the apparatus through L and to escape through J until the voided gas showed a constant and high degree of purity. Tube H charged with 50 g. of activated chabasite and highly evacuated was now chilled to −192° for hydrogen, −182° for oxygen and −78° for carbon dioxide and the gas adsorbed in it up to a pressure of about 1900 mm. A portion of this gas was then discarded, a large fraction of the remainder was drawn into the reservoirs I or K and the residue removed from H by evacuation at room temperature. This procedure was repeated one or more times and the finally purified gas stored in I or K. In the case of carbon dioxide the purification was also frequently carried out using the dehydrated chabasite itself in D. When enough of the gas had been added to raise the pressure there to the maximum desired, a small measured portion containing practically all of the impurities was removed and replaced by an equal volume of the pure original gas (99.88%). This was repeated (usually two repetitions were ample) until the first sample withdrawn showed a purity of 99.88%. We could then be certain that the residual gas was of a considerably higher purity.

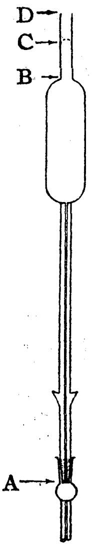

Fig. 2.—Adsorption cell.

Procedure

The water vapor was drawn off from the sample through stopcock 2 into the phosphorus pentoxide tube E, by means of a mercury diffusion pump backed by an oil pump. After suitable intervals of heating and pumping, tube E was disconnected and weighed. By the use of an identical counterpoise and by careful control of the humidity this could be done with an accuracy of ±0.2 mg. which corresponds to an uncertainty of only about 0.004% with the usual 5-g. sample of chabasite.

Adsorption Measurements.—The gas after final purification was transferred to the buret F and from there measured volumes of it were admitted to the evacuated cell D containing the suitably dehydrated adsorbent. Pressure readings were taken until no further change could be detected. This was usually the case within at most twenty minutes. Additional amounts of gas were then introduced until the limit of the manometer had been reached. The points thus obtained gave an "in-going" isotherm. The process was now reversed, measured volumes of gas being removed and an "out-going" isotherm obtained.

Experimental Results

A typical set of experimental data as obtained for a single "out-going" point on an oxygen isotherm is given in Table I in order to illustrate the application of the corrections and the methods of calculation.

TABLE I

OXYGEN ISOTHERM AT 0° ON AUSSIG CHABASITE

Run 120: 78.4% dehydrated at 255°; 2.775 g. anhydrous chabasite; 5.88 cc. free space

Time:—1:30–2:30 P.M., Dec. 17		Volume gas	
Barometer, corr., mm.	750.5	Removed, cc.	11.00
Manometer, mm.	768.0	Removed, corr., cc.	10.10
Manometer, mm.	10.0	Total in system, cc.	23.95
Pressure, mm.	758.0	Free, cc.	5.85
Pressure, corr., mm.	755.4	Adsorbed, cc.	18.10
Temperature buret, °C.	19.9	Adsorbed cc. per g.	6.52

Our experimental data are collected in Tables II–V and are shown graphically in Figs. 3–9.

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[5] The most pertinent previous information appears to be the observations of Rothmund [*Rec. Trav. Chim.*, **44**, 329 (1925)] that chabasite dehydrated at a temperature of 400–600° loses most of its water but can regain it fully on exposure to water vapor at room temperature. At higher temperatures this reversibility becomes less complete and at 800° is wholly lost.

TABLE II

HYDROGEN ADSORPTION ISOTHERMS AT 0° ON CHABASITE DEHYDRATED TO VARIOUS DEGREES

Chabasite Sample											
9		9		9		9		10		7	
Dehydration, %											
61.4		78.4		91.3		96.3		96.7		97.5	
Dehydration temperature, °C.											
180		255		380		630		634		640	
Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.
1833	0.25	1796	1.0	1850	1.9	1918	5.6	1802	5.8	1870	5.2
857.8	.10	1193	0.8	1203	1.4	1276	4.0	1225	4.2	605.7	2.1
364.7	< .05	722.5	.5	671.7	0.9	906.8	3.0	780.7	2.8	276.7	0.9
		366.4	.3	279.0	.4	542.1	1.9	432.2	1.6	45.0	.4
		137.1	.1	101.6	< .1	366.8	1.4	168.4	0.6		
						188.4	0.8				
						52.8	.3				
						13.0	.1				

TABLE III

ADSORPTION ISOTHERMS AT 0° OF OXYGEN ON CHABASITE DEHYDRATED TO VARIOUS DEGREES

Chabasite Sample															
8		8		10		9		10		9		10		8	
Dehydration, %															
40.0		74.0		90.7		94.5		95.5		96.3		96.7		97.8	
Dehydration temperature, °C.															
250		306		390		460		575		635		635		730	
Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.
822.5	1.3	927.0	7.3	1962	19.8	1864	25.9	1950	33.2	1847	36.3	1894	33.0	1315	23.2
575.8	0.8	554.7	4.1	1615	18.2	1545	23.4	1484	29.0	1441	33.3	1510	30.4	801.7	18.5
298.5	.3	356.5	2.8	1235	14.4	1260	20.8	1016	24.5	1144	31.0	1153	27.2	352.6	12.4
10.0	.0	10.5	0.1	876.7	11.1	999.8	18.2	647.6	19.9	906.4	28.6	832.3	23.9		
				514.0	6.7	779.5	15.6	302.8	13.7	740.4	26.5	462.6	18.9		
				259.3	3.4	580.9	12.8	169.4	10.0	551.5	23.8				
				133.5	1.6	390.7	9.8	79.7	6.3	391.8	20.9				
				70.8	0.7	239.2	7.1	58.8	5.1	269.1	17.6				
						138.6	4.7			172.4	14.7				
						52.8	2.1			64.8	8.9				
										25.9	5.5				

Since however a total of 30 isotherms for oxygen and 15 for carbon dioxide were measured at 0°, because of limitations of space only a part of these have been included in the tables.[6] The temperatures of dehydration given in the tables are the respective maximum temperatures attained during the dehydration which was usually continued for four to ten hours until no appreciable amount of water came off at pressures less than 0.1 mm. The volumes of gas adsorbed as given in the tables represent the number of cubic centimeters, corrected to standard temperature and pressure, adsorbed at the given pressure, per gram of anhydrous adsorbent.

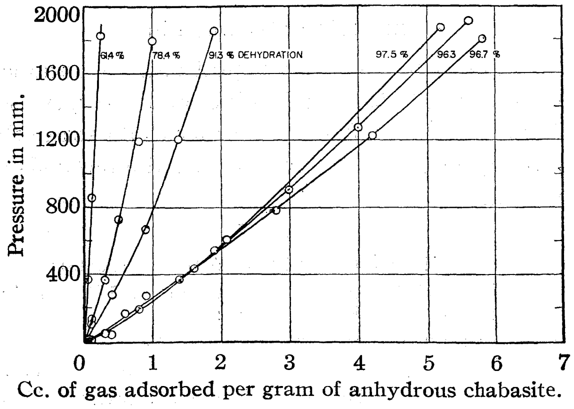

Fig. 3.—Adsorption isotherms at 0° of hydrogen by chabasite at various degrees of dehydration.

Incomplete results with ammonia, which so far as we know is the most highly adsorbed of all gases upon these adsorbents, show that it is somewhat adsorbed upon chabasite when even less than 5% of the total water is removed; and there is some evidence that ammonia actually drives water out of partially dehydrated chabasite. Moreover, ammonia when once adsorbed is held with extreme tenacity. It was found, for example, that all of the ammonia adsorbed on 90% dehydrated chabasite could only be removed by prolonged heating of the adsorbent above 400° at vacua obtainable by mercury diffusion pumps.

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(6) All of these data in tabular form are available as Science Service Document No. 1003 (9 pages, 25 cents in microfilm form or 55 cents in photoprint form; payable in advance by check or money order to Science Service, 2101 Constitution Avenue, Washington, D. C.).

TABLE IV

CARBON DIOXIDE ADSORPTION ISOTHERMS AT 0° ON CHABASITE DEHYDRATED TO VARIOUS DEGREES

Chabasite Sample															
10		10		10		10		9		10		10		9	
Dehydration %															
33.2		61.2		77.0		90.7		91.3		93.8		95.7		96.3	
Temperature of dehydration, °C.															
120		180		250		390		380		512		608		635	
Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.
605.5*	32.3	149.6*	65.9	1010*	105.0	2.0*	78.7	684.1*	128.1	373.5*	112.1	109.6*	103.9	25.0*	75.8
1405*	34.9	1202*	79.0	1741	108.1	20.0*	105.8	1559	132.8	1922	125.1	1518*	123.1	597.7*	114.0
1972	35.1	1574	80.6	1315	106.3	762.0*	128.0	1051	130.6	1260	123.2	1901	125.0	1700	123.0
1372	34.6	1259	79.5	924.3	104.6	1892	133.1	683.0	128.4	686.2	117.8	1224	122.0	501.0	114.2
1092	33.7	916.4	77.9	570.7	101.9	1304	131.1	391.6	125.2	411.2	113.3	833.4	119.6	148.7	103.5
657.2	32.7	586.6	75.8	368.5	99.2	749.8	127.9	236.2	122.1	249.0	108.7	415.8	116.3		
523.8	32.0	358.5	72.9	207.1	95.0	402.3	124.5	114.7	118.3	194.3	106.0	240.2	110.8		
388.3	31.1	147.5	66.3	115.4	89.4	203.2	120.3	57.3	113.7	74.8	95.8	167.4	107.8		
103.7	26.4	74.7	61.7	38.8	82.1	97.7	115.1	33.8	109.3	39.9	89.8	81.7	102.0		
20.8	19.4	33.9	54.2	19.9	74.1	38.8	109.6	14.9	103.0	14.0	77.5	47.8	96.3		
		14.5	46.1	12.5	66.1	12.0	101.7	8.0	94.6	4.3	61.3				
				5.0	49.9	2.4	85.8			1.6	45.0				
										1.2	37.4				

Under these conditions there was actual decomposition of the ammonia, and very probably a further removal of water. For these reasons no attempt has been made to treat the ammonia results quantitatively as has been done with hydrogen, oxygen and carbon dioxide.

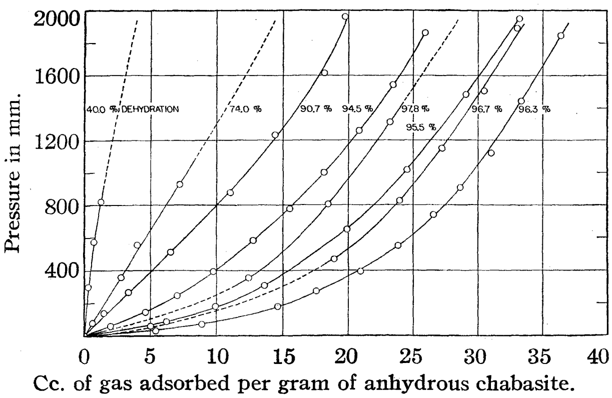

Fig. 4.—Adsorption isotherms at 0° of oxygen by chabasite at various degrees of dehydration.

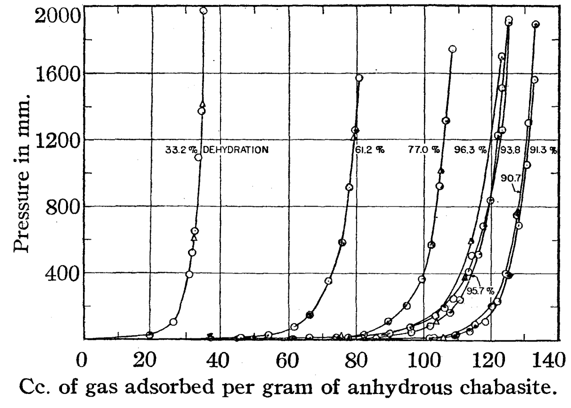

Fig. 5.—Adsorption isotherms at 0° of carbon dioxide by chabasite at various degrees of dehydration. Triangles represent "in-going" values.

The displacement of water by ammonia and the subsequent removal of the latter by evacuation at these relatively low temperatures does, however, facilitate the preparation of highly active adsorbents.

Reproducibility of the Measurements

In the measurements upon samples of chabasite which were only slightly dehydrated the adsorption equilibria adjusted themselves slowly, but in the measurements made with samples considerably dehydrated, for instance 50% or more, equilibrium was attained rapidly, usually in less than twenty minutes.

Hysteresis was also substantially absent, the "in-going" points corresponding closely to the "out-going." This has been indicated in the case of the data for the adsorption of carbon dioxide at 0° by labeling the "in-going" points in the Tables with a * and in the figures with a Δ. It can be seen that they agree closely with corre-

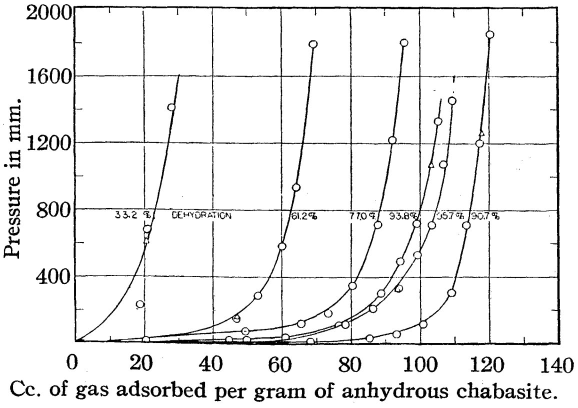

Fig. 6.—Adsorption isotherms at 34.5° of carbon dioxide by chabasite at various degrees of dehydration. Triangles represent "in-going" values.

TABLE V

CARBON DIOXIDE ISOTHERMS AT TEMPERATURES OF 34.5 TO 306° ON CHABASITE DEHYDRATED TO VARIOUS DEGREES

Chabasite Sample 10

Dehydration, %													
33.2		61.2		77.0		90.7		93.8		95.5		95.7	
Temperature of dehydration, °C.													
120		180		250		390		512		575		608	
Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.	Press., mm.	Cc./g.
34.5°													
597.7*	20.8	150.1*	47.4	1798	95.8	1250*	118.1	1064*	103.8			314.4*	94.0
1398	28.3	1778	69.5	1210	92.5	1840	120.8	1321	105.9			1444	109.9
665.8	21.2	926.2	64.5	707.2	88.1	1195	117.8	716.9	99.6			1067	107.4
219.0	19.0	572.5	60.5	338.9	80.9	652.3	113.7	483.0	94.7			755.2	103.9
		278.9	53.6	174.3	73.7	294.8	109.7	288.8	89.1			527.9	99.7
		139.6	47.2	111.7	65.9	107.6	101.2	104.7	77.3			324.7	94.2
				65.0	49.8	47.8	93.6	32.9	61.4			204.2	86.8
						27.9	85.8	14.0	45.0			109.6	78.6
						7.5	68.6	6.9	37.4			17.0	50.2
												0.5	20.8
61.2°													
2020	22.3	1763	56.8	1943	85.2	1593	111.5	1270	93.0	876.5	94.8	1793	102.0
981.0	17.3	970.9	52.2	1041	79.7	926.0	107.4	871.3	87.8	498.0	88.1	1331	99.9
		482.9	45.0	577.8	72.8	378.4	100.8	332.6	76.8	328.7	82.5	941.2	96.7
				370.6	65.3	169.2	93.1	115.6	61.1	214.2	76.1	632.5	92.9
				165.5	49.6	99.7	85.6	43.8	44.9	159.5	71.8	400.5	87.6
						25.9	68.6	23.0	37.4			206.2	79.2
												110.6	66.2
												56.8	50.0
												1.6	20.8
100.0°													
		1991	40.7	1516	62.8	1548	98.3	1900	79.8	796.7	70.4	1803	82.0
				1031	55.8	826.7	91.7	1297	74.7	488.1	62.9	1444	7.2
				718.0	48.4	527.8	84.6	808.4	67.7	323.7	56.1	1056	75.3
						209.0	68.0	499.8	60.2	219.2	50.5	757.0	70.8
						49.4	46.1	320.6	52.7	149.5	44.4	456.3	64.1
								211.2	45.0			219.2	52.7
								121.6	37.2			86.2	36.5
218°													
								1949	25.6	1919	32.0	1909	38.1
								1111	19.8	1327	28.0	1591	35.9
								585.4	14.6	885.2	24.4	1193	28.9
								219.0	9.0	404.5	18.5	804.7	25.2
								144.4	7.4	237.4	15.6	438.1	20.5
								66.7	5.0			189.2	15.5
												61.8	11.6
												28.9	8.6
												18.0	7.5
306°													
								748.1	7.9			1842	19.1
								398.2	5.1			1190	16.2
								225.0	3.2			695.2	12.6
								119.5	2.2			388.4	10.2
								73.8	1.7			154.5	7.3
								24.9	1.0			17.0	4.3

sponding "out-going" points. A similar reproducibility was obtained in the other measurements with carbon dioxide, oxygen and hydrogen.

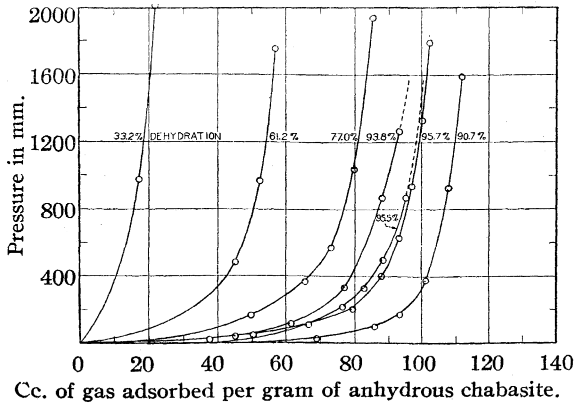

Fig. 7.—Adsorption isotherms for carbon dioxide at 61.2° by chabasite at various degrees of dehydration.

Isotherms obtained from different samples of chabasite of nearly the same degree of dehydration were also usually quite concordant. This is evidence not only of a still broader reproducibility of the phenomenon, but also of the absence of any displacement of water from the partially dehydrated chabasite during the adsorption and desorption of the gases within the range of temperatures and pressures employed. This fixity of the residual water was confirmed by passing the desorbed gases through weighed tubes containing phosphorus pentoxide and ascertaining that there was no increase in weight.

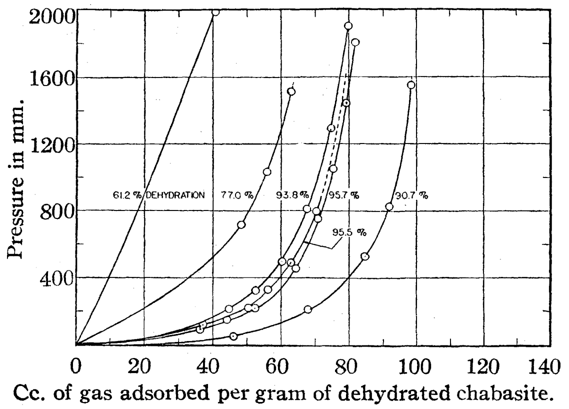

Fig. 8.—Adsorption isotherms of carbon dioxide at 100° by chabasite at various degrees of dehydration.

Utilizing large-scale plots for these isotherms, isobars were now constructed where the amounts adsorbed per gram of anhydrous chabasite were plotted against percentages of water removed. The resulting curves for hydrogen and oxygen on the same scale and for carbon dioxide on a four times smaller scale all at 0° are shown in Fig. 10. Those for carbon dioxide at successively higher temperatures are shown in Fig. 11.

These isobars are also indicative of the reproducibility of our results. The isotherms from which they are derived were obtained in some instances from as many as six different samples of chabasite. These samples not only were independent at the start but were independently dehydrated at somewhat different temperatures and pressures and according to different schedules. In spite of this, the resultant individual points lie smoothly on the isobaric curves. This shows that the adsorptive capacity of this variety of chabasite at a given degree of dehydration is definite and independent, within the limits tried, of the mode of dehydration.

It is also of interest that the adsorptive capacity of a highly dehydrated chabasite remains undiminished after repeated adsorptions and desorptions have occurred both with the same gas and other gases. Thus for example, using chabasite Sample 1, where 19.05% of water of the total of 22.25% originally present had been removed, a later isotherm with carbon dioxide checked closely an earlier isotherm made with this gas, although in the interim several other isotherms at other temperatures had been measured upon the same sample. Similarly chabasite Sample 11, where 21.41% of water had been removed, gave an isotherm substantially identical with an earlier one although in the meantime a dozen isotherms at other temperatures and with other gases had been measured upon it.

Discussion

It can be seen from Figs. 10–11 that the adsorption increases steadily as water is removed from the chabasite, but that ultimately a sharp maximum is reached at a point where only a little water remains. From there on the adsorption diminishes rapidly until at complete dehydration practically no gas is adsorbed. It should be pointed out also that while the adsorption equilibria up to the maximum are reversible, as noted above, after the maximum is passed the reversibility diminishes, and when the water has been largely removed, the equilibria are only slowly attained and are of somewhat doubtful reproducibility. Continued heating after the maximum activity has been developed lessens the activity even when no measurable loss of water occurs.

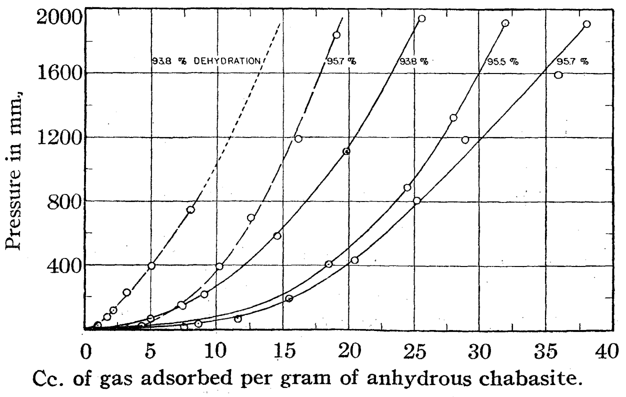

Fig. 9.—Adsorption isotherms at 218 and 306° of carbon dioxide by chabasite at various degrees of dehydration: broken lines, 306°; solid lines, −218°.

From Fig. 11 it can be seen that the same characteristic maximum adsorption at 93% dehydration observed at 0° persists at the higher temperatures. There is also a secondary maximum which is barely suggested in the curve for adsorption at 0° but becomes well marked in the curves for 34.5, 61.2 and 100°. Incomplete results at 218 and 300° show that this secondary maximum is also well marked at these temperatures. It is noteworthy that this secondary maximum occurs at nearly the same percentage dehydration (96%)

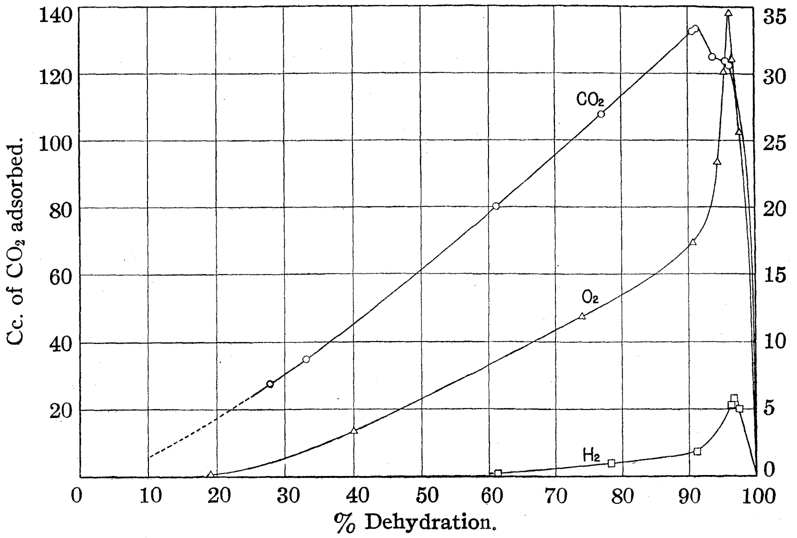

Fig. 10.—Adsorption at 0° and 1600 mm. of CO_2, O_2 and H_2 by chabasite at various degrees of dehydration: ○ = CO_2; △ = O_2; □ = H_2.

where the primary and sole maxima occur for oxygen and for hydrogen.

A reasonable interpretation of the general course of these curves is that the porosity of the adsorbent, and hence its inner surface and its adsorptive capacity, steadily increase as water is removed, so long as the original crystal lattice persists. At the high temperatures required to remove the last traces of water, the crystal lattice begins to collapse, with a consequent decrease in the adsorptive capacity. The sharp drop from the maximum is then to be attributed to a sintering that takes place at the high temperatures of dehydration.

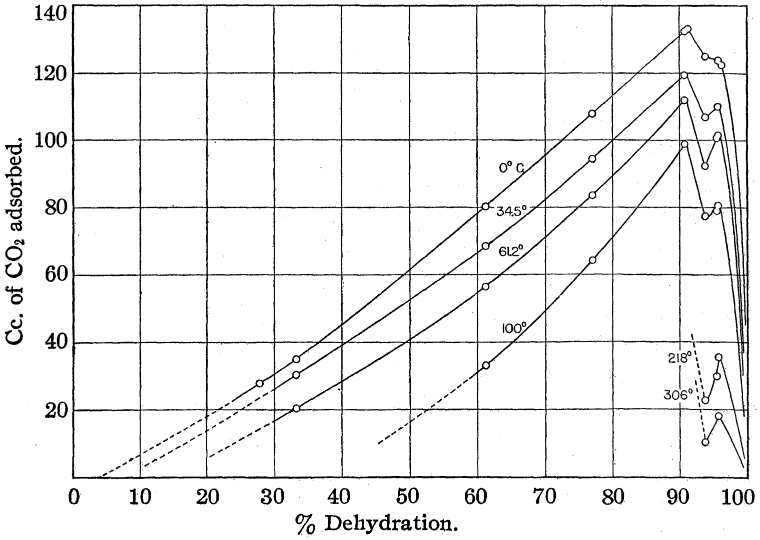

Fig. 11.—Adsorption isobars at 1600 mm. of carbon dioxide by chabasite at various degrees of dehydration.

Another feature of these curves is of great interest. They do not run linearly from the origin (no water removed), but appear to approach the horizontal axis rather abruptly at points at some distance to the right of the origin. In other words, significant quantities of the carbon dioxide, oxygen and hydrogen only appear to be adsorbed when, respectively, 5, 17 and 50% of the total water have been removed. It follows that chabasites dehydrated by these amounts exhibit an astonishing specificity in their behavior toward these gases. Our data in this range are too meager and too inaccurate to fix the exact ratios between the adsorptions of these gases under these conditions, but at 17% dehydration 15 cc. of carbon dioxide and less than 0.2 cc. of oxygen are adsorbed and at 50% dehydration 6 cc. of oxygen and less than 0.1 cc. of hydrogen are adsorbed. These amounts correspond to ratios at least of the order of 75:1 and 60:1, whereas the ratios between the volumes of these gases adsorbed under the same conditions on active charcoal are approximately 3:1 and 4:1, respectively. This remarkable specificity makes possible a simple and effective separation of such gases out of their mixtures.

A reasonable explanation of the negligible adsorption of these gases at and below these critical degrees of dehydration is as follows: The first 5% of the water removed appears to come from the "outer" surface of the crystals or crystallites and its removal provides only an insignificant increase in surface and a consequent insignificant increase in adsorption. The next water removed (up to 17%) opens up relatively coarse pores into which all three gases readily penetrate. The surface thus developed is sufficient to adsorb carbon dioxide largely but oxygen and hydrogen only in negligible amounts. When more water is removed (up to 50%), some additional coarse pores are produced into which carbon dioxide can enter, but the chief effect is to open up a great number of smaller pores into which only oxygen and hydrogen can enter. The resultant inner surface is sufficiently large to adsorb a significant amount of oxygen but is not large enough to adsorb more than a negligible amount of hydrogen. The removal of still more water (50–95%) not only increases the number of coarser and finer pores and thus increases the adsorption of carbon dioxide and oxygen, but it opens up a multitude of the very finest pores into which hydrogen alone can enter. This finest porosity provides a correspondingly great surface with a consequent considerable adsorption even of hydrogen.

This explanation does not, on first thought, seem to help in understanding the marked specificity exhibited by the chabasite dehydrated to 17 and 50% as compared, for instance, with the adsorption of these gases on active charcoal. The negligible adsorption of oxygen compared with that of carbon dioxide at 17% dehydration (1:60), or of hydrogen compared with that of oxygen, cannot be due to any difficulty in the access of the oxygen or the hydrogen, respectively, to the inner surface of the adsorbent, for the oxygen molecule is smaller than the carbon dioxide molecule and the hydrogen molecule in turn is smaller than the oxygen molecule.

On further thought, however, it is clear that this disparity between the ratio of 60:1 for these partially dehydrated chabasites and of 4:1 for charcoal is due to the marked difference in the nature of the porosity of the two types of adsorbent. Whereas in the former at this degree of dehydration the two gases compared both have ready access to all the porosity, in the latter there is a considerable porosity into which only the smaller and less adsorbable of the two gases can enter. Charcoal therefore appears to be a relatively better adsorbent for the less adsorbable gas than would otherwise be the case.

Stated somewhat differently, it may be said that since the same area of adsorbent surface in these specially dehydrated chabasites is available to both gases, the observed ratio between the amount of each gas adsorbed, though extreme, is nevertheless presumably normal.

Another interesting feature of these curves is the relative location of the point of maximum adsorption as disclosed by the data in Table VI.

TABLE VI

LOCATION OF THE MAXIMA

	Percentages		
	Water removed	residual water	Dehydration
Hydrogen	21.6	0.48	97.8
Oxygen	21.4	.68	96.9
Carbon dioxide	20.5	1.58	92.9

The maxima for hydrogen and oxygen are displaced slightly in the direction of more complete dehydration, the maximum for hydrogen being displaced somewhat farther than that for oxygen. These maxima clearly represent the resultant of two opposing effects of the dehydration, namely, the continuing exposure of additional inner surface which increases, and the accelerating collapse of the crystal structure which decreases the adsorption. If the second porosity to be developed is finer than the first and impenetrable by carbon dioxide while the third porosity is still finer and impenetrable by oxygen and if these porosities are correspondingly more extensive, it would be expected that with oxygen and even more with hydrogen the effect of the increase in porosity and inner surface would prevail over the progressive collapse of the crystal lattice to higher degrees of dehydration than in the case with carbon dioxide. This displacement then of the maxima is in full accord with the inference drawn from the other parts of the curves.

A final point of interest with regard to these curves is the very considerable volumes of gases adsorbed at the maxima as compared, for instance, with corresponding volumes for charcoal. Thus the most highly activated coconut charcoal adsorbs at 0° and under atmospheric pressure about 1.5 cc. H_2, 20 cc. O_2 and 87 cc. CO_2, while as can be seen from the above curves, dehydrated chabasite at the several maxima adsorbs, respectively, 2.7 cc. H_2, 27 cc. O_2 and 130 cc. CO_2.

Summary

Chabasite shows a maximum adsorption of hydrogen, oxygen and carbon dioxide at 0°, when 97.8, 96.9 and 92.9%, respectively, of its original water has been removed at suitable temperatures. It shows a similar maximum adsorp-

tion of carbon dioxide at the same percentage dehydration at temperatures of 34.5, 61.2 and 100°. This behavior is explained as due to the collapse of the crystal skeleton when the last fractions of the water are removed.

Slightly dehydrated chabasite exhibits a pronounced specificity of adsorption toward hydrogen, oxygen and carbon dioxide. This behavior is explained on the assumption of several limiting pore sizes and of differing extents of the corresponding inner surfaces.

CAMBRIDGE, MASS. RECEIVED AUGUST 19, 1936

NOTES

The Ethyl Esters of Triiodophenoxyacetic Acids and Potassium Triiodophenoxyacetate

BY T. C. DANIELS AND R. E. LYONS

Several hitherto undescribed triiodophenoxy substitution products of ethyl acetate have been prepared because of their possible opacity to x-rays. The procedure followed was similar to that used by Hewett, Johnson and Pope[1] in preparing tribromophenoxyacetic esters. A mixture of 0.05 mole of triiodophenol, with equivalent quantities of sodium and of ethyl mono-, di- or trichloroacetate, dissolved in 50 cc. of absolute alcohol, was heated on a water-bath for two, three and one-half, or seven hours, respectively, and then poured into 250 cc. of cold water. The monophenoxy derivative, after two recrystallizations from alcohol, was obtained in 40% yield as colorless silky crystals; the diphenoxy, after two recrystallizations from chloroform (in which iodine was liberated slowly) as colorless needles. Attempts to secure the triphenoxy derivative in crystalline form were unavailing, only a yellow, amorphous mass being obtained.

The mono-substituted ester was hydrolyzed incompletely by heating with 30% aqueous potassium hydroxide for several hours. The reaction mixture was poured into water, filtered and the free acid precipitated by dilute hydrochloric acid. Saponification of the di- and tri-substituted esters does not occur under similar conditions.

TABLE I

Phenoxyacetate	M. p., °C.	Formula	Iodine, % Calcd.	Iodine, % Found
Ethyl triiodo-	128.5	$C_{10}H_9O_3I_3$	68.27	67.98
Ethyl ditri-iodo-	160.0	$C_{10}H_{10}O_4I_6$	74.02	73.77
Ethyl tri-tri-iodo-	208–211[a]	$C_{22}H_{11}O_5I_9$	76.23	76.06
Potassium triiodo-	211 (free acid)	$C_8H_4O_3I_3K$	67.07	66.63

[a] Decomposition point.

INDIANA UNIVERSITY
BLOOMINGTON, INDIANA RECEIVED OCTOBER 12, 1936

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[1] Hewett, Johnson and Pope, *J. Chem. Soc.*, **103**, 1630 (1913).

The Effect of Helium on the Kinetics of the Thermal Decomposition of Acetaldehyde

BY C. J. M. FLETCHER

The extent to which organic molecules decompose by way of a free radical and chain mechanism, or by a simple rearrangement, has been a matter of considerable debate. Although there is an increasing body of experimental evidence which indicates that free radicals and chain processes do exist in the decomposition of such molecules, there is still the alternative that molecular rearrangement can compete with the chain mechanism often to its virtual exclusion. Acetaldehyde is a substance for which a chain mechanism has been proposed,[1] and it has been suggested that the kinetics of its chain decomposition in the presence of free radicals produced either photochemically,[2] or by the thermal decomposition of azomethane,[3] support such a mechanism. However, the concentration of free radicals present,[4] the influence of small amounts of nitric oxide,[5] and the catalysis of acetaldehyde by diethyl ether[6] do not support this hypothesis.

[1] F. O. Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

[2] Leermakers, *ibid.*, **56**, 1537 (1934).

[3] Allen and Sickman, *ibid.*, **56**, 2031 (1934).

[4] Patet, *Z. physik. Chem.*, **B32**, 294 (1936).

[5] Staveley and Hinshelwood, *J. Chem. Soc.*, 812 (1936).

[6] Fletcher and Rollefson, THIS JOURNAL, **58**, 2129 (1936).

The effect of inert gases on the rate of reaction also indicates that the decomposition does not follow the chain mechanism:

$$\begin{array}{rlll} CH_3CHO \longrightarrow CH_3 + CHO & k_1 & E_1 & (1) \\ CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO & k_2 & E_2 & (2) \\ CH_3.CO \longrightarrow CH_3 + CO & k_3 & E_3 & (3) \\ 2CH_3 \longrightarrow C_2H_6 & k_4 & E_4 & (4) \\ 2CH_3 + M \longrightarrow C_2H_6 + M & k_5 & E_5 & (5) \end{array}$$

but rather the direct rearrangement

$$CH_3CHO \longrightarrow CH_4 + CO \quad k_6 \quad E_6 \quad (6)$$

for whereas at temperatures above 440°, the recombination of methyl radicals is mainly a homogeneous reaction which takes place partially at ternary collisions so that the rate of the chain reaction is retarded by helium,[7] the thermal decomposition of acetaldehyde itself is accelerated by nitrogen,[8] and by helium (Table I).

TABLE I

TEMPERATURE 552°

$p_{Acet.}$, mm.	p_{He}, mm.	$t_{1/3}$, sec.	$t_{1/2}/t_{1/3}$	Increase in $1/t_{1/3}$, %
93.9	429	148	1.97	11
82.0	375	160	1.95	10
96.4	...	163	1.94	..
83.0	...	175	1.93	..

The last column of Table I gives the increase in rate (as determined from values of the time taken for the pressure to increase by one-third of the initial pressure of acetaldehyde) in the presence of helium compared to the rate for the same initial pressure of pure acetaldehyde.

The results with helium were obtained with the same experimental procedure as that for which it was found that the rate of the chain decomposition in the presence of ethylene oxide was retarded by about 10% at 441° for a 2:1 helium ratio.[7] As the heterogeneous recombination of methyl radicals decreases with temperature, the acceleration given in Table I cannot be accounted for by the inert gas preventing the diffusion of radicals to the walls. Neither can it be explained on the chain mechanism by an increase in the rate of production of methyl radicals such as might occur if reaction 1 were second order; for the initial rate of the chain mechanism is

$$-(dp/dt) = p^{(n/2)+1} k_2 \sqrt{k_1/[k_4 + k_5\,(M)]} \quad (1)$$

where n is the order of reaction 1, so that to explain the observed order of approximately 1.5, Reaction 1 has to be first order.

As the chain mechanism competes so ineffectively with the direct rearrangement, it may be assumed that its over-all energy of activation, $E_{ald.}$, is considerably higher. If the variation with temperature of the recombination of free radicals at ternary collisions can be neglected, then, from equation 1, $E_{ald.} = E_2 + {}^1/_2(E_1 - E_4)$. Values of $(E_2 - {}^1/_2E_4)$ may be obtained from the decompositions induced by azomethane and ethylene oxide; from the results with azomethane, Allen and Sickman[3] derived the value 13,800 cal. on the assumption, which is probably justified,[9] that all the azomethane decomposes to give free radicals. With ethylene oxide the fraction of molecules which gives free radicals is approximately 14%;[7] if the temperature independent factors are the same for both types of decomposition, such a proportion would be obtained if the energies of activation differ by about 3000 cal., *i. e.*, that for the production of free radicals would be approximately 56,000 cal. Making a calculation similar to that for azomethane, $(E_2 - {}^1/_2E_4)$ is therefore 13,500 cal., in good agreement with the value from azomethane. Thus $E_{ald.} \simeq {}^1/_2E_1 + 13{,}700$ cal., so that for the chain mechanism to have a larger energy of activation than that actually observed (50,000 cal.[10] or 45,700 cal.[11]), the energy of activation (E_1) for the breaking of the C–C bond must be closer to 80,000 cal. than to the value of 70,000 cal. assumed by Rice and Herzfeld.

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[7] Fletcher and Rollefson, THIS JOURNAL, **58**, 2135 (1936).

[8] Hinshelwood and Askey, *Proc. Roy. Soc.* (London), **A128**, 91 (1930).

[9] O. K. Rice and Sickman, *J. Chem. Phys.*, **4**, 242 (1936).

[10] Fletcher and Hinshelwood, *Proc. Roy. Soc.* (London), **A141**, 41 (1933).

[11] Letort, *Compt. rend.*, **199**, 1617 (1934).

THE CHEMICAL LABORATORY
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RECEIVED SEPTEMBER 15, 1936

The Standard Electrode Potential of Silver

BY J. J. LINGANE AND W. D. LARSON

The value for the standard potential of the silver electrode, $Ag \mid Ag^+ (a = 1)$, given by Lewis and Randall[1] is −0.7995 v., whereas the value given in the "International Critical Tables"[2] is −0.7978 v. Both of these values apparently are based on the measurements of Noyes and Brann[3] on cells involving liquid junction potentials. Evaluation of the standard potential of the silver electrode from these measurements

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[1] Lewis and Randall, "Thermodynamics," McGraw Hill Book Co., Inc., New York, 1923, p. 414.

[2] "International Critical Tables," Vol. VI, p. 333.

[3] Noyes and Brann, THIS JOURNAL, **34**, 1016 (1912).

necessitates the use of the standard potential of the calomel electrode, and the difference between the two values given above apparently is due to the revision of the accepted value of the standard potential of the calomel electrode.

We wish to call attention to a simple unambiguous method by means of which the standard electrode potential of silver may be calculated from the standard potential of the silver–silver chloride electrode, $Ag\,|\,AgCl(s),\ Cl^-\ (a = 1)$, and the activity product of silver chloride. The relation between the standard potential of the silver–silver chloride electrode, E^0_{AgCl}, the activity product of silver chloride, K, and the standard potential of the silver electrode $E^0_{Ag,\,Ag^+}$, is given by the thermodynamic equation

$$E^0_{AgCl} = E^0_{Ag,\,Ag^+} - (RT/F)\ln K \qquad (1)$$

The value of E^0_{AgCl} has been determined by several investigators[4] from measurements of the cell $H_2\,|\,HCl,\ AgCl(s)\,|\,Ag$. A critical examination of the data of these authors has led us to believe that the measurements of Carmody, who used quartz cells and was the only one of these investigators who was able to obtain very concordant results in extremely dilute solutions, are the most reliable. By graphical extrapolation Carmody obtained the value −0.2223 v. for E^0_{AgCl}. We have recalculated the value of E^0_{AgCl} from Carmody's data for the three most dilute solutions (0.0007280, 0.0005518 and 0.0003288 *m*) by application of the limiting law of Debye and Hückel. This leads to the equation

$$E^0_{AgCl} = -E_{cell} - \frac{RT}{F}\ln m^2 + 2 \times 0.5045\,\frac{RT}{F}\,S^{1/2} \qquad (2)$$

in which S is the total ionic strength of the solution corrected for the solubility of silver chloride. This equation leads to the same value of E^0_{AgCl} for each of the three most dilute solutions, namely, −0.2222 v. at 25°. We consider this to be the most reliable value of E^0_{AgCl}, and it is in excellent agreement with the value −0.2221 v. estimated by Randall and Young.[5]

The activity product of silver chloride has been determined recently by Brown and MacInnes[6] by a highly precise electrometric titration method. They found a value of K equal to 1.721×10^{-10} at 25°, and this result is apparently reliable to a few tenths of one per cent.

By substituting these values into equation (1) we obtain for the standard electrode potential of silver at 25°

$$E^0_{Ag,\,Ag^+} = -0.2222 + 0.05913\log(1.721 \times 10^{-10}) = -0.7996\text{ v.}$$

The close agreement between this result and the value given by Lewis and Randall is remarkable in view of the fact that the value calculated above is based on entirely independent measurements by different investigators. This result therefore constitutes strong evidence in favor of accepting the value −0.7996 v. as the standard potential of the silver electrode, rather than the value −0.7978 v. given in the "International Critical Tables."

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RECEIVED AUGUST 1, 1936

Beta-Octyl Thiocyanate

BY W. GORDON ROSE AND H. L. HALLER

In the course of studies on the relative toxicity to insects of optical isomers of secondary alkyl thiocyanates, the results of which will be reported elsewhere, occasion has been had to prepare the dextro and levo forms of beta-octyl thiocyanate (alpha-methylheptyl thiocyanate). By the action of phosphorus tribromide (138.0 g.) on dextro-beta-octanol (66.0 g.), $[\alpha]^{20}D$ +9.70° homogeneous, $[\alpha]^{20}D$ +11.88° in ethanol ($c = 5.67$), there was obtained 81.3 g. of beta-octyl bromide, $[\alpha]^{20}D$ −32.15° homogeneous, $[\alpha]^{20}D$ −45.30° in ethanol ($c = 5.99$). The latter (81.0 g.), on being refluxed in 100 cc. of methanol with 45.0 g. of potassium thiocyanate, yielded 51.7 g. of beta-octyl thiocyanate, b. p. 98.5–99.0° at 4 mm., d^{20} 0.919, $n^{20}D$ 1.4635, MR_D(obsd.) = 51.30, MR_D(calcd.) = 51.09, $[\alpha]^{20}D$ +51.7° homogeneous, $[\alpha]^{20}D$ +59.1° in ethanol ($c = 5.06$). *Anal.* Calcd. for $C_9H_{17}NS$: C, 63.08; H, 10.01; N, 8.18. Found: C, 63.14, 63.17; H, 10.02, 10.08; N, 8.44, 8.32.

Beta-octyl thiocyanate has been obtained previously by the interaction of beta-octyl-*p*-toluenesulfonate and potassium thiocyanate.[1] The beta-octyl sulfonate was obtained on oxidation of the corresponding sulfinate, which in turn

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[4] (a) Noyes and Ellis, THIS JOURNAL, **39**, 2532 (1917); (b) Linhart, *ibid.*, **41**, 1175 (1919); (c) Scatchard, *ibid.*, **47**, 708 (1925); (d) Nonhebel, *Phil. Mag.*, [7] **2**, 1085 (1926); (e) Carmody, THIS JOURNAL, **54**, 188 (1932).

[5] Randall and Young, *ibid.*, **50**, 989 (1928).

[6] Brown and MacInnes, *ibid.*, **57**, 459 (1935).

[1] Kenyon, Phillips and Pittman, *J. Chem. Soc.*, 1081 (1935).

was obtained from beta-octanol and *p*-toluenesulfinyl chloride. Starting with a dextro-beta-octanol, $[\alpha]^{20}_{5893}$ +9.48° homogeneous, $[\alpha]^{20}_{4359}$ +22.40° in ethanol (c = 4.992), Kenyon and his co-workers obtained, through this series of reactions, a levo-beta-octyl thiocyanate, $[\alpha]^{20}_{5893}$ −71.41° homogeneous, $[\alpha]^{20}_{5893}$ −64.68° in ethanol (c = 5.010), $n^{17°}_{D}$ 1.4651, $d^{20°}_{4}$ 0.795.

In the series of reactions used by the writers a dextrorotatory octanol yielded a dextrorotatory thiocyanate, while in the procedure used by Kenyon a levo-octyl thiocyanate was obtained from a dextrorotatory octanol. Since an asymmetric carbon atom is involved in both series of reactions, the difference in the results may be explained by the occurrence or absence of the Walden inversion.

The refractive index of the thiocyanate prepared by the writers agrees with that reported by Kenyon and his co-workers, indicating that the compounds are of the same degree of chemical purity. The density of the writers' compound, however, was 0.919, whereas Kenyon reported 0.795.

The molecular refraction of beta-octyl thiocyanate, calculated from the revised values of Eisenlohr for the atomic refractions[2] and employing 13.21 for the thiocyanate radical, is 51.09. The observed molecular refraction for the writers' compound, obtained with the Lorentz–Lorenz formula, is 51.31, whereas with the values for refractive index and density reported by Kenyon 59.31 is obtained.

These results indicate that the value for the density found by the writers is closer to the true value than is that found by Kenyon, *et al.* Since the specific refraction (homogeneous) is dependent on the density, this value is also subject to revision.

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(2) Landolt–Börnstein, "Physikalisch-chemische Tabellen," Aufl. 5, Bd. 2, Julius Springer, Berlin, 1923, p. 985.

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A Stopcock Substitute

By Walter C. Schumb and H. Irving Crane

In the course of a certain investigation in this Laboratory it was found necessary to devise a means of interrupting the flow of a benzene solution. A stopcock could not be used, since the ordinary organic stopcock lubricants are readily attacked by benzene, and the reactivity of the solute toward moisture or reactive hydrogen made the use of certain other types of lubricant, such as phosphoric acid, out of the question. The device shown in the diagram is an adaptation of Stock's stopcock for gases [*Ber.*, **58,** 2058 (1925)].

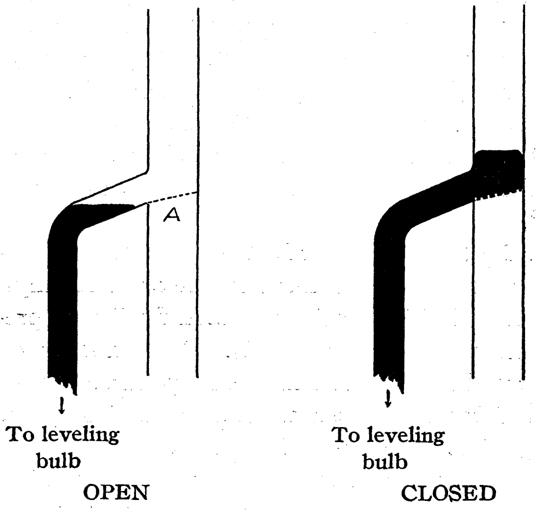

Fig. 1.

The device, constructed of Pyrex glass, consists essentially of a fritted glass plate (A) (80 mesh), so placed that mercury can be flowed over it at will by means of a suitable leveling bulb.

Obviously the device is applicable to any liquid of not too high viscosity, which does not attack mercury. The high surface tension of mercury prevents any of it passing through the fritted plate.

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The Rearrangement of Alkyl Aryl Thioethers

By Wendell H. Taylor

In a recent study of the reaction between aromatic mercaptals and formaldehyde, the author[1] postulated a rearrangement of formaldehyde diaryl mercaptals involving the migration of the —CH_2 group from sulfur to the benzene nucleus, with regeneration of the —SH groups. Such a change would be essentially similar to the rearrangement of the alkyl aryl thioethers and it was therefore of interest to investigate such thioether rearrangements under conditions comparable to those under which the analogous oxygen com-

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(1) W. H. Taylor, This Journal, **57,** 1065 (1935).

pounds isomerize, and comparable also to the conditions of the above-mentioned mercaptal reaction.

The rearrangement of two allyl aryl thioethers has previously been reported,[2] both, however, involving "pyrolysis" of the compounds at their rather high boiling points (215–264°) in the absence of solvents or rearranging agents. The present communication reports briefly on the rearrangement of allyl *p*-tolyl sulfide, *s*-butyl *p*-tolyl sulfide and *s*-butyl phenyl sulfide in the presence of zinc chloride–acetic acid reagent which has been found[3] a satisfactory rearranging medium for the oxygen ethers at temperatures as low as 112°.

In the three cases studied the thioether underwent partial rearrangement to one or more alkyl-substituted thiophenols, obtained finally by precipitation as lead mercaptides. Simultaneously a scission of the thioether molecule appeared to take place, fairly large amounts of allene and butylene being evolved. This is in sharp contrast to the non-production of unsaturated gases reported[4] in thioether and oxygen ether pyrolysis, but corresponds exactly to the observations of Sprung and Wallis. The presence of thiophenol and *p*-thiocresol as the other scission products was indicated by the high percentage of lead found by analysis of the total lead mercaptide precipitate, and by interpolation an approximate ratio of rearrangement product to decomposition product was obtained. Although a part of the thiophenols set free in the reaction suffered oxidation to disulfides and could not be weighed as lead mercaptides, thereby rendering an accurate estimate of the extent of the rearrangement impossible, the isomerization of $\text{—CH}_2\text{—S—R}$ to $\text{R(CH}_2\text{—)SH}$ was definitely established.

For assistance with a part of the experimental work the author wishes to thank Messrs. W. A. Bastedo, Jr., and R. W. Storer.

Experimental

The thioethers were prepared in good yields by heating the appropriate alkyl bromide for twenty-four hours at 110–120° with the sodium salt of thiophenol or *p*-thiocresol. Allyl *p*-tolyl sulfide had the properties described by Hurd; *s*-butyl phenyl sulfide, b. p. 104–105° (25 mm.); *s*-butyl *p*-tolyl sulfide b. p. 135–138° (22 mm.). All were colorless liquids of not unpleasant odor, giving no reaction with alcoholic lead acetate solution. The zinc chloride–acetic acid reagent contained 10 g. of fused zinc chloride in 26 cc. of solution.

In a typical experiment 20–30 cc. of the zinc chloride solution was heated for three hours at 135–150° in a flask provided with a dropping funnel and connected *via* a reflux condenser to a gas buret. After the air thus had been displaced partially, 2.5–10 g. of the thioether was run in and the heating continued for twenty-four hours more, by which time the evolution of gas had practically ceased. By passing steam into the reaction flask all remaining gas was easily driven over into the buret, the contents of which were tested from time to time during the reaction period. The heavy, brownish product which remained in the flask was extracted with ether, and the portion of this which then dissolved in warm 95% alcohol was treated immediately with a saturated alcoholic solution of lead acetate. The precipitate of lead mercaptides was filtered off, washed, dried and analyzed for lead by the usual method of gentle ignition followed by treatment with nitric and sulfuric acids to give lead sulfate.

In the rearrangement of allyl *p*-tolyl sulfide, the volume of gaseous product having the properties of allene—odor, inflammability with luminous flame, reaction with bromine water and with mercuric chloride, inertness toward ammoniacal silver nitrate—amounted to 30–60 cc. per gram of thioether originally taken, the yield decreasing as the reaction temperature was raised from 135 to 150°. The orange lead mercaptide precipitate, presumably a mixture of the lead salts of *p*-thiocresol and 2-allyl-4-methyl thiophenol, gave on analysis 40.2–40.8% Pb. Calcd. for $Pb(SC_6H_4CH_3)_2$: Pb, 43.4; calcd. for $Pb(S\cdot C_6H_3\cdot C_3H_5\cdot CH_3)_2$: Pb, 38.9. The value obtained by analysis would correspond to a mixed mercaptide precipitate containing from 57.5–71% of the lead salt of 2-allyl-4-methyl thiophenol.

In the case of the butyl aryl ethers similar results were obtained. The gaseous product had the properties of butylene but was produced in smaller quantity—from 25–37 cc./g. of the butyl phenyl sulfide, and from 10–15 cc./g. of the butyl *p*-tolyl sulfide. Only in the case of the former was a quantitative analysis of the mercaptide precipitate made. The heavy yellow powder was found to contain 41.8% Pb. Calcd. for $Pb(SC_6H_5)_2$: Pb, 48.7; calcd. for $Pb(SC_6H_4C_4H_9)_2$: Pb, 38.5. This would correspond to a mixture of the two mercaptides containing 69% of the lead salt of *s*-butyl thiophenol.

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[2] Hurd and Greengard, THIS JOURNAL, **52**, 3356 (1930).

[3] Sprung and Wallis, *ibid.*, **56**, 1715 (1934).

[4] Hurd and Webb, *ibid.*, **58**, 943 (1936).

The Spinning Top Ultracentrifuge and the Sedimentation of Small Molecules

BY J. W. WILLIAMS AND C. C. WATSON

In recent articles McBain and O'Sullivan[1] have discussed their development of the air-driven spinning top as transparent ultracentrifuge. As we read these reports we cannot escape the feeling that a certain pronouncement in them requires further analysis. In the "Communication" a

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[1] McBain and O'Sullivan, THIS JOURNAL, **57**, 780, 2631 (1935).

"fortunate accident" is mentioned which made it possible "to observe the sedimentation velocity of a boundary in aqueous solution of mercuric chloride: $s = 0.891 \times 10^{-13}$ cm./sec./dyne; theory $= 0.890 \times 10^{-13}$." Later, in the definitive article, McBain and O'Sullivan make the claim that they have recorded for the first time the sedimentation velocity of an ordinary molecule (mercuric chloride), this as a footnote to the statements "For sedimentation equilibrium of ordinary molecules, powers ranging from 100,000 to 1,000,000 times gravity are essential. Still higher powers will be required for observing their sedimentation velocity."

It has seemed worth while to examine this extremely important claim, which is made more striking because of the remarkable agreement between theory and observation (about 0.1%) which is reported. Such examination is extremely difficult because definite information is lacking as regards the speed at which the rotor was turning, how the position of the boundary was observed and located at the ends of the several intervals of time during the centrifuging, how the distances from the center of the cell were measured, how the absence of convection effects was proved, what was the concentration of the solution and the temperature of the cell used in the experiment, how long the centrifuging was continued, etc. However, by making calculations which involve the dimensions of the apparatus, the rotor speeds, and strengths of the materials of construction mentioned in other parts of the longer article, it is concluded that their sedimentation power was not over 350,000 times gravity. For a molecule of weight and density of mercuric chloride in water at ordinary temperatures, one may calculate that the actual sedimentation rate with such centrifugal force would be of the order of 1 mm. per hour.

With the apparatus as described and with the assumption of technique and evaluation of the data according to the methods developed by Svedberg, it is highly improbable that such a rate could be measured with the precision claimed. Also, a serious difficulty is that the back diffusion would so blur the boundary that the distance of travel of the latter in any ordinary interval of time would be hard to estimate. Experiments of Pedersen[2] made in the Svedberg laboratory may be cited in this connection. Working with aqueous solutions of mercuric chloride and at 350,000 times gravity, this investigator was able to establish equilibrium in a cell with liquid column about 5 mm. in height after something like seven hours of centrifuging. However, no mention is made by Pedersen of the observations of the velocity of the sedimentation.

Actually, in view of the very careful Pedersen experiments and several statements contained in the article in question, there may be some doubt that a true sedimentation velocity was observed. In addition to the two sentences quoted above, McBain and O'Sullivan define an ultracentrifuge as being "any centrifuge of low or high power in which convection does not occur, and in which it is possible to measure any redistribution of the contents." Again in referring to the behavior of a rotor which is described as having several advantages (speed, uniformity of temperature, strength) over the one in which the experiment in question took place, there is the statement "With the driving air arbitrarily thermostated to within ±0.02° and the room temperature controlled, the same rotor will sometimes sediment molecules as small as purified egg albumin (molecular weight about 35,000)."

It is a matter of some surprise to find the theoretical sedimentation velocity constant for mercuric chloride molecules in aqueous medium expressed to three significant figures when no temperature is specified. The value of the constant varies considerably with temperature because the viscosity of the solvent is involved. The variation amounts to approximately 2% per degree in aqueous solution at ordinary centrifuge temperatures. For mercuric chloride the theorectical sedimentation constant expressed to two significant figures is 0.73 at 20°, 0.82 at 25° and 0.89 at 30°. The temperature of the cell during the experiment was not determined with precision.

Since the records of the experiment and the calculation for the corresponding theoretical specific sedimentation velocity for mercuric chloride are so incomplete, we are impelled to suggest that a further account of the work be presented before it can be given serious consideration as the first measurement of the sedimentation velocity of an ordinary molecule.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

RECEIVED MARCH 31, 1936

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[2] Pedersen, *Z. physik. Chem.*, **A170**, 53 (1934).

Addendum to the Note of Williams and Watson

By James W. McBain

I do not consider that the note by Williams and Watson calls for any detailed comment. The two sentences published by McBain and O'Sullivan, one sentence in a preliminary communication and the other single sentence in a footnote in a paper of eleven printed pages entitled "The Development of the Air-Driven Spinning Top as a Transparent Ultracentrifuge," still appear to be ample notice of the physical phenomenon that was observed, on November 15, 1934, with the old circular cell whose use was discontinued that year. The cell contained pure water and a crystal of mercuric chloride. Sufficient of the latter dissolved in the lower portion of the cell and then through an accident of convection currents, the absorbing material ($HgCl_2$) was sedimented downward again with a fairly sharp boundary as shown by the photographs and microphotometer photographs, moving 0.102 cm. in 8400 seconds at 108,600 r. p. m. with an average radius of 1.054 cm., giving an observed $S = MD \times (1 - V)/RT = 0.890 \times 10^{-13}$, which, as a mere scientific curiosity, agreed with the value predicted. The precise agreement is of course fortuitous and should not have been expressed to three significant figures, as is obvious to anyone who has any knowledge of an ultracentrifuge.

Professor Williams has acknowledged Dr. O'Sullivan's statement that the sedimentation force was 138,000 times gravity, but Williams and Watson prefer to state "it is concluded that it was not over 350,000 times gravity."

McBain and O'Sullivan stated that this result was an accident and that in the ordinary course, where convection does not occur, a higher order of magnitude of centrifugal force than that in any existing ultracentrifuge anywhere today would be required to obtain sedimentation velocities of such small molecules regularly.

It is entirely a matter of individual opinion as to whether any significance whatsoever attaches to this photographed and microphotometered observation, and Williams and Watson are convinced on the basis of their experience that none does. We still think that it did offer an actual semi-quantitative measurement.

As regards the fourth paragraph of the note of Williams and Watson devoted to discussing the state of development of our air-driven ultracentrifuge as described at the April, 1935, meeting of the Society, it is only necessary to say that our statements were carefully made and stand accordingly as referring to the now superseded models as developed at that time; and that the appreciable modifications and the very simple temperature control in the later model referred to in the footnote by H. J. Fouts inserted at the end of that paper in the final proofs have resulted in uniform success in sedimenting smaller protein molecules such as carbon monoxide hemoglobin—as was, for example, demonstrated at the Western Protein Conference, June 6, 1936. There appears now to be no reason why any sedimentation velocity or equilibrium observable in the Svedberg ultracentrifuges, or the equally good air-driven models now developed, for example, at the Rockefeller Institute for Medical Research [see for example *J. Exptl. Medicine*, **64**, 39 (1936)], or the model supplied by the Sharples Specialty Company of Philadelphia should not also be capable of quantitative study in the McBain–O'Sullivan–Fouts transparent ultracentrifuge. All parts of this cell are easily kept at any desired *constant* measured temperature within 0.02°. All forms of the air-driven ultracentrifuge appear to be in process of still further rapid improvement.

Stanford University
California
Received July 21, 1936

Chemical Nature of δ-Follicular Hormone

By O. Wintersteiner, E. Schwenk, H. Hirschmann and B. Whitman

In 1932 Schwenk and Hildebrandt[1] reported the isolation from the urine of pregnant mares of a new oestrogenic substance, isomeric with oestrone (theelin), which they designated δ-follicular hormone. Wintersteiner, Schwenk and Whitman[2] subsequently showed that this substance (m. p. 209°) was not a ketone, but a dihydroxy compound. Recently larger amounts of crude phenolic fractions from mares' urine were separated in the laboratories of the Schering Corporation into ketones and alcohols. The alcoholic portion was worked up for δ-hormone at Columbia University. Our present experience with material of this type makes it appear doubtful whether the earlier preparations represented a chemical individual,

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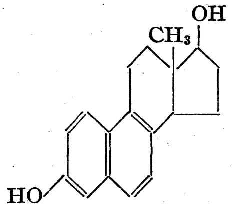
(1) Schwenk and Hildebrandt, *Naturw.*, **20**, 658 (1932).

(2) Wintersteiner, Schwenk and Whitman, *Proc. Soc. Exptl. Biol. Med.*, **32**, 1087 (1935).

a possibility discussed in the first publication. Fractional crystallization yielded an apparently homogeneous product which did not change its melting point (226° corr.) on repeated recrystallization from various solvents. However, the analytical composition and specific rotation varied with different preparations ($[\alpha]_D$ +31 to +37°). The preponderant constituent of these mixtures appears to be a molecular compound consisting of two components. Only one component forms a picrate, and this property as well as its stronger acidic character enabled us to isolate this component in pure form.

The new compound melts at 215–217° and has the composition $C_{18}H_{20}O_2$ (calcd.: C, 80.55; H, 7.52; found: C, 80.53, 80.47; H, 7.61, 7.52); $[\alpha]^{25}_D$ −4.7° (0.7% in dioxane). A di-*p*-nitrobenzoate (m. p. 250–252° corr.) and a monobenzoate (m. p. 203–205° corr.) have been prepared. The compound gives the color reactions originally attributed to the δ-follicular hormone.[1,3] Its absorption spectrum coincides with that of equilenin. Our measurements on equilenin reveal two new bands in addition to those found by Dirscherl and Hanusch,[4] namely, at 2310 Å., log ε 4.78, and at 2920 Å., log ε 3.58.

The monobenzoate was oxidized with chromic acid to a ketone which gave no depression of its melting point (223° corr.) when mixed with equilenin benzoate. The dihydroxy compound (m. p. 217°) is therefore dihydroequilenin.



Contrary to the rule, established for other oestrogenic compounds, that reduction of the C_{17} keto group to carbinol enhances the physiological activity, the dihydroequilenin isolated from urine possesses only about one-half of the potency of equilenin. On the other hand, David[5] found that the oily product which he obtained by reduction of equilenin with sodium was about three times as potent as equilenin. The possibility that our diol differs from the potent oestrogenic diols, obtained by reduction, in the configuration of the C_{17} hydroxyl group will be investigated. Whether the high potency originally reported for the δ-hormone resides in the other, as yet unidentified, component of the molecular compound (m. p. 226°) or in other diols present in the impure preparations, remains to be determined.

We wish to express our sincere thanks to Dr. A. Girard of Paris for sending us samples of equilenin and its benzoate for comparison.

DEPARTMENT OF BIOCHEMISTRY
COLLEGE OF PHYSICIANS AND SURGEONS
COLUMBIA UNIVERSITY.
RESEARCH LABORATORIES
SCHERING CORPORATION
BLOOMFIELD, NEW JERSEY
RECEIVED NOVEMBER 12, 1936

[3] Schwenk and Hildebrandt, *Biochem. Z.*, **259**, 240 (1933).

[4] Dirscherl and Hanusch, *Z. physiol. Chem.*, **233**, 13 (1935).

[5] David, *Acta brevia Neerl.*, **4**, 63 (1934).

Phenylmercuric Fluoride

BY GEORGE F. WRIGHT[1]

The recent discovery[2] of mercuric fluoride as a new fluorinating agent recalls the investigation in this Laboratory of phenylmercuric fluoride. This preparation was incidental in the study of the relative strengths of C–Hg and Hg–X bonds in organomercuric halides. According to our knowledge of organomercurials the tendency toward the dissociation reaction $2RHgX \rightleftarrows R_2Hg + HgX_2$ decreases in the order HgI > HgBr > HgCl. It was hoped that the introduction of fluorine would so stabilize the Hg–X bond as to favor the primary reaction $RHgX \longrightarrow R— + HgX$ which, it is considered, accounts for the interconversion possible with compounds like furyl and thienylmercuric halides containing more reactive, though unfortunately less stable, radicals.[3] The compound did not, however, fulfil these expectations. Instead of reacting with acetyl chloride to give acetophenone, acetyl fluoride was formed as easily as from mercuric fluoride.[2] Likewise when the compound was pyrolyzed at a temperature lower than that required to decompose diphenylmercury, only the latter substance, and no diphenyl, was produced.

In connection with the assertion of Henne and Midgley that pure mercuric fluoride cannot be prepared by treating mercuric oxide with aqueous hydrofluoric acid it may be significant that treatment of such a solution with phenyldiazonium fluoride, and subsequent treatment with copper, produced no trace of phenylmercuric fluoride.

[1] National Research Fellow in Chemistry.

[2] Henne and Midgley, THIS JOURNAL, **58**, 884 (1936).

[3] Steinkopf and Bauermeister, *Ann.*, **403**, 50 (1914); Gilman and Wright, THIS JOURNAL, **55**, 3302 (1933).

I wish to thank Professor E. P. Kohler for suggestions offered during this investigation.

Experimental

Phenylmercuric Fluoride.—A solution of 40.6 g. (0.17 mole) of freshly precipitated silver oxide and 14 g. (0.35 mole) of 50% hydrofluoric acid in 400 cc. of water was shaken for five hours with 78 g. (0.25 mole) of phenylmercuric chloride, previously moistened with ethanol. The solid was filtered off and extracted with 400 cc. of boiling ethanol. After a small amount of precipitation by cooling, the solution was decanted and concentrated *in vacuo.* The residue was extracted with boiling ethanol and filtered. The cooled solution yielded 32 g. of phenylmercuric fluoride, m. p. 170°, or 43% of the theoretical. The chlorine-free compound was soluble in hot alcohol, hot xylene and hot chloroform and was crystallized from the latter solvent for analysis (m. p. 171°). It was insoluble in carbon tetrachloride, ethyl acetate, ether and hot acetone. The extracted silver chloride from the reaction mixture contained much unreacted phenylmercuric chloride; no doubt the yield can be increased by a longer period of reaction.

Anal. Calcd. for C_6H_5HgF: C, 24.27; H, 1.70. Found: C, 24.25; H, 1.99.

Reaction with Acetyl Chloride.—When 2.96 g. (0.01 mole) of phenylmercuric fluoride was refluxed with 1.57 g. (0.02 mole) of acetyl chloride, the acetyl fluoride was evolved immediately through the reflux condenser. After five hours the reaction was poured into iced sodium carbonate solution. No mercuric oxide precipitated. The solid was filtered off and crystallized from xylene to weigh 2.80 g. and melt at 257°. This 90% yield of phenylmercuric chloride was substantiated by mixed melting point.

Diphenylmercury.—When phenylmercuric fluoride was slowly destructively distilled at 200° under 10 mm. only diphenylmercury, and no diphenyl, could be found in the distillate.

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

RECEIVED SEPTEMBER 14, 1936

COMMUNICATIONS TO THE EDITOR

METAL ION ACTIVATION IN ENZYMATIC CATALYSIS. ARGINASE

Sir:

Recent investigations [Hellerman, Perkins, and Clark, *Proc. Nat. Acad. Sci.*, **19,** 855 (1933); Hellerman and Perkins, *J. Biol. Chem.*, **107,** 241 (1934); Bersin, *Z. physiol. Chem.*, **220,** 209 (1933)] support the idea that reversible chemical actions upon substituent thiol groups of certain enzymes (urease, papain, etc.) may account largely for their reversible inactivations by oxidation and by silver ion, phenylmercuric hydroxide, etc. However, the enzyme, arginase [Hellerman and Perkins, *J. Biol. Chem.*, **112,** 175 (1935)], was found to be little sensitive to phenylmercuric hydroxide, and most readily activated, not by reduction in the usual sense but rather by the use of reduced ions of the transition elements, manganese, cobalt or nickel, as well as ferrous ion, which had been associated previously with arginase activation. This, and other evidence cited, was considered to point strongly to metal coördination as a factor not merely in arginase activation but actually in the functioning of the enzyme itself. For example, dissociable, labile enzyme-substrate intermediates might be constructed by the "binding" to a metal ion of both enzyme and substrate through donor groupings of each. If so, an effective metal ion should alter the activity–*p*H curve of arginase in a characteristic way.

We have now studied the effect of such ions upon the arginase–arginine reaction in buffers of widely varying *p*H values but having approximately constant ionic strength ($\mu = 1$). Activity–*p*H curves constructed from the data clearly show characteristic differences. Liver-arginase action is enhanced greatly by nickelous and especially cobaltous ion from *p*H 5 to 7.7; activation by manganous ion is not significant below *p*H 6.7. The optima for cobaltous, nickelous and manganous ion are, respectively, *p*H 7.5 to 7.7, 6.7 to 7.7 and 10 as compared with the optimum for our arginase, without added metal, 7.7 to 9.0. The variations may be considered in relation to the corresponding stabilities of the coördination complexes of these ions with substituted ammonias. For example, we ascertained (by a potentiometric titration method) that the dissociation constants of the complex ions derived from *d*-arginine with cobaltous, nickelous and manganous ion, respectively, are approximately of the order, 2×10^{-10}, 4×10^{-11} and 1×10^{-6}. Manganous ion apparently cannot appreciably activate arginase in the more acid *p*H range where it coördinates only slightly.

A similar study has also been made with the new catalyst for *d*-arginine hydrolysis, which Hellerman and Perkins found was "elicited," in the presence of cobaltous, nickelous or manganous ion from some constituent of their preparations of jack bean urease. This "urease-metal" effect, in contrast to liver–arginase activity, is negligible below *p*H 7.0; "with Co^{++}" the curve relating activity (ordinate) with *p*H (abscissa) rises sharply from *p*H 7.1 to 7.7, the optimum. This practically proves the non-identity of the two catalysts. Nevertheless, the characteristics of the kinetics of arginine hydrolysis with either enzyme (plus Co^{++}) are similar (pseudounimolecular at *p*H 7.5). Moreover, the striking specificity of liver–arginase is retained in the new catalyst; this was tested with argininic acid, δ-guanidinovaleric acid, etc.

The results will be published in detail in another place.

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY
THE JOHNS HOPKINS UNIVERSITY LESLIE HELLERMAN
BALTIMORE, MARYLAND C. CHESTER STOCK

RECEIVED OCTOBER 23, 1936

AN ANTIRACHITIC SUBSTANCE FROM TUNA LIVER OIL

Sir:

Drummond and Haslewood [*Chem. & Ind.*, **55**, 598 (1936)] report the isolation of an antirachitic substance from tuna liver oil and indicate that their substance may not be identical with that of Brockman [*Z. physiol. Chem.*, **241**, 104 (1936)]. Our own findings may be of interest, particularly since we arrive at essentially the same end product as Brockman by a somewhat different route. We have not used the chromatographic technique which he deems essential.

Starting with an alcohol-soluble fraction from the non-saponifiable of tuna liver oil, the sterols were esterified with phthalic acid, leaving the hydrocarbons behind. This was followed by distribution of the sterol mixture between solvents in the manner described for a number of similar mixtures by various investigators. Removal of cholesterol by digitonin, freezing, treatment with decolorizing carbon and finally formation of the 3,5-dinitrobenzoic ester gave a crystalline product which melted sharply at 128.5°. The alcohol from this showed a narrow absorption band with a peak at 2650 Å. and an extinction coefficient $E^{1\%}_{1\text{cm.}} = 350$ in Normalbenzin (Kahlbaum). The dinitrobenzoic ester showed 4.94% of nitrogen; calcd. 4.83%. The biological activity was 30×10^6 international units per gram. No evidence of any considerable amount of biological activity residing in substances with other absorption peaks was obtained, although in the stages of lesser purity low absorption peaks at both longer (Drummond) and shorter wave lengths were very evident.

We agree with Brockman that the material he identified essentially characterizes the Vitamin D of this type of liver oil. Our slightly higher biological activity as well as our slightly but distinctly narrower absorption band (calculated to the same units as Brockman uses), cause a little hesitation in concluding that either Brockman's D_3 or our material is pure. The difference in absorption is not likely to be a solvent effect (hexane *vs.* Normalbenzin), particularly since the position of the peak is identical. All these findings have as yet no bearing on the question of multiplicity of forms of naturally occurring Vitamin D.

DEPARTMENT OF PATHOLOGY E. J. H. SIMONS
COLLEGE OF PHYSICIANS AND SURGEONS T. F. ZUCKER
COLUMBIA UNIVERSITY

RECEIVED NOVEMBER 14, 1936

NEW BOOKS

Collateral Readings in Organic Chemistry. By L. A. Goldblatt, University of Pittsburgh. Edwards Brothers, Inc., Ann Arbor, Michigan, 1936. iii + 128 pp. 21.5 × 27.5 cm. Price, $1.00.

This book is an attempt, on the part of the author, to place at the disposal of students in Elementary Organic Chemistry, at a nominal expense, articles in the current literature. The articles have been taken from the journals sponsored by the American Chemical Society.

The author states in the preface that he desires to bring to the attention of the student of Elementary Organic Chemistry the existence of a literature in Organic Chemistry. The articles have been carefully chosen. The experiment is an interesting one and the book seems worth while.

Samuel T. Arnold

An Elementary Chemistry. By A. H. B. Bishop, Headmaster of Warwick School, and G. H. Locket, Assistant Master at Harrow School. Oxford University Press. 114 Fifth Ave., New York, N. Y., 1936. 398 pp. 133 figs. 13 × 19 cm. Price, $1.75.

This textbook of elementary chemistry, following the usual English method, presents more material than the ordinary American secondary school book, and rather less than most regular college texts. The topics and presentation in general are well adapted for a course emphasizing either general knowledge or college preparation. The authors have tried to avoid what they believe to be a fault of many texts, by offering more than the customary amount of information on the metallic elements and their metallurgy, and stressing the everyday and industrial uses of the elements and compounds described. The amount of chemical theory in the book has been minimized by careful presentation and judicious elimination, the latter perhaps having been carried too far for the best interests of college preparatory classes. Questions and problems are introduced frequently, many of them taken from various examination papers. One useful feature of the book is the directions for experiments which are inserted in the text at the proper places; many of them being suitable for desk demonstration. The book may well be chosen by instructors giving a thorough high school or brief college course.

Allen D. Bliss

Das Ausblühen der Salze. (The Efflorescence of Salts.) By Dr. Phil. Karl Schultze, Hygienisches Staatsinstitut zu Hamburg. Separate printing, from *Kolloid-Beiheften*, edited by Prof. Dr. Wo. Ostwald, Leipzig. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1936. 99 pp. 36 figs. 15.5 × 23.3 cm. Price, RM. 4.

The German word *ausblühen* refers usually to the shedding of blossoms; its intent is probably broader than that of the English, creeping of salts, and corresponds more nearly to that of efflorescence by which we are accustomed to designate both the loss of water from hydrated crystals with the consequent formation of powder and the deposition of dissolved salts in masses which resemble vegetation, as when we speak of the efflorescence upon a piece of masonry or the walls of a cellar. The phenomena in question are of interest to the colloid chemist, the geologist, the mineralogist, and others; they play an important part in the economy of nature and are of practical significance to the artist, the architect and the engineer.

The author of the present brochure has published extensively on the subject, and now presents an interesting, well-illustrated, and well-documented survey of the whole field. The seven sections of the monograph deal respectively with (1) the multiplicity of the names (for the phenomenon of efflorescence) and the first descriptions, (2) *Bodenausblühen* (creeping within deep masses of crystals), (3) climate and local conditions, (4) efflorescence of structural materials, (5) experiments toward an explanation of the mechanism of efflorescence, (6) capillary theory of efflorescence, and (7) influence of dispersion. The early work of Lemery on chemical vegetation, published with three handsome engravings in *Mem. Acad. Roy. des Sciences*, 1706, pp. 411–418; 1707, pp. 299–328, is not mentioned in the list of references.

Tenney L. Davis

Grundriss der chemischen Technik. (An Outline of Chemical Technology.) By Dr. F. A. Henglein, Professor and Director of the Institute of Chemical Technology, Technical College of Karlsruhe. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany, 1936. viii + 470 pp. 435 figs. 19.5 × 27.5 cm. Price, RM. 16.80.

This book is the outgrowth of a series of lectures given at two well-known German universities and is based on the author's long practical experience in chemical industry. It is divided into two main parts, the first dealing with the general technology common to all branches of the industry and the second with the more specialized techniques of particular industries.

Part I opens with a brief review of some of the more important physicochemical laws governing chemical reaction, and some general observations on the economics of chemical processes and on the analysis of processes into unit operations. This is followed by a long section describing typical equipment for carrying out the more common unit operations—a purely descriptive and non-quantitative treatment, very well illustrated by diagrams and photographs.

The remaining sections of Part I deal with a number of matters which are of the utmost importance to the success of any chemical manufacturing enterprise, but which are frequently omitted or only casually mentioned in typical American texts on so-called "Industrial Chemistry." For example, such factors as power, water supply, storage, transportation, safety, shops and laboratories, organization of personnel, patents, buildings, etc., are treated briefly but with sufficient detail to emphasize their importance.

Part II, dealing with the more specialized procedures, has two main subdivisions, the first of which treats the more strictly chemical industries such as nitrogen fixation, acids, alkalies, dyestuffs, pharmaceuticals and the like, while the second is concerned with those industries producing consumption goods with the aid of chemicals and chemical control, but in which the products are not the direct result of chemical reactions. Examples are the rubber, textile, leather, perfume and photographic film industries. As an Introduction to Part II, there is a good general discussion of the raw materials of chemical industry.

The most outstanding feature of the book is the excellence of the illustrations of which there are more than 500. They contribute very greatly to its value, but even without them the reviewer believes that the book is a distinct contribution to the chemical engineering literature. It seems to him to give an unusually well balanced picture of chemical industry as a whole.

BARNETT F. DODGE

Colloid Symposium Monograph. Papers Presented at the Twelfth Symposium on Colloid Chemistry, Ithaca, New York, June, 1935. Edited by HARRY BOYER WEISER, Professor of Chemistry, The Rice Institute. The Williams and Wilkins Company, Mt. Royal and Guilford Avenues, Baltimore, Maryland, 1936. 156 pp. 18 × 26 cm. Price, $3.00.

This volume contains the papers presented at the Twelfth Symposium on Colloid Chemistry, held in June, 1935, at Ithaca, New York. All but two of these papers, namely, one entitled "The Adsorption of Water Vapor by the Growth Elements of the Sapwood and by the Heartwood of Southern Pine," by C. J. Frosch, and another, "A Hydrate Decomposition Mechanism," by V. R. Damerell and O. F. Tower, have already been published in Volume 40 of *The Journal of Physical Chemistry*. It is, however, a convenience to have them available in a separate volume, particularly for persons who have sets of Colloid Symposium Monographs and Colloid Symposium Annuals.

ARTHUR B. LAMB

The Thermochemistry of the Chemical Substances. By F. RUSSELL BICHOWSKY, Editor for Thermochemistry for the "International Critical Tables," and FREDERICK D. ROSSINI, Scientist in Physical Chemistry at the National Bureau of Standards. Reinhold Publishing Corporation, 330 West 42d Street, New York, N. Y., 1936. 460 pp. 15.5 × 23.5 cm. Price, $7.00.

The sub-title of this book "The Assembly of a Self Consistent Table of "Best" Values for the Heats of Formation of the Chemical Substances (Except Carbon Compounds Containing More Than Two Carbon Atoms), Including Heats of Transition, Fusion, and Vaporization" clearly defines the contents. The authors have retained the order of arrangement of the section of thermochemistry in the "International Critical Tables," of which this is essentially a revision and extension. Accurate descriptions of the electron configurations of many of the substances are added. The return to the calorie (1 defined calorie = 4.1850 absolute joules = 4.1833 International joules = 0.04337 absolute volt-electrons) is welcome.

In determining the best value, the authors first recalculated the experimental data to consistent units, molecular weights, etc., so far as possible. The values are tabulated as the heat evolved when the clearly indicated reaction takes place at a constant temperature of 18° and a constant pressure of 1 atm. Only the selected best value appears in the main table. There follows (pp. 171–405), arranged in the same "I. C. T." order as the main table, a discussion of the source and methods of measurement and sometimes the individual values from which the selection of the best value was made. This section is especially welcome to research workers in thermochemistry. The system of references to the original data is clear, concise, and is a great improvement over that used in the "I. C. T." or other tables of thermochemical data. The abbreviations used are clearly defined, and as the "I. C. T." order of arrangement is used the material is self indexed. But for those unfamiliar with the "I. C. T." standard arrangement, an index showing the locations of the elements in the table and text is given.

The authors are thoroughly familiar with the field and have succeeded in assembling, recalculating and tabulating the extensive data relating to heat of formation in a practical, accurate, and understandable way.

MERLE RANDALL

Experimental Enzyme Chemistry. By HENRY TAUBER, New York Medical College and Flower Hospital, New York City. Burgess Publishing Company, 426 South Sixth Street, Minneapolis, Minnesota, 1936. v + 118 pp. Illustrated. Price $3.50.

This mimeographed edition is a successful attempt to present certain of the more important advances in enzyme chemistry during the past few years. Experimental results, rather than theoretical considerations, are emphasized and no attempt is made to cover the material given in earlier monographs. At times the text is vague and shows haste in writing, and certain sections are rather sketchy due to the size of the book. However, this is in part offset by a well selected list of over 800 references.

The first chapter deals with the nature of enzymes and their mode of action as influenced by various factors. The protein nature of many enzyme systems, shown largely by American workers, is discussed. Such topics as buffers, "anti-enzyme," activators and inhibitors are either omitted or given too scant treatment. Then come chapters on the following specific systems: esterases, proteolytic enzymes and those acting upon related nitrogen compounds, carbohydrases, catalase, oxidizing enzymes and the flavine system, carbonic anhydrase, zymase and luciferase.

Especially in the cases of the proteases and the carbohydrases certain groupings are attacked by specific enzymes and these relationships are pointed out in this book. During the past ten years theories as to the role of cytochrome and the flavine pigment of Warburg and Christian in oxidizing enzyme systems have been developed; this difficult field is also well summarized.

Dr. Tauber has performed an excellent service in summarizing the latest material in several fields of enzyme chemistry and we can only wish that the manuscript were extended to cover more fully certain sections and to include other topics. An index would greatly increase the usefulness of the book. The monograph will scarcely serve as an introduction to the study of enzyme chemistry but it will be read with profit by those acquainted with the field.

W. M. SANDSTROM

Enzymologia. Vol. I, Nos. 1–2. Edited by CARL OPPENHEIMER. W. Junk Verlag, 74 Scheveningsche Weg, Den Haag, Holland. 160 pp. 20 × 28 cm. Price, per volume, Dutch florins, 15.00.

This journal, first issued in June, 1936, is devoted entirely to enzymes and will cover the whole range of enzyme research. Original articles and brief preliminary reports will be accepted, but summarizing reviews are to be accepted only when asked for by the editor. The manuscripts, which are to be as concise and comprehensive as possible, may be written in German, English, French and Italian. Publication will be prompt. Authors are to receive 120 free copies of their articles as honorarium. The editor, Dr. Oppenheimer, well known as the author of many authoritative volumes dealing with enzymes, will have the assistance of 101 collaborators from various countries who are recognized for their interest in enzyme chemistry and for past contributions in this field.

The first two numbers of the journal, containing seventeen research papers, have already appeared. These papers are of such quality that the reviewer believes that *Enzymologia* can be expected to deserve a place in every biochemical library. In view of the present high cost of German journals one wonders what the price will be per year. Because of the fact that *Enzymologia* will appear at indefinite intervals, it is difficult to make any positive statement, but it is probable that the cost per year will be inconsiderable.

In view of the present broadcast distribution of enzyme articles in so many different scientific publications it will be a distinct advantage to find a considerable number grouped together in one journal. The reviewer is of the opinion that *Enzymologia* deserves the support and interest of chemists and biologists, and that the existence of this new journal will raise the standards of enzyme research.

JAMES B. SUMNER

BOOKS RECEIVED

October 15, 1936–November 15, 1936

HEINRICH BILTZ. "Die neure Harnsaürechemie. Tatsachen und Erklärungen." Verlag Johann Ambrosius Barth, Salomonstrasse 18B, Leipzig C 1, Germany. 164 pp. RM. 5.80.

CHRISTIAN BOMSKOV. "Methodik der Hormonforschung." Vol. I. Georg Thieme Verlag, Rossplatz 12, Leipzig C 1, Germany. 251 pp. RM. 54; bound, RM. 56.

LUCIUS JUNIUS DESHA. "Organic Chemistry. The Chemistry of the Compounds of Carbon." McGraw-Hill Book Company, Inc., 330 West 42d St., New York, N. Y. 750 pp. $3.75.

HERBERT FRÖHLICH. "Elektronentheorie der Metalle." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 386 pp. RM. 27; bound, RM. 28.80.

WILHELM KLEMM. "Magnetochemie." Akademische Verlagsgesellschaft m. b. H., Sternwartenstrasse 8, Leipzig C 1, Germany. 262 pp. RM. 16; bound, RM. 18.

J. F. MCCLENDON and C. J. V. PETTIBONE. "Physiological Chemistry." Sixth edition. C. V. Mosby Co., 3523 Pine Boulevard, St. Louis, Mo. 454 pp. $3.50.

ADDITIONS AND CORRECTIONS

Notice to Readers.—For the convenience of those who may wish to cut out the corrections and attach them to the margins of the articles corrected, they have been printed only upon one side of the page.

1935, Vol. 57

Madison Hunt and C. S. Marvel. **The Reaction between Sulfur Dioxide and Olefins. II. Propylene.**

Page 1696. Column 1, lines 12 and 13 should read: "*Anal.* Calcd. for $C_4H_9S_2O_3Na$: S, 33.33. Found: S, 32.82, 32.62."—C. S. Marvel.

J. W. McBain and Margaret D. Betz. **Straight-Chain Sulfonic Acids in Water. III. Electromotive Force.**

Page 1914. The authors report: "The activity data of Randall and Young quoted in column 3 of Table II are those for 0° instead of 25°. This does not affect any of the more dilute solutions, but it increases the discrepancy which is emphasized between the best standard e. m. f. data for 1 *m* hydrochloric acid and accepted theory to no less than 10.8 and 11.6 millivolts, leaving it 1.3 or 2.1 millivolts for 0.1 *m* hydrochloric acid."—J. W. McBain.

Donald D. Coffman. H. B. Dykstra. **Acetylene Polymers and their Derivatives. XXIII-XXV.**

Pages 1978, 1981, 2255. The authors write: "The more recent articles in our Acetylene Polymers series have been numbered incorrectly:

Page number	1978	1981	2255
Number assigned	XXII	XXIII	XXIII
Correct number	XXIII	XXIV	XXV

"We wish to report also that on page 2257 ... the data given in the last line of Table IB are not for $CH_2{=}CHC(OC_2H_5)_2CH_3$, as indicated, but for $CH_2{=}CHC(OC_2H_5)(OC_6H_5)CH_3$."—H. B. Dykstra.

Louis F. Fieser and Emanuel B. Hershberg. **The Synthesis of Phenanthrene and Hydrophenanthrene Derivatives. II. The Hydrocarbon Synthesis.**

Page 2196. Line 25. "Dr. Haworth's melting point for 2,3-dimethylphenanthrene styphnate was given incorrectly as 137–148° instead of 147–148°."—L. F. Fieser.

1936, Vol. 58

E. D. Farley and C. S. Marvel. **Rearrangements of Polyynes. VIII. Formation of Diallenes.**

Page 30. The authors write: "In the chart the neutral compound in the upper right-hand corner should be $C_{33}H_{30}O_2$. Also, in the last line of the chart, the compound $C_{38}H_{42}$, m. p. 181°, should be $C_{38}H_{42}$, m. p. 197°."—C. S. Marvel.

E. C. Pitzer, N. E. Gordon and D. A. Wilson. **The Reduction of Uranyl Ion in the Uranyl Oxalate Actinometer.**

Page 69. Column 2, line 11 should read "$\alpha = K/[K + (H^+)]$." Line 17 should read "$[UO_2(C_2O_4)_2^=] = 0.0201$."—E. C. Pitzer.

George H. Tomlinson, 2nd, and Harold Hibbert. **Studies on Lignin and Related Compounds. XXIII. The Preparation and Methylation of Spruce Lignin Sulfonic Acids.**

Page 343. In column 2, line 12, for "100°" read "110°."—Harold Hibbert.

George H. Tomlinson, 2nd, and Harold Hibbert. **Studies on Lignin and Related Compounds. XXIV. The Formation of Vanillin from Waste Sulfite Liquor.**

Page 346. In Table I, column 4, item 5, for "Digest 100 cc. liquor ..." read "Digest 1000 cc. liquor ..."—Harold Hibbert.

B. Sullivan and C. H. Bailey. **The Lipids of the Wheat Embryo. I. The Fatty Acids.**

Page 386. In column 2 the third formula should read "$Ln = -(100 - G) + 1.104$ (thiocyanogen number)."—C. H. Bailey.

S. R. Benson and H. N. Calderwood. **The Chemical Examination of the Seed of Abies Balsamea (L) Miller.**

Pages 524–525. In item 7 of the Summary the second word should be "linolenic" instead of "linoleic," and in the last line for "9-octadecanoic" read "9-octadecenoic."—H. N. Calderwood.

Lee Irvin Smith and C. W. MacMullen. **The Reaction between Quinones and Sodium Enolates. IV. Pseudocumoquinone, Sodium Acetoacetic Ester and Sodium Malonic Ester.**

Page 630. "In formula I a methyl and hydroxyl group should be interchanged so that the hydroxyl will be para to the bridge oxygen and not meta."—Lee Irvin Smith.

Walter Fuchs. **Investigations Concerning Phenol Lignin and β-Methoxyethanol Lignin from Spruce Wood.**

Pages 673 ff. The compound described as "Methoxy Glycol" should have been named "β-Methoxyethanol."—The Editor.

William F. Bruce. **The Preparation of Platinum Oxide for Catalytic Hydrogenations.**

Page 688. In column 1, footnote 4 should read "(4) The addition of a trace of $FeSO_4$ served to promote the reaction."—William F. Bruce.

R. F. Miller and Roger Adams. **Contribution to the Multiplanar Isomerism of Cyclohexanes.**

Page 788, Column 2, line 18. The sentence, "On the basis of only one 'C' form, five isomers remain." should read, "On the basis of only two 'C' forms produced by interchange of a and b or c and d, six isomers remain."—R. F. Miller and Roger Adams.

Earl M. Bilger and Harold Hibbert. **Mechanism of Organic Reactions. IV. Pyrolysis of Esters and Acetals.**

Page 825. In the first column of the table, item 4 should read "Ethylene *n*-butyral" instead of "Ethyl *n*-butyral."—Harold Hibbert.

Samuel C. Hooker. **Condensation of Aldehydes with β-Hydroxy-α-naphthoquinone. Synthesis of Hydrolapachol.**

Page 1163. Note 1, Lines 10 and 11. The word "purification" should read "publication."

Henry E. Bent and N. B. Keevil. **The Electron Affinity of Free Radicals. X. A Potentiometric Method for Determining ΔF for the Addition of Sodium to an Organic Compound.**

Page 1230. Column 1, line 9 from the end, for "10^{12}" read "10^{10}."—Henry E. Bent.

P. C. Jurs and C. R. Noller. **Saponins and Sapogenins. IV. The Isolation of Amolonin and Determination of the Products of Hydrolysis.**

Page 1254. In the captions of Figs. 2 and 3 and at the bottom of column 1, for "polarigram" and "polarigraph" read "polarogram" and "polarograph."—C. R. Noller.

Henry E. Bent and Norman B. Keevil. **The Electron Affinity of Free Radicals. XI. The Free Energy of Addition of Sodium to Ketones and Unsaturated Hydrocarbons.**

Page 1371. Column 1, line 4, for "not" read "now."—Henry E. Bent.

Russell E. Marker, Oliver Kamm, Thomas S. Oakwood and Joseph F. Laucius. **Sterols. VI. Synthetic Preparation of Oestrone (Theelin).**

Page 1503. The authors write: "In the formulas for ergosterol, neoergosterol, dehydro-neoergosterol and tetrahydro-dehydro-neoergosterol, the radical attached to the 17-position should be C_9H_{17} instead of C_9H_{18}. The analysis formulas also should be changed accordingly."—Russell E. Marker, Oliver Kamm, Thomas S. Oakwood and Joseph F. Laucius.

Charles M. Mason, Roger D. Gray and Grace L. Ernst. **The Magnetic Rotation of Lanthanum and Neodymium Chlorides in Aqueous Solution.**

Page 1602. In column 2, lines 8 and 14, for "λ5460.8 Å," read "λ5460.7 Å."

Page 1604. In column 2, lines 12 and 24, for "λ5460.8 Å." read "λ5460.7 Å."—C. M. Mason.

James P. Danehy and J. A. Nieuwland. **The Reactions of Metal Halides with Acetylenic Grignard Reagents.** Charles A. Young, R. R. Vogt and J. A. Nieuwland. **The Reaction of Butylacetylene with Hydrogen Bromide.**

Pages 1609 and 1806. The first of these two papers should have been numbered XVI, and the second XV instead of XIV.—G. F. Hennion.

Theodore Soller, Seymore Goldwasser and Ralph A. Beebe. **A Sensitive Manostat for Low Pressures and its Application to the Adsorption of Hydrogen and Deuterium on Copper.**

Page 1706. In the Summary, paragraph 2, line 3, for "3.35" read "5.5."—Ralph A. Beebe.

G. H. Cartledge and W. P. Ericks. **Equilibrium between the Trioxalatomanganiate and Dioxalatodiaquomanganiate Ions.**

Page 2068. Footnote (6) should read "(6) Johnson, *Trans. Faraday Soc.*, [5] 28, 845 (1932)."—G. H. Cartledge.

Frank T. Gucker, Jr., Fred D. Ayres and T. Richard Rubin. **A Differential Method Employing Variable Heaters for the Determination of the Specific Heats of Solutions, with Results for Ammonium Nitrate at 25°.**

Page 2122. In column 1, the third line from the end should read "$= 1.24741 + [0.10(1.2471 - 1)]/79.6 = 1.24772 = x_1$."—Frank T. Gucker.

F. H. Norton and H. B. Hass. **The Action of Diethylmagnesium upon the Methyl Substituted Derivatives of Epoxyethane.**

Page 2150. In Table VIII, first part, after "Ref. cpd." insert a line reading "Et_2Mg 157.1 750 82.5 1.4390 0.8549 40.04 0."—H. B. Hass.

David E. Adelson and Marston Taylor Bogert. **Investigations in the Retene Field. VII. Certain Fluorenones and Phenanthridones from Retenediphenic Acid.**

Page 2236. Column 1, in formula (II) the "HOOC—" on the upper ring should be ortho to the bond connecting the rings instead of ortho to the "—$CH(CH_3)_2$."—Marston T. Bogert.

L. F. Fieser, M. Fieser and E. B. Hershberg. **The Synthesis of Phenanthrene and Hydrophenanthrene Derivatives. VI. 1′,3′-Diketocyclopentenophenanthrenes.**

Page 2323. In formula V the carbonyl groups should be at the 1′- and 3′-positions, rather than at 2′ and 3′.—L. F. Fieser.

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Subject Index to Volume LVIII, 1936